Defects and diffusion in metal oxides: Challenges for first-principles modelling

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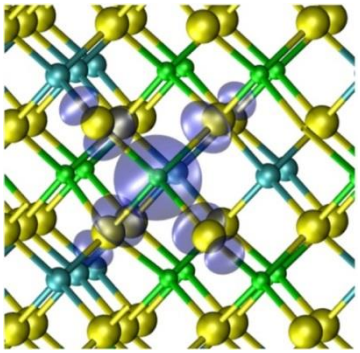
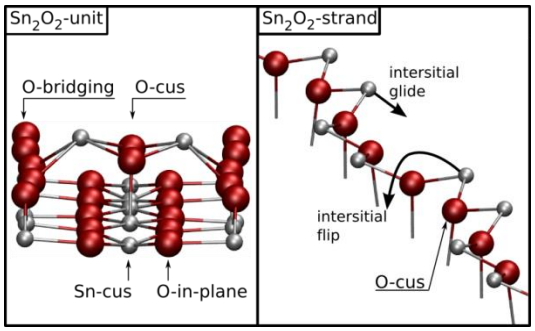
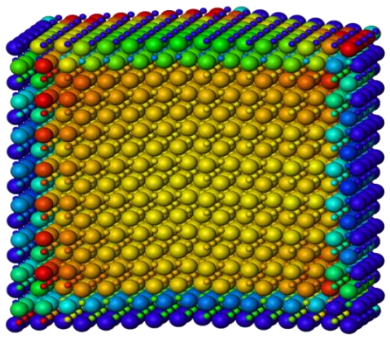
Karsten Albe, FG Materialmodellierung, TU Darmstadt

Johan Pohl, Peter Agoston, Paul Erhart, Manuel Diehm







FUNDING: DFG-SFB 595, BMBF „Gracis“, Helmholtz Virtual Institute „MiCo“, Schott Solar

How To Get Hydrogen?

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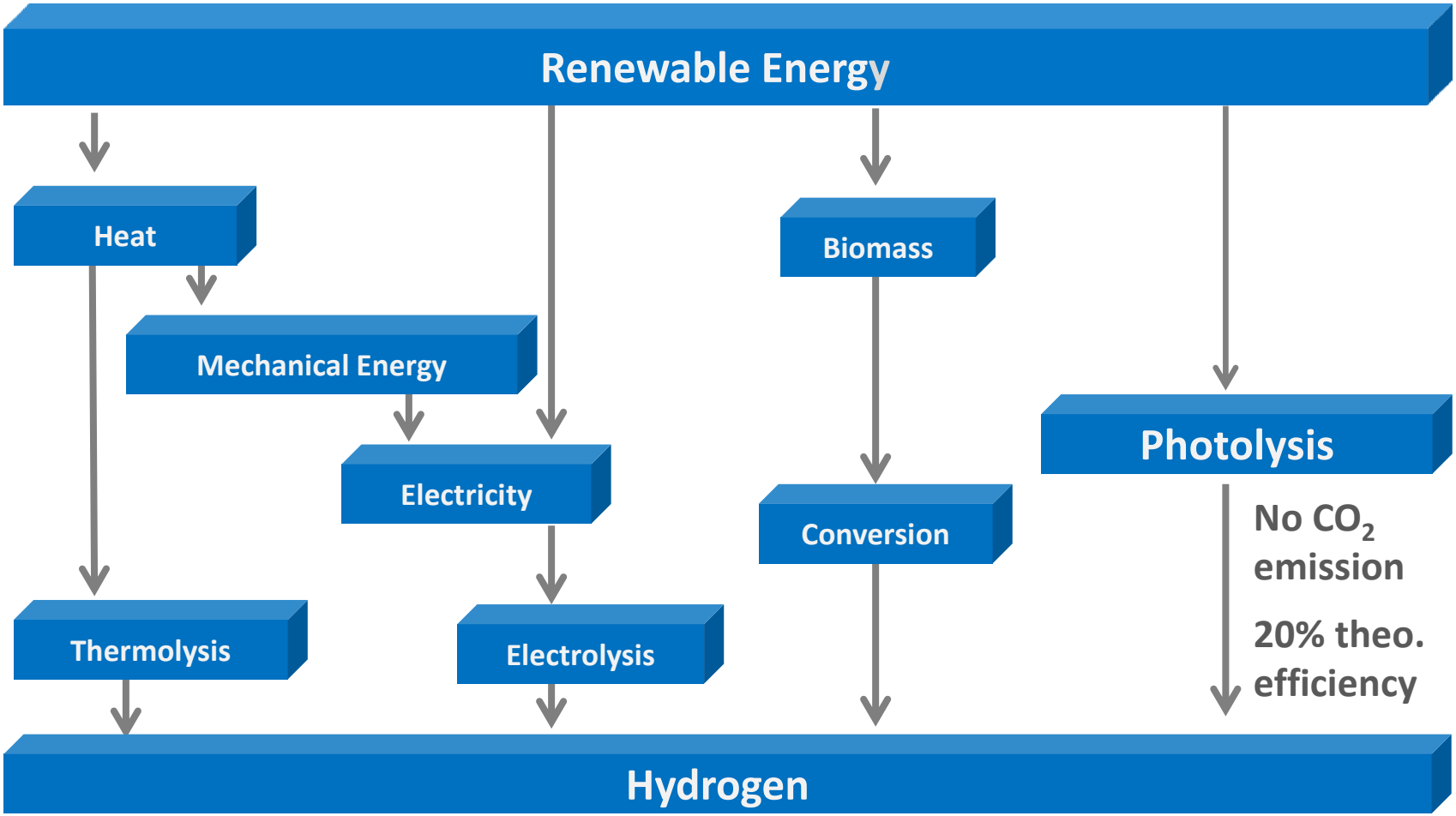

Photocatalysis: Desired Materials Properties

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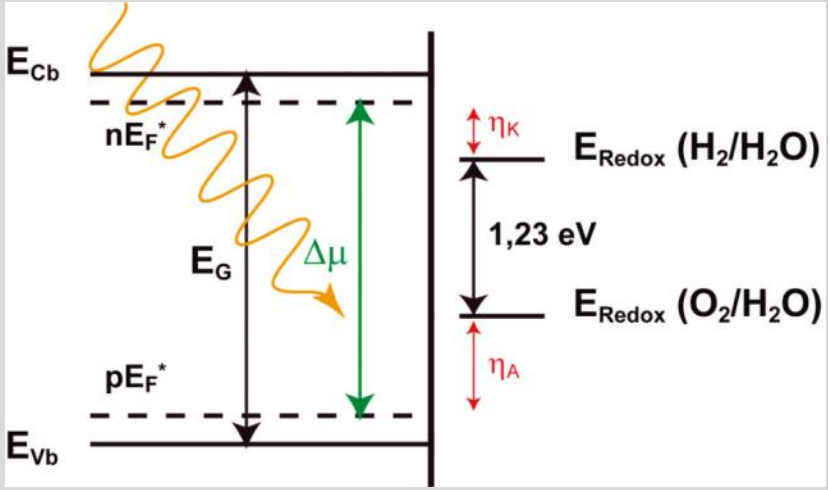
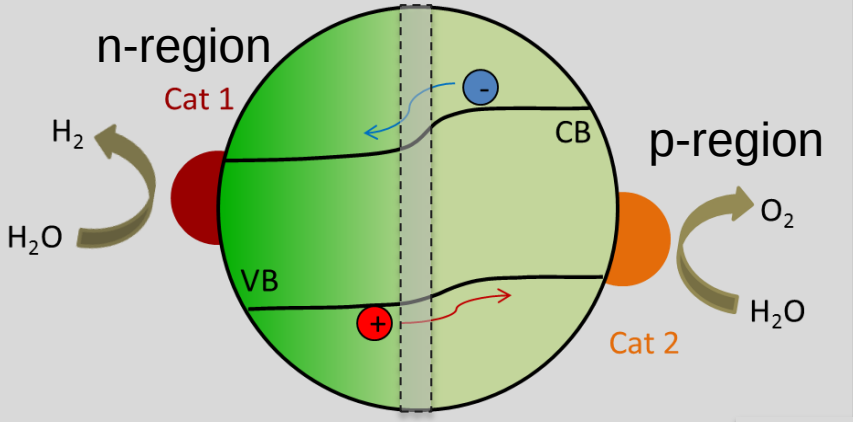
- 1.23 eV < band gap ≤ 3eV
- Engineered pathways of electron-hole pairs
- No defects acting as recombination sites
- Charge transfer used for water splitting instead of corrosion
- Efficient H_2 production and low overvoltages η
- Identify transparent passivating surface layer
- Couple Fermi level of metal catalyst to the quasi-Fermi levels of the semiconductor under illumination
- Design a working device
- Design and implement assembling procedures





Materials by Design

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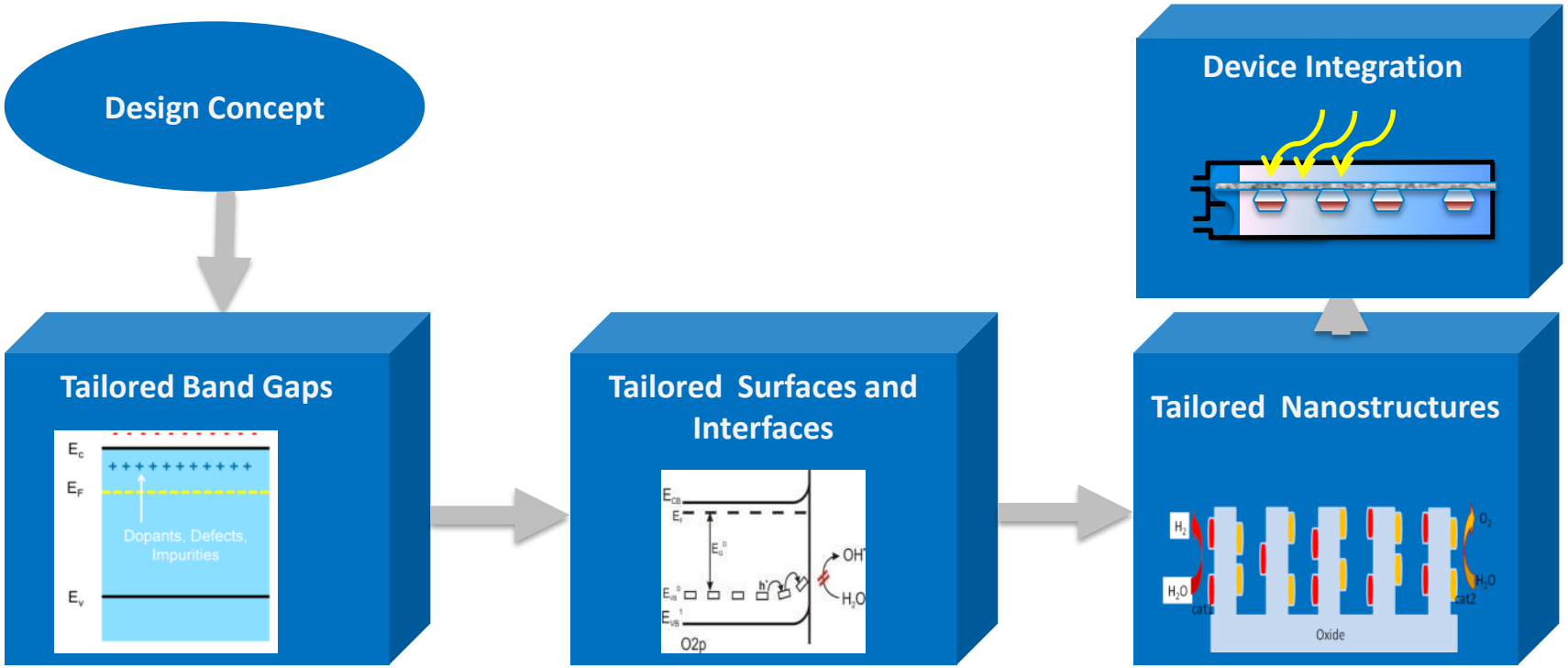

Materials by Design

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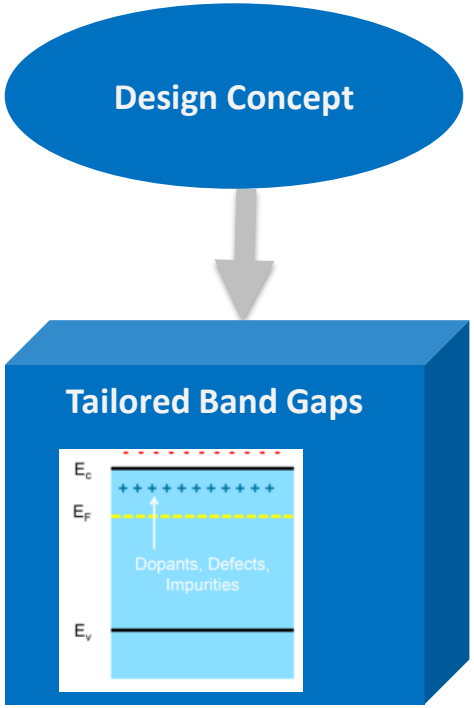

Electronic Structure Theory

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Basic material properties

Density functional theory

- Crystal structure
- Thermodynamic stability

Band-structure properties (perfect crystal lattice)

Many-body theory
Quasi-particle energy calculations (GW)

- Band gap
- Absorption spectrum
- Effective masses

Defect properties (imperfect lattice)

Supercell calculations
Defect theory

- Doping (electrical properties)
- Defects
- Self-trapped carriers

Defects in Semiconductors

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Defect formation energy	$\Delta H = \Delta H_{D,q}(\mu, E_F)$
Defect concentration	$c_D \approx N_{site} \times \exp(-\Delta H/kT)$
Electron/hole density	$c_e = \int f_{FD}(E-E_F)\, g(E)\, dE$
Charge neutrality	$-c_e + c_h + \Sigma\,[q \cdot c(D^q)] = 0$
Self-consistent solution	$\Delta H(E_F) \longrightarrow c_D(\Delta H) \longrightarrow E_F$
pO_2 dependence of μ_O	$\Delta\mu_O(T,P_0) = \frac{1}{2}[H_0+\Delta H(T)] - \frac{1}{2}T\cdot[S_0+\Delta S(T)]$
(ideal gas)	$\Delta\mu_O(T,P) = \Delta\mu_O(T,P_0) + \frac{1}{2}kT\ln(P/P_0)$

High conc.	Account for competition of defects and host atoms for N_{site} Association/dissociation of ***defect-clusters*** (law of mass action)
Direct	Given $\Delta H(\mu)$, find concentrations c_D
Inverse	Given a target concentration, find ΔH (i.e., find μ)

Ab-initio Thermodynamics of Point Defects

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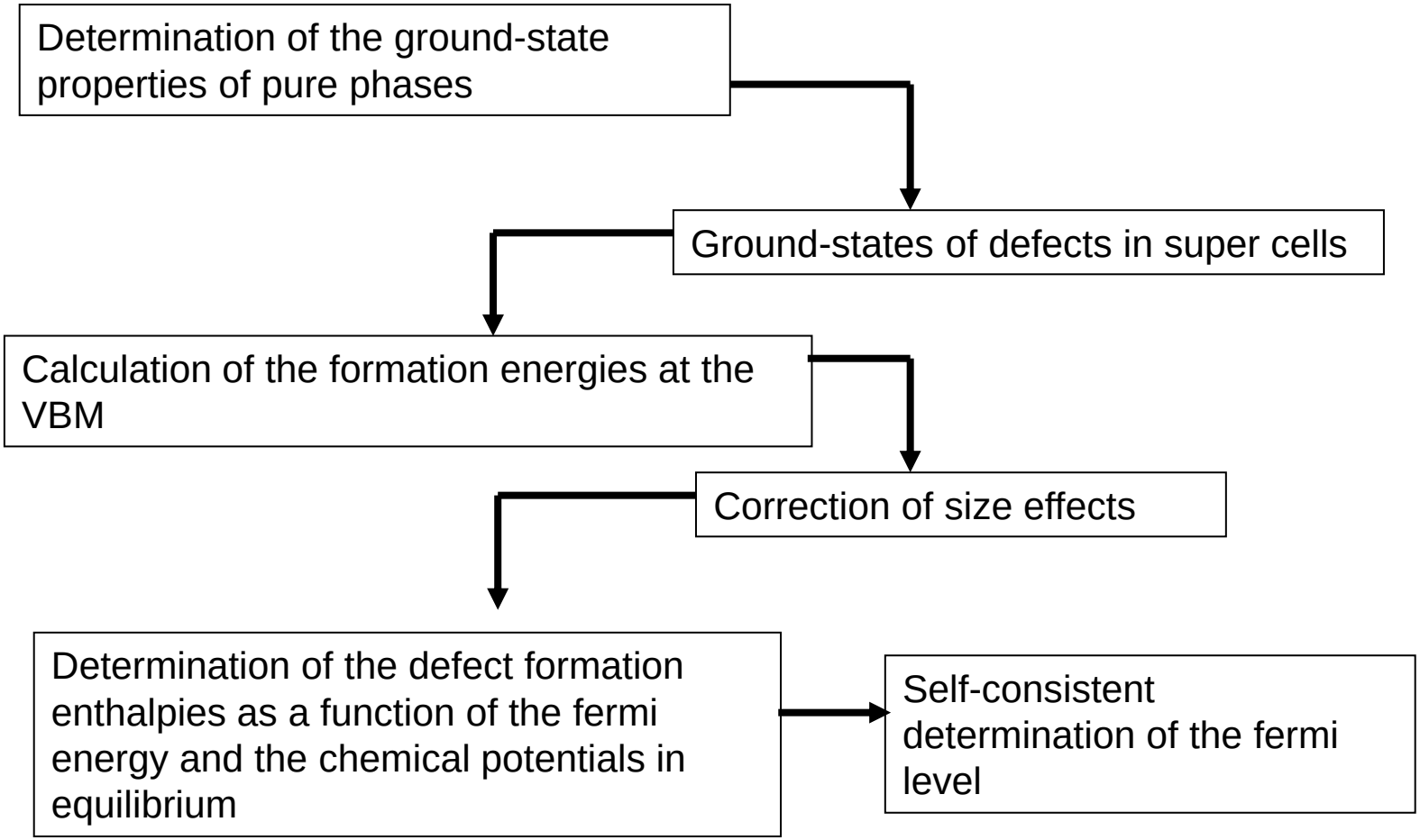

When DFT fails…

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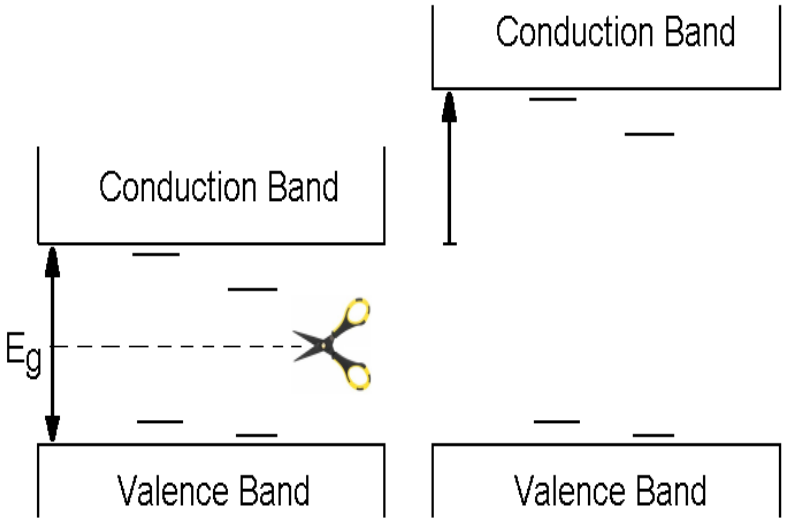
In defect calculations: band gaps

- Heavily underestimated
- Both LDA/GGA functionals
- Affects:
  - Defect levels
  - Defect formation energies



Correction: scissor operation!

- Shift the conduction band
- Align E_g(DFT) and E_g(EXP)
- Donor type defects follow CB
- Correct formation energies

Alternative: hybrid or semi-empirical functionals

Pt/CuGaSe2 and Pt/CdS/CuGaSe2 as Photoelectrode

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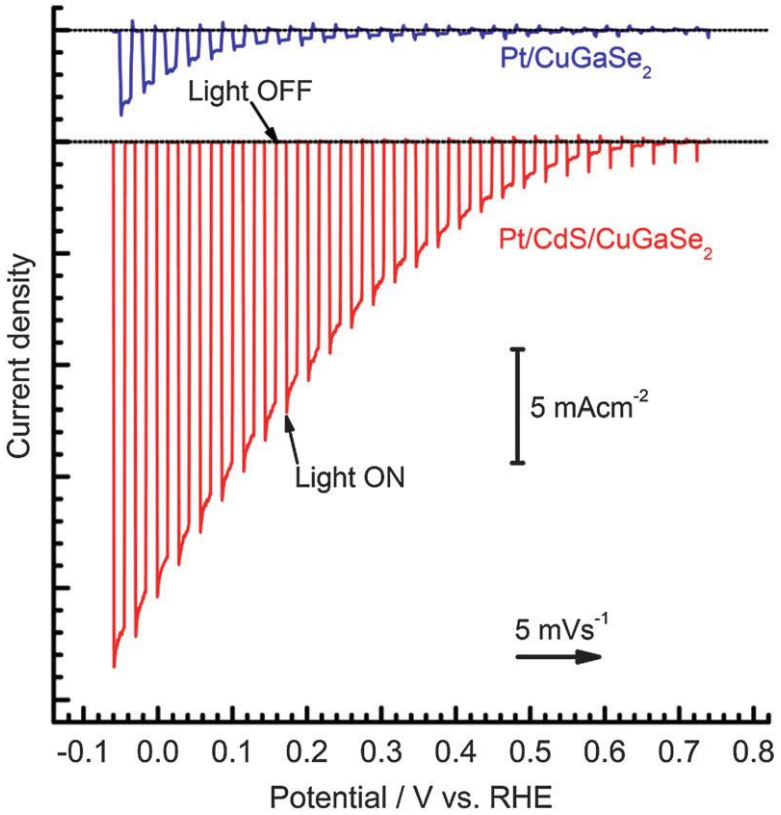

0.1 M Na_2SO_4 aq. (pH 9),
300 W Xe lamp, 5 mV s^{-1}

Chem Soc Rev

TUTORIAL REVIEW

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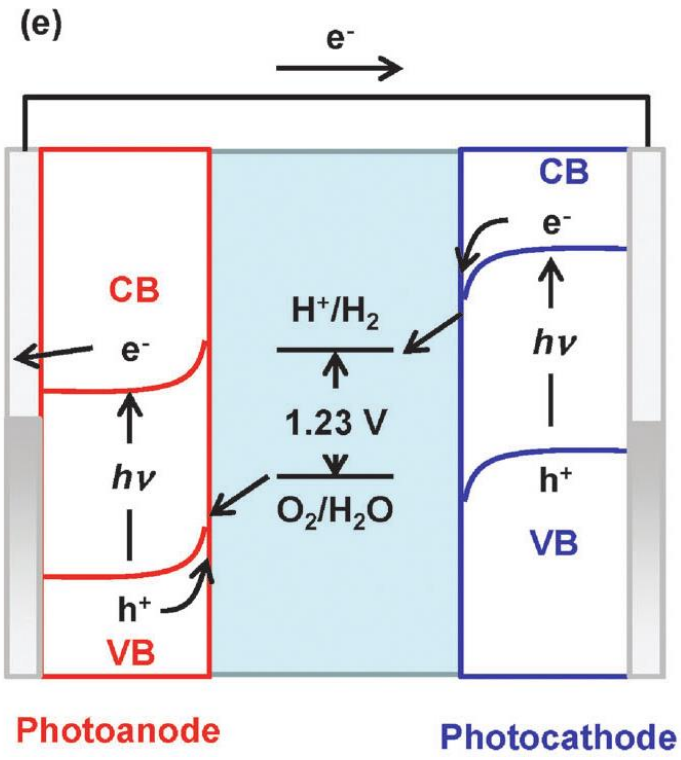
Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting

Cite this: DOI: 10.1039/c3cs60378d



Chalcopyrite Band Gaps from HSE06

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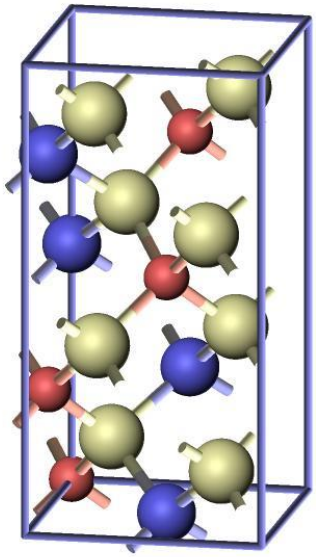
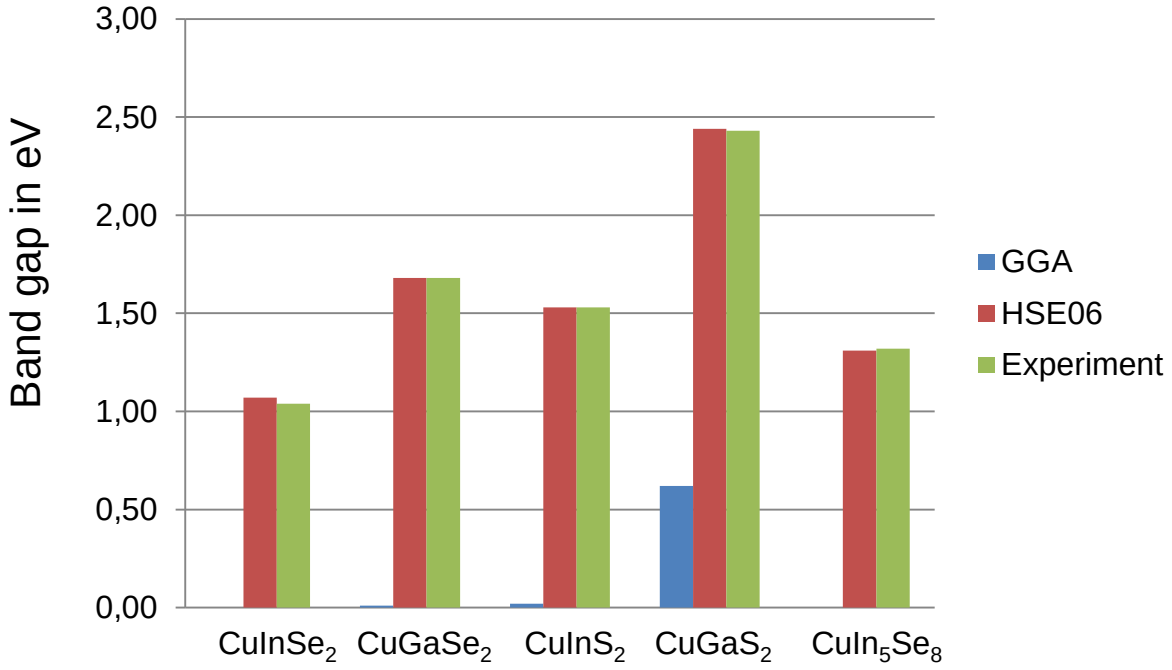


Chalcopyrite

Electronic band gaps (eV) with optimized exchange screening parameter ω = 0.13:



J. Pohl, K. Albe, J. Appl. Phys. **108**, 023509 (2010)

Defects in $CuInSe_2$

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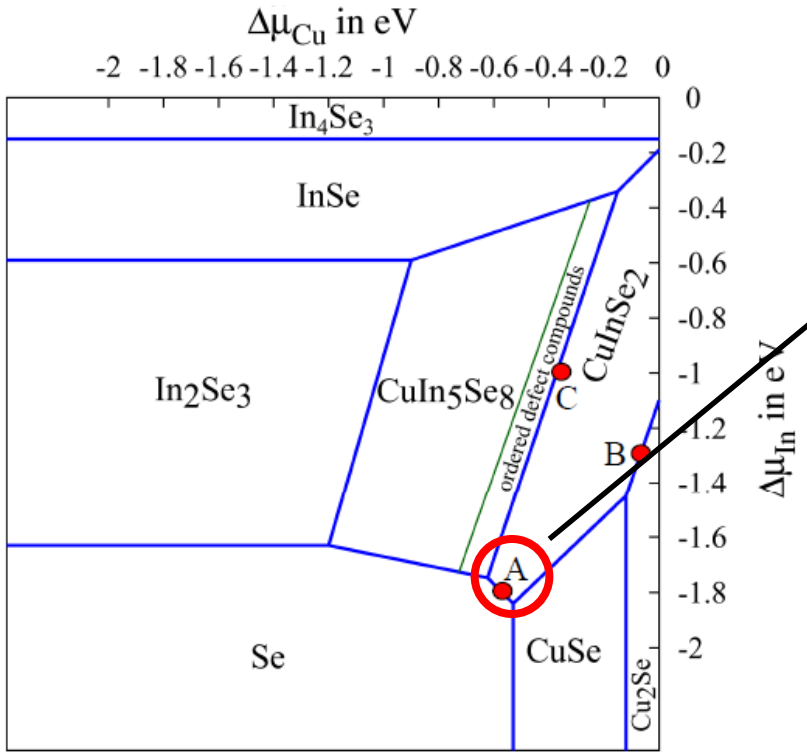
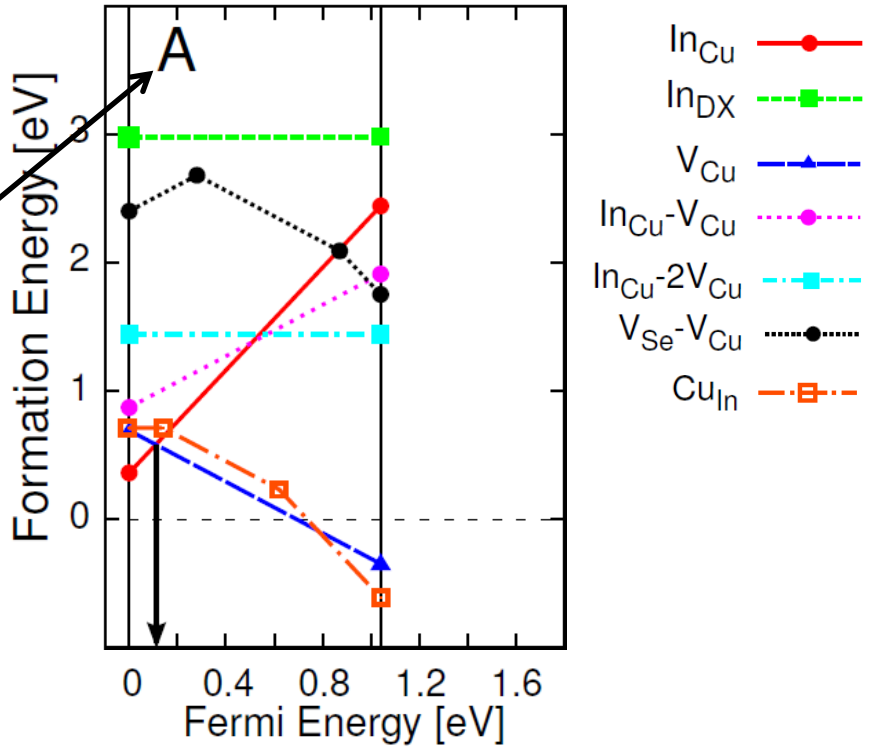
Phase stability



Point defect formation enthalpies



J. Pohl, K. Albe, Phys. Rev. B **87**, 245203 (2013)

Defects in $CuInSe_2$

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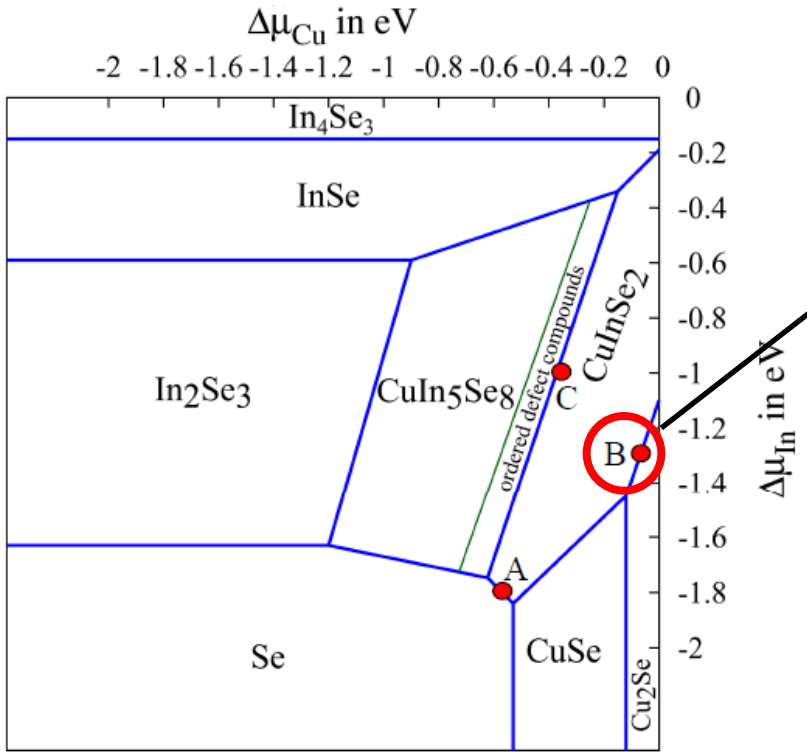
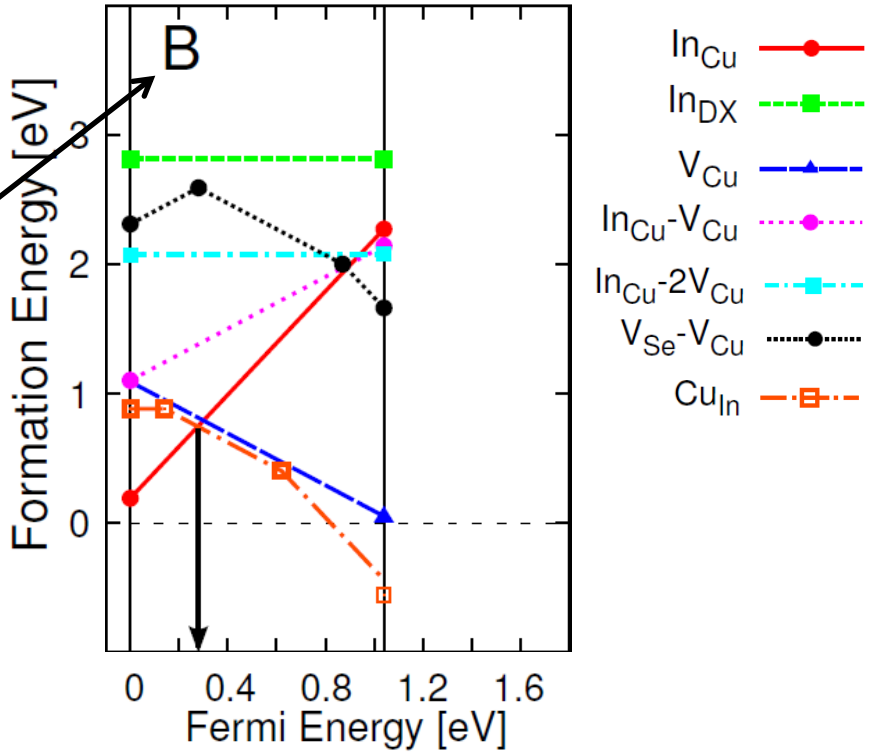
Phase stability



Point defect formation enthalpies



J. Pohl, K. Albe, Phys. Rev. B **87**, 245203 (2013)

Defects in $CuInSe_2$

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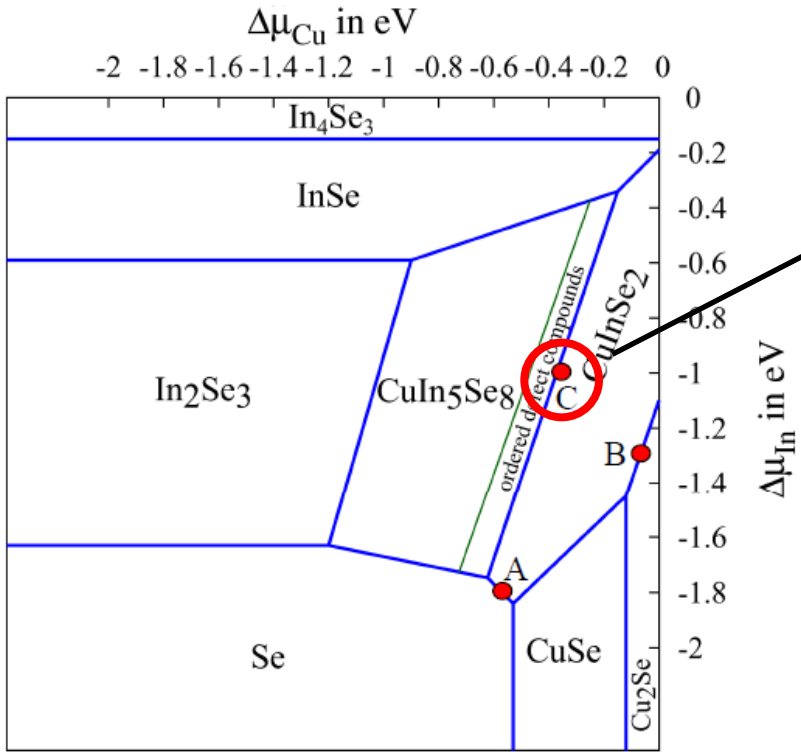
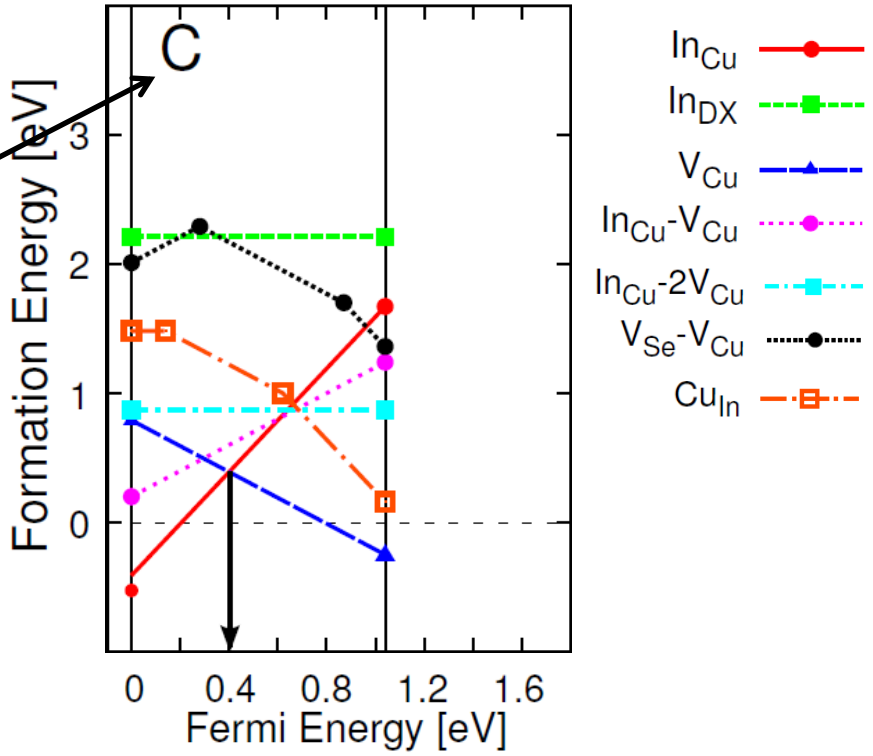
Phase stability



Point defect formation enthalpies



J. Pohl, K. Albe, Phys. Rev. B **87**, 245203 (2013)

Defects in $CuGaSe_2$

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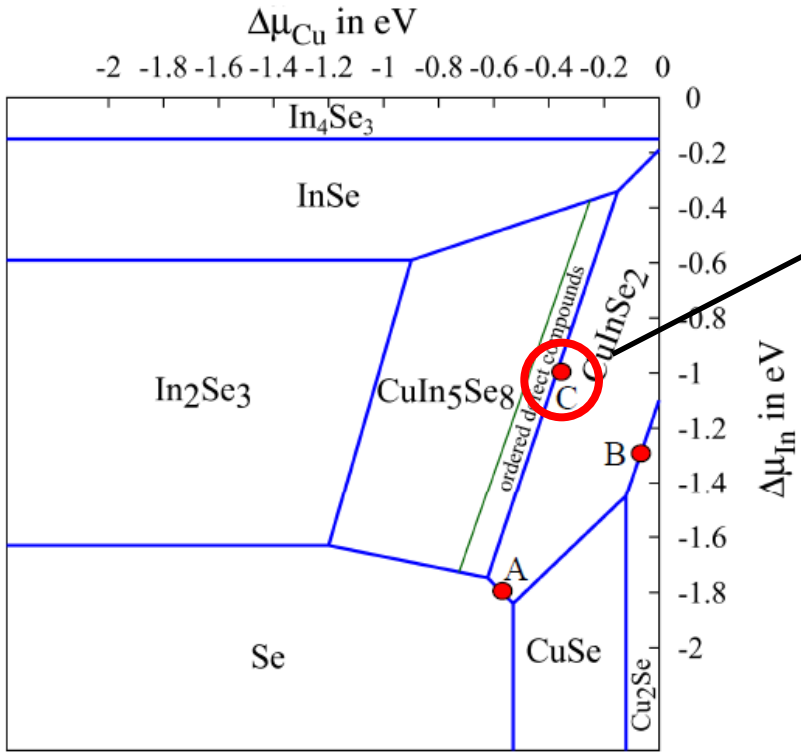
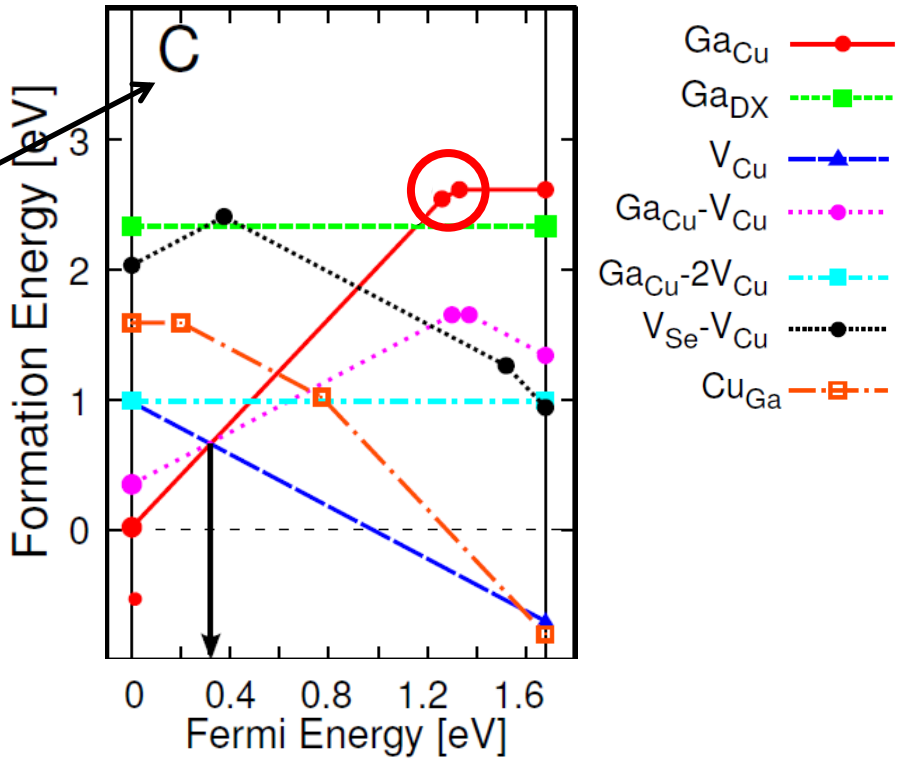
Phase stability



Point defect formation enthalpies



J. Pohl, K. Albe, Phys. Rev. B **87**, 245203 (2013)

Antisite Defects in $CuInSe_2$ and $CuGaSe_2$

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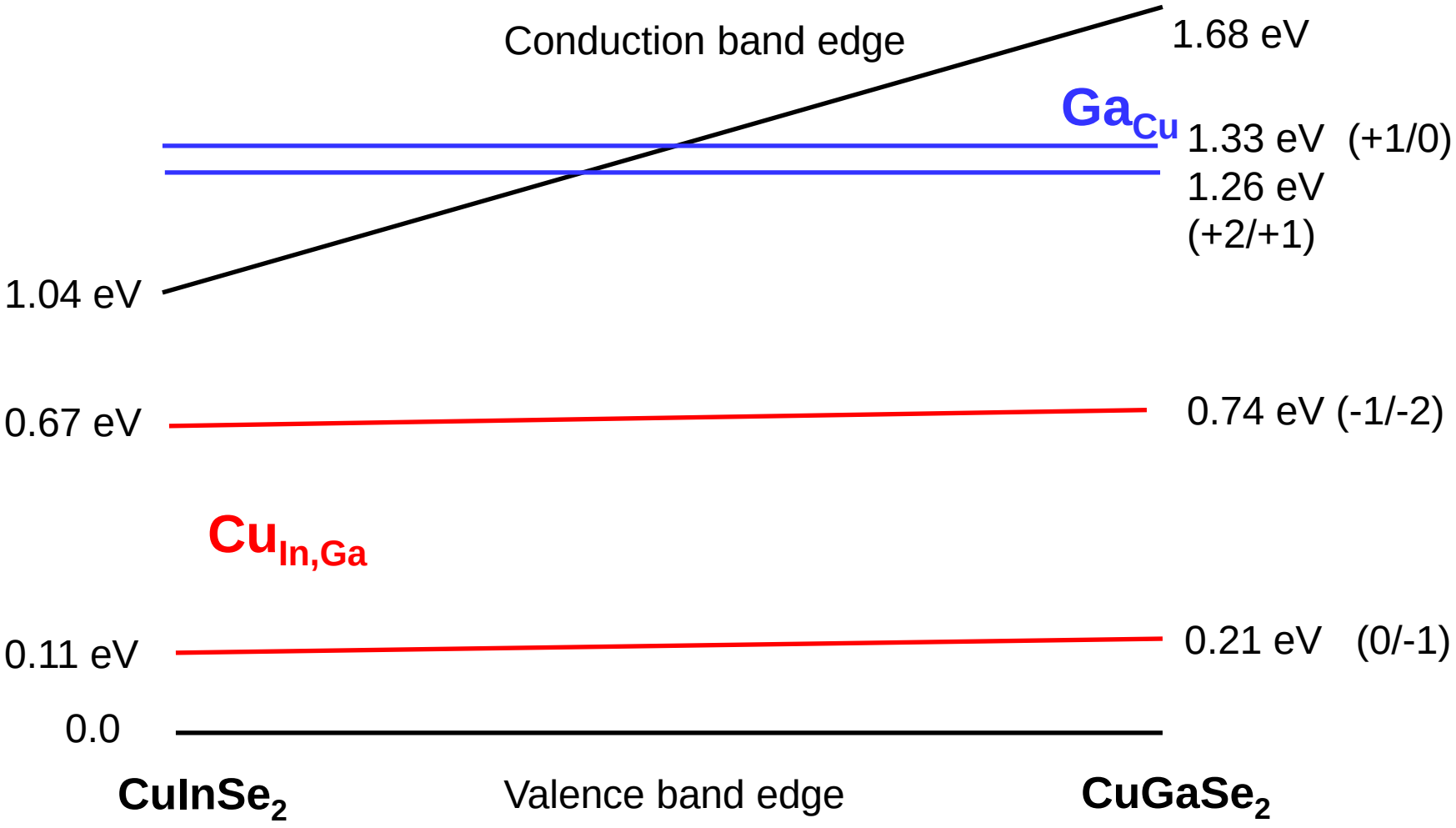

Conclusions on CIGS

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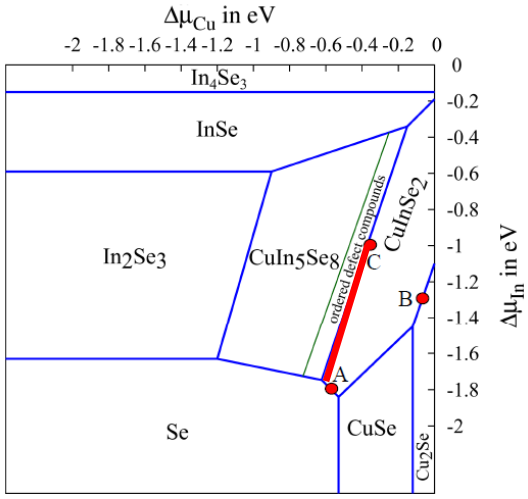
- For a typical Cu(In,Ga)Se_2 absorber with [Ga]/[Ga]+[In]=0.25, Cu_{In} and Cu_{Ga} hole traps are the most detrimental defects! Copper-rich conditions maximize the concentration of this defect.
- For [Ga]/[Ga]+[In] > 0.5, Ga_{Cu} becomes a deep minority carrier trap and can limit device efficiency.

- Optimal conditions to minimize Cu_{In} and Cu_{Ga} are located on the copper-poor side, with not too high Se/metal-ratio!



SnO_2: Intrinsic Conductivity and $p(O_2)$

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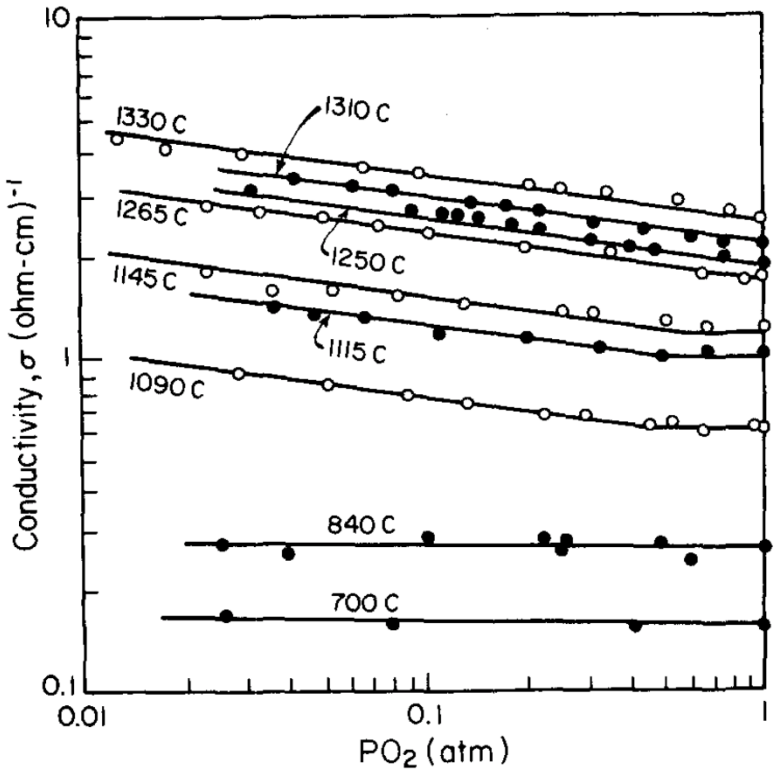

J. Appl. Phys., Vol. 44, No. 10, October 1973

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \rightleftharpoons O_O$$

$$K_O(T) = \frac{1}{P_{O_2}^{1/2}[V_O^{\bullet\bullet}][e']^2}$$

- Is standard defect chemistry correct ?
- Whats about other intrinsic defects ?

TCO: What do we expect?

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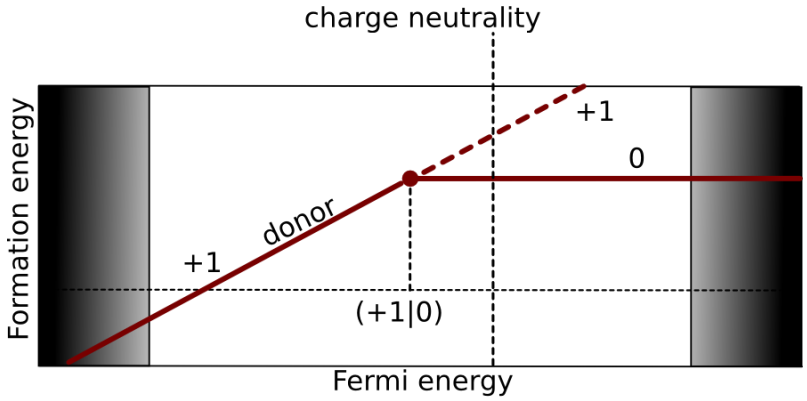
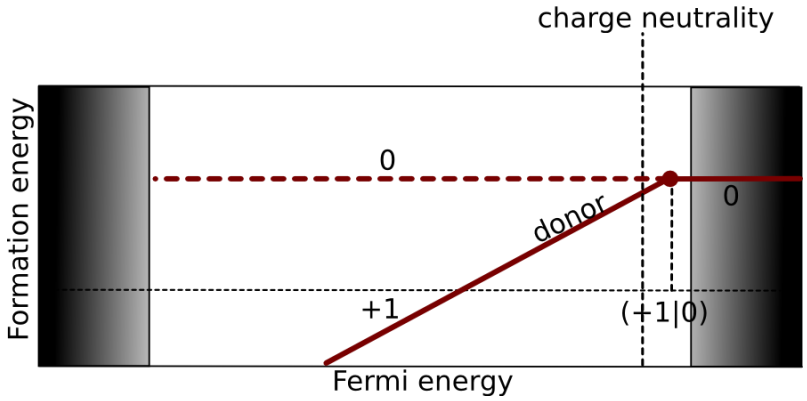
"deep" - Donor



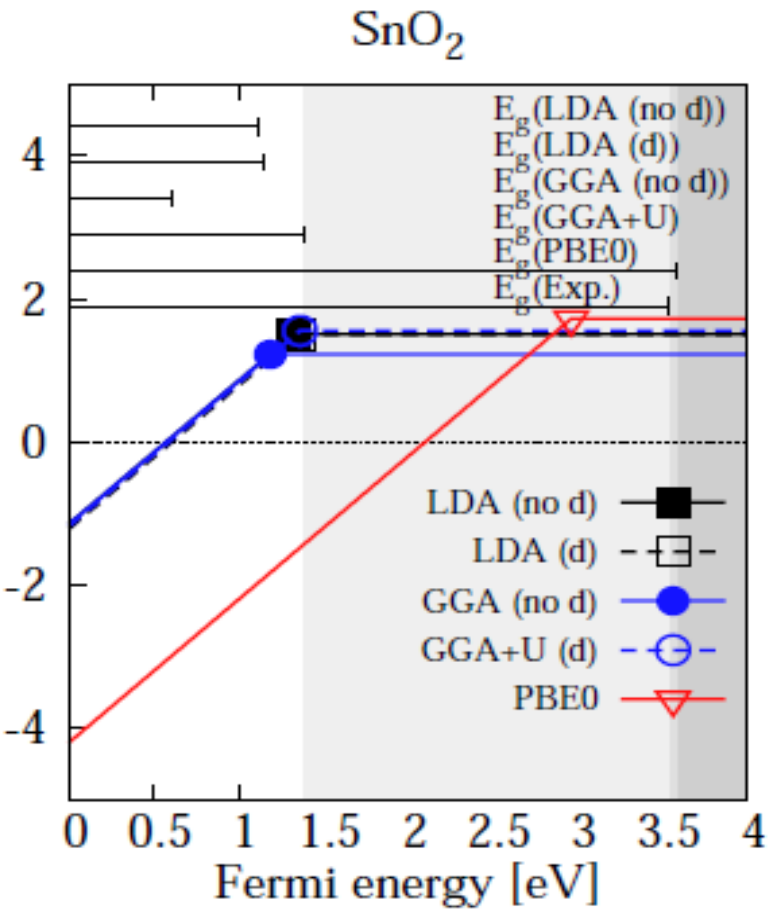
Intrinsic
n-typeTCO



"shallow" - Donor

In principle oxygen vacancies or cation interstitals can be donors

O-Vacancy



- Constant formation energies for the neutral charge state
- Strongly reduced formation energies for positive charge states
- Indium oxide and tin oxide are truly intrinsically n-type semiconductors
- The behavior is more complex for ZnO

Agoston, Albe/ Phys. Rev. Lett. **103** (2009) 245501, Phys. Rev. Lett. **106** (2011) 069602

Band Gaps and Defect States

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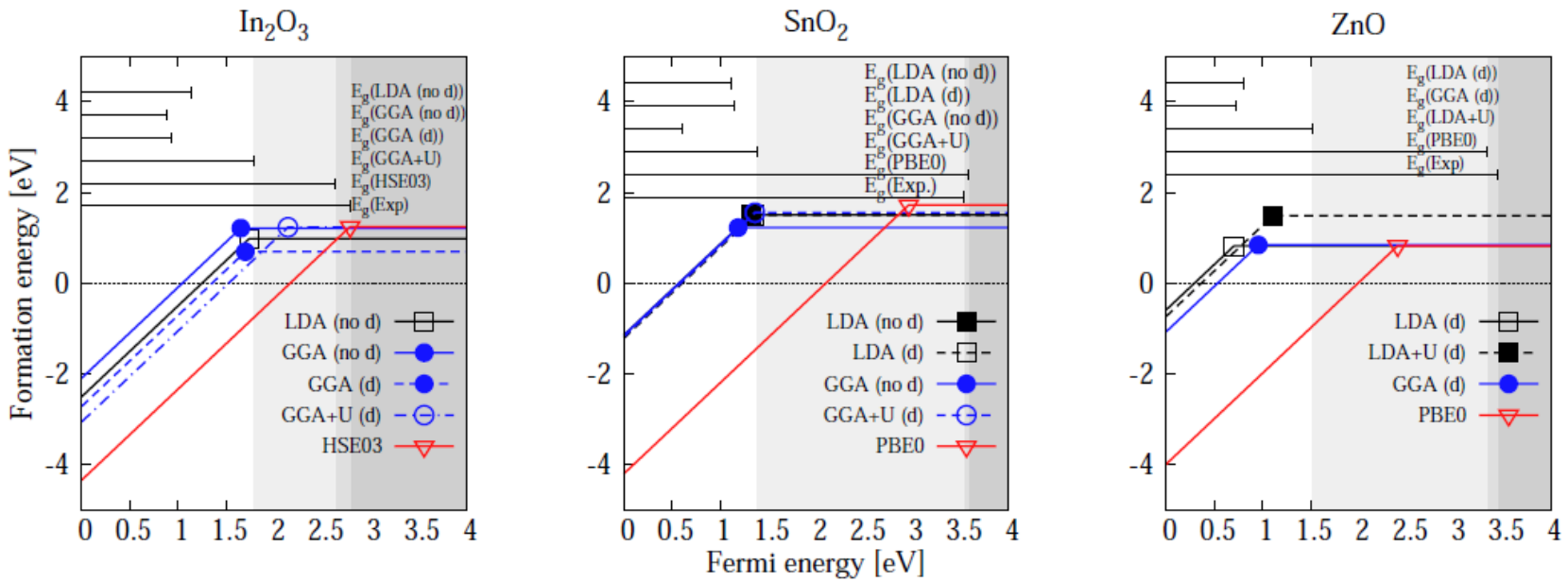

Phys. Rev. Lett. **103** (2009) 245501, Phys. Rev. Lett. **106** (2011) 069602

Acceptor Defects

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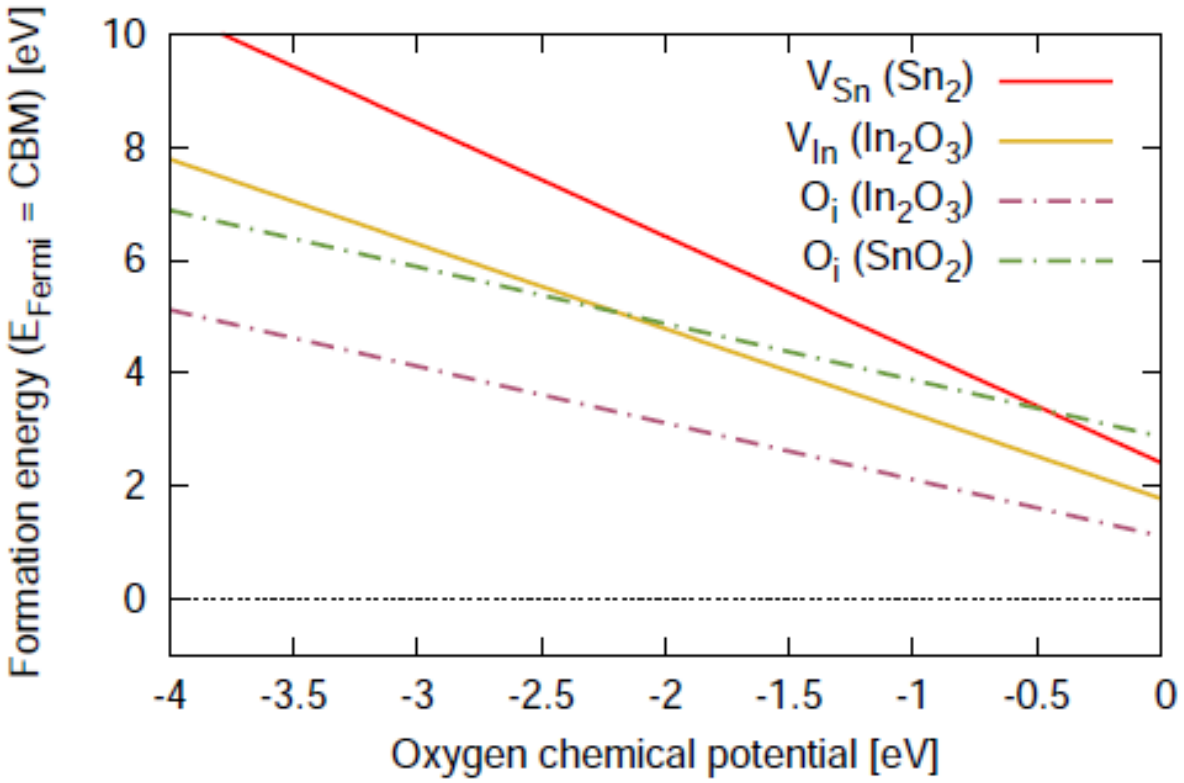

- Increased formation energies of acceptor defects in all TCOs
- Doping limits agree with experiment for In_2O_3 but not for SnO_2

SnO_2 vs. In_2O_3

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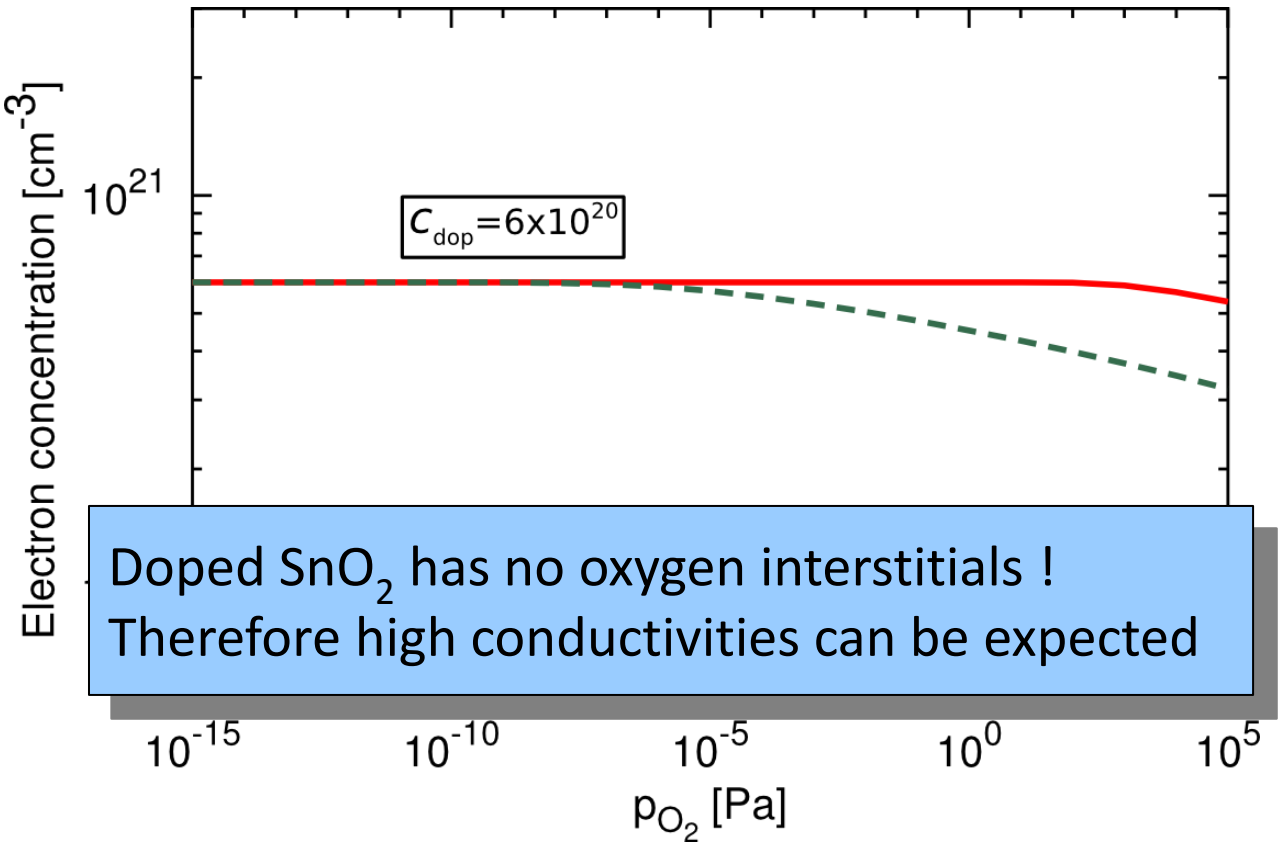

Doped SnO_2 has no oxygen interstitials !
Therefore high conductivities can be expected

P. Agoston, C. Körber, A. Klein, M. J. Puska, R. M. Nieminen and K. Albe, J. Appl. Phys
C. Körber P. Ágoston, A. Klein Sensors and Actuators B 139 2 665-672 (2009)

Diffusion: Migration Barriers

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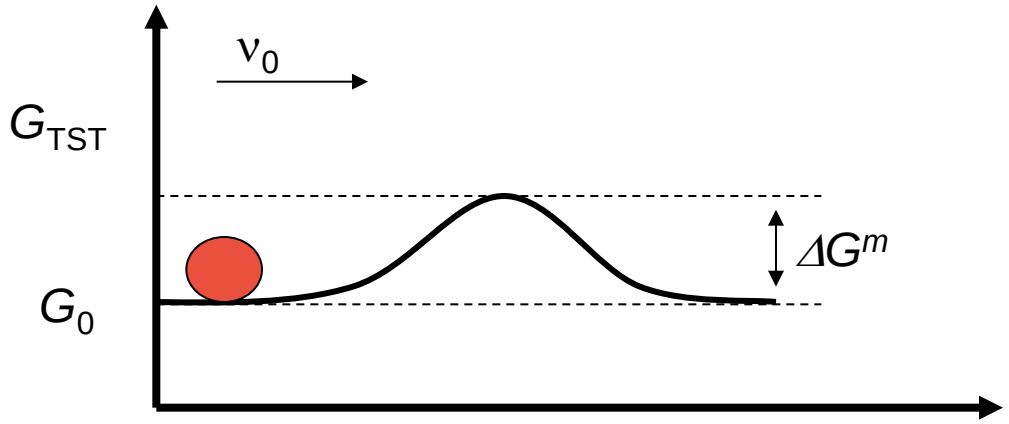
$$D^* = \underbrace{\nu_0 \cdot \lambda^2 \cdot f \cdot \exp\left(\frac{\Delta S^f + \Delta S^m}{k}\right)}_{D_0} \cdot \exp\left(\frac{\Delta H^f(E_f, p^{O_2}) + \Delta H^m(E_f)}{kT}\right)$$



Point defects in ZnO: Kinetics

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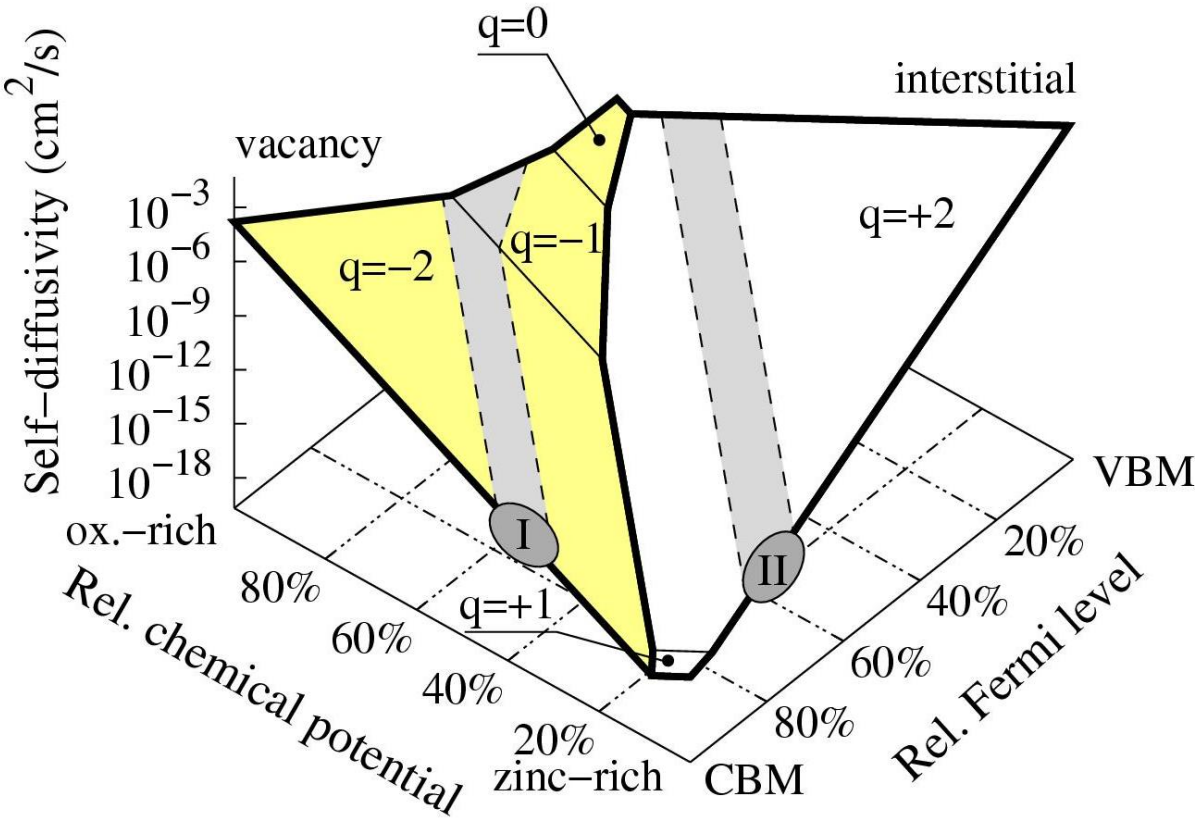

Appl. Phys. Lett.
88, 201918 (2006)

Materials by Design

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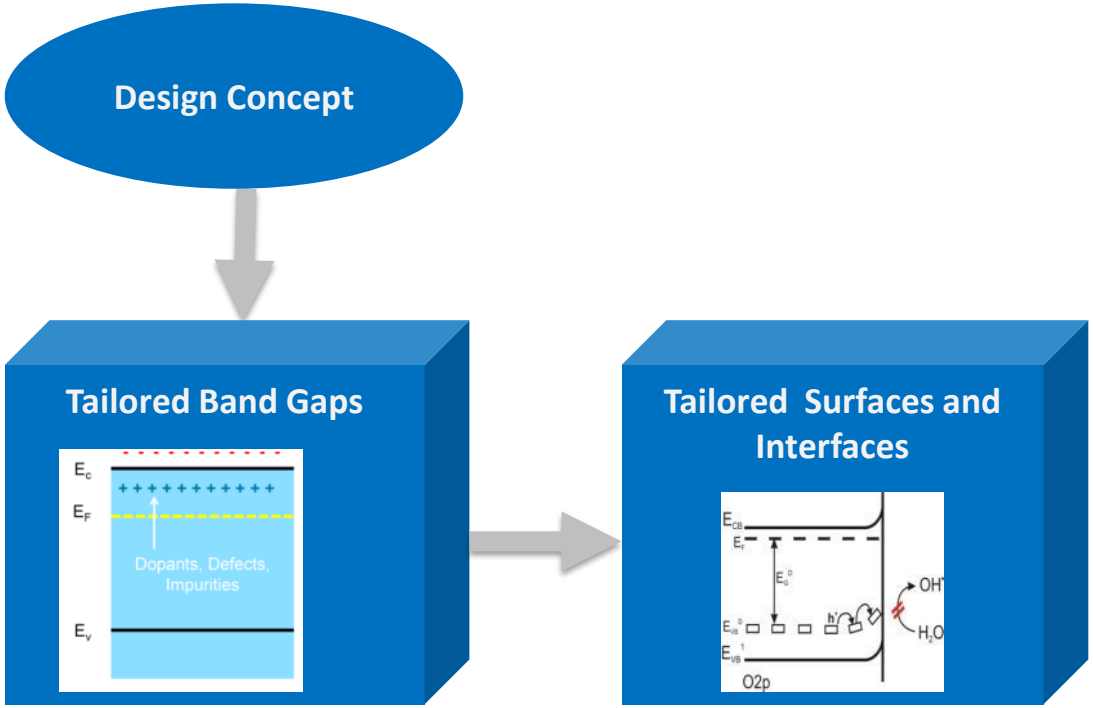

ITO-(001)

Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

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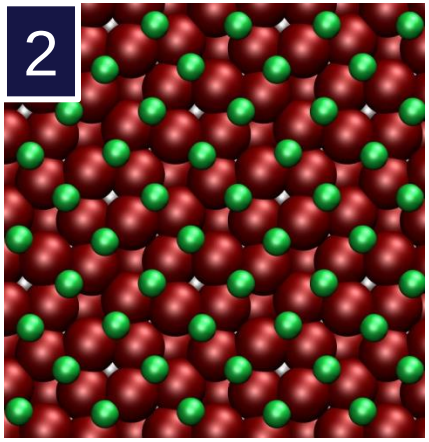

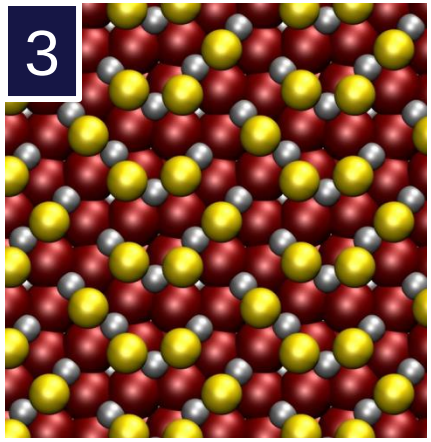

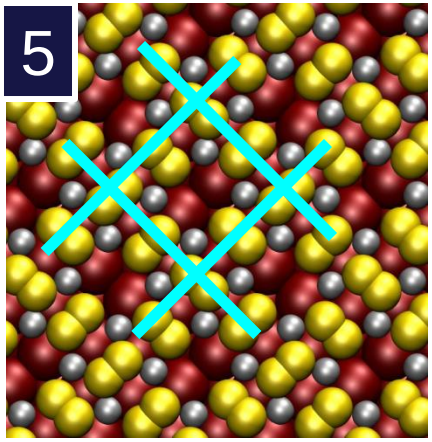

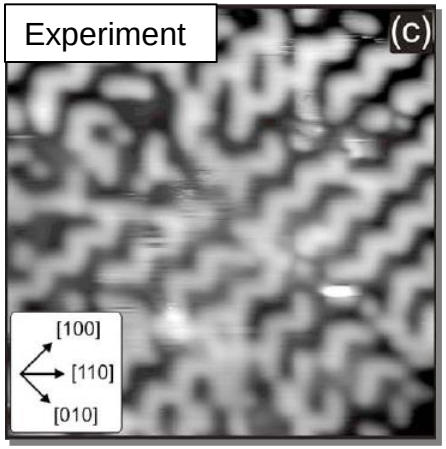

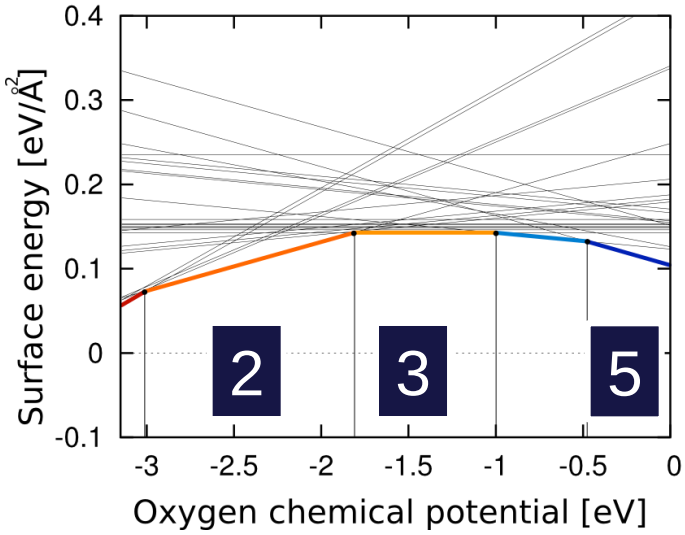

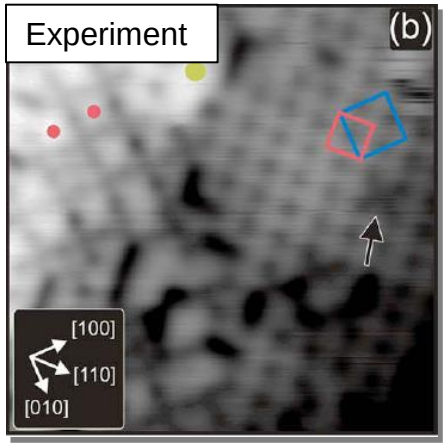

E. Morales, U. Diebold, Appl. Phys. Lett. , **139**, 665-672 (2009)

In_2O_3-(001)

Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

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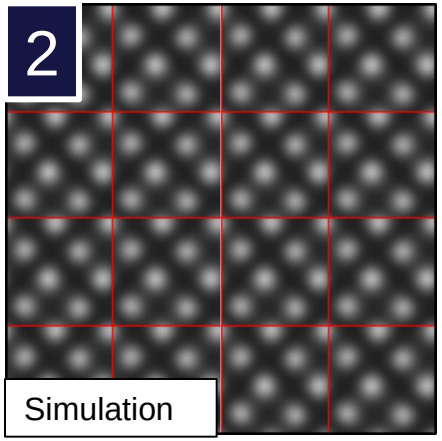

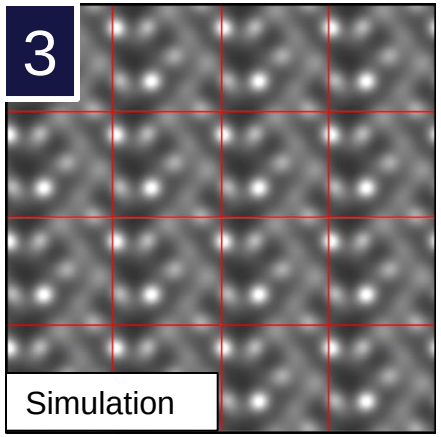

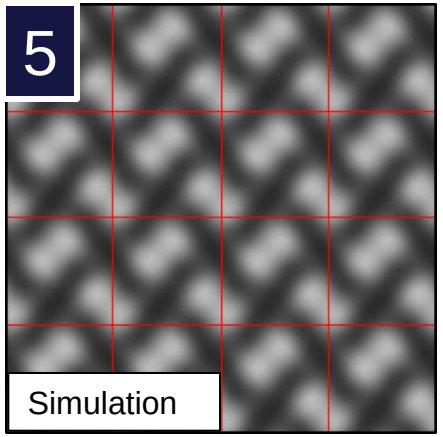

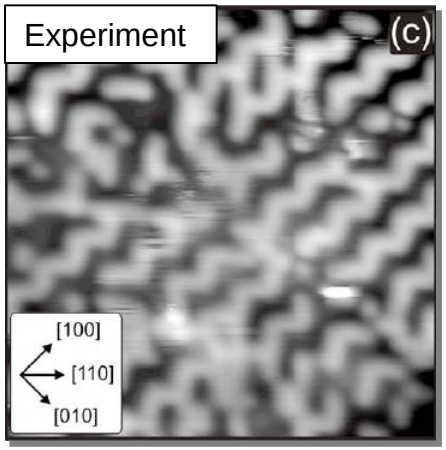

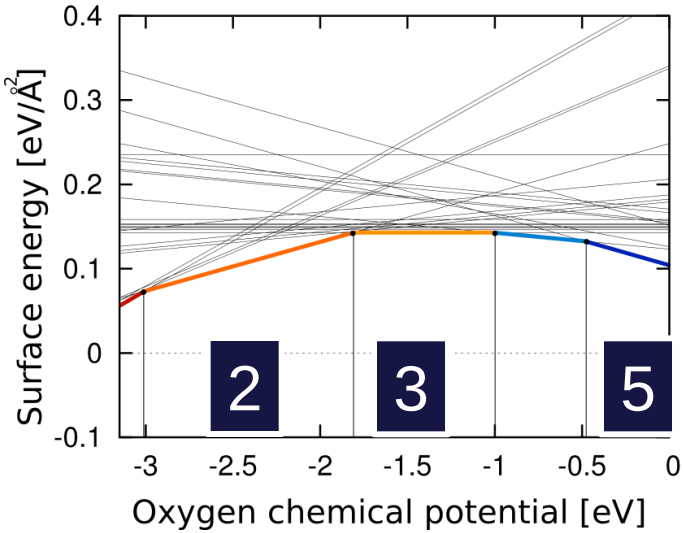

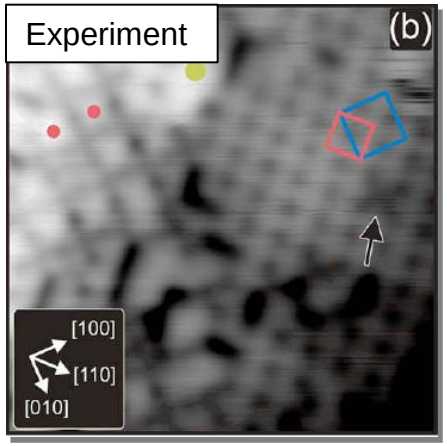

In_2O_3-(001)

Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

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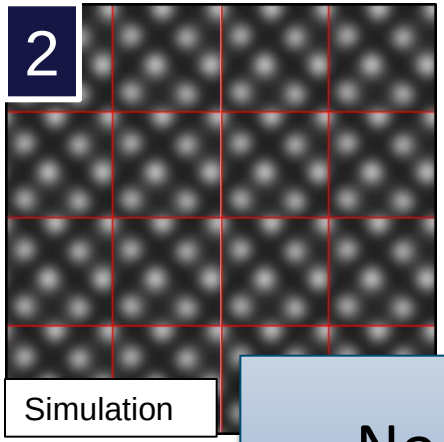
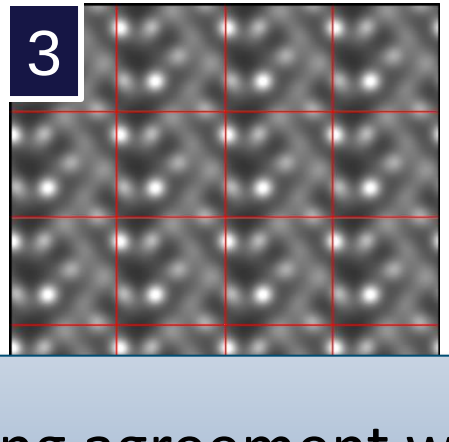
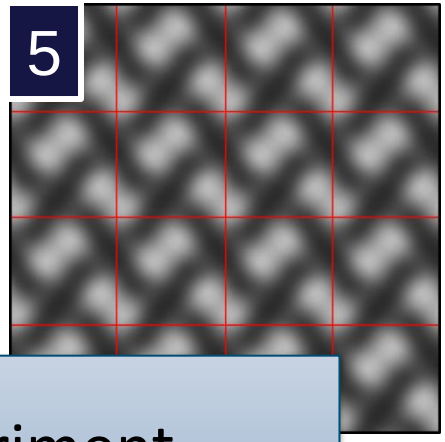


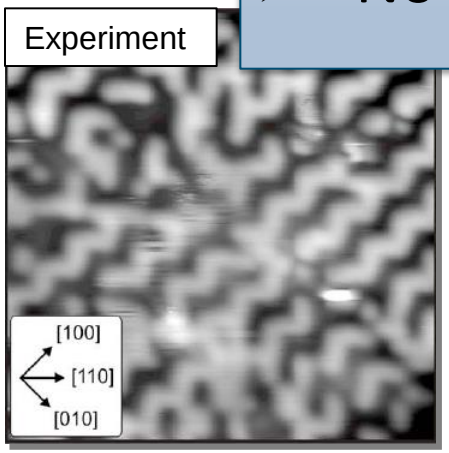


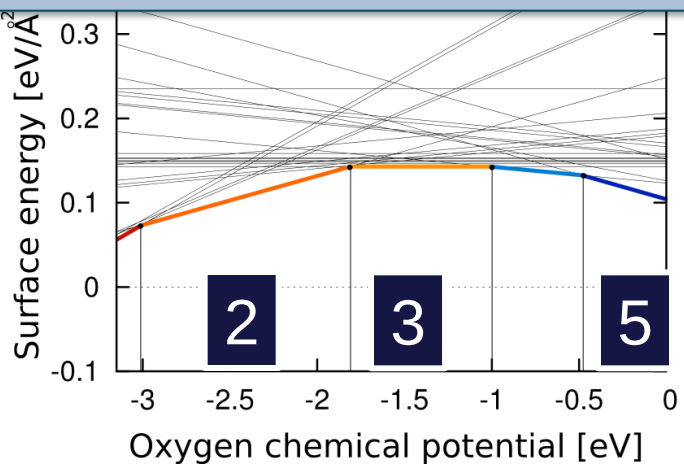


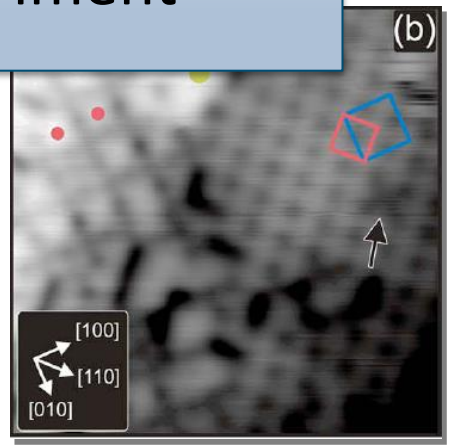
Simulation

Experiment

- No compelling agreement with experiment







Doping Effect

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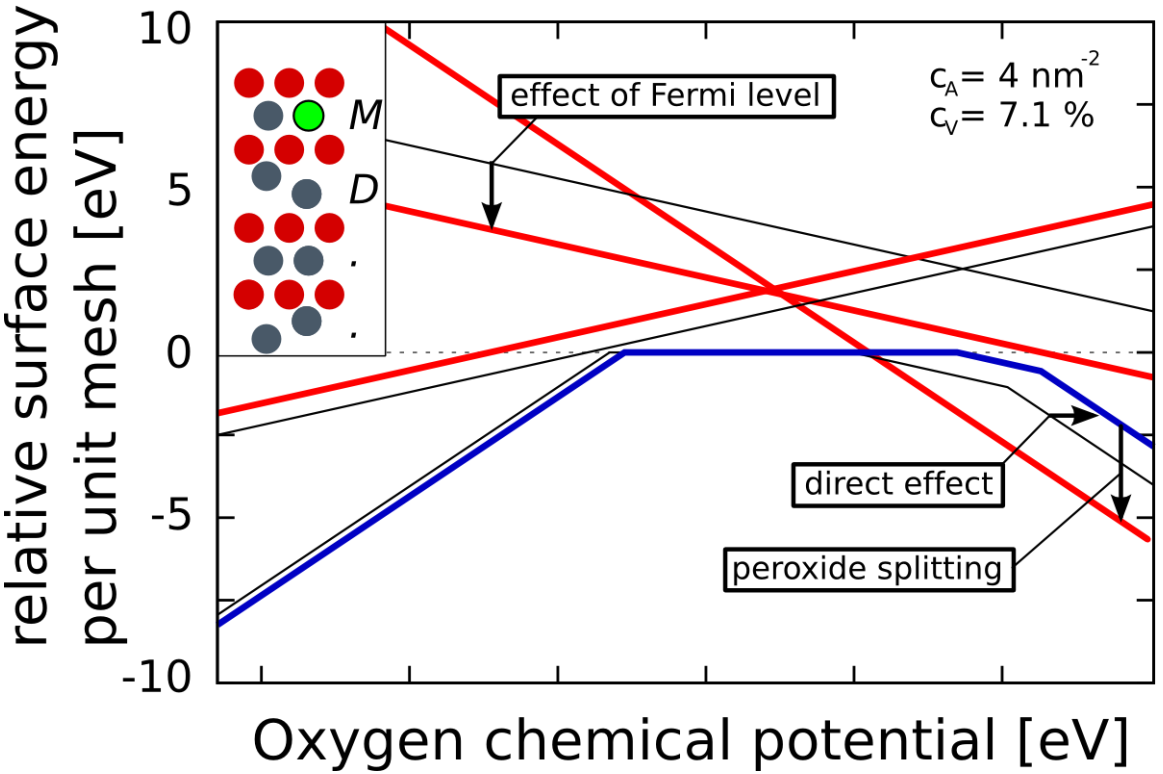

- Peroxide splitting highly favorable

ITO-(001)

Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

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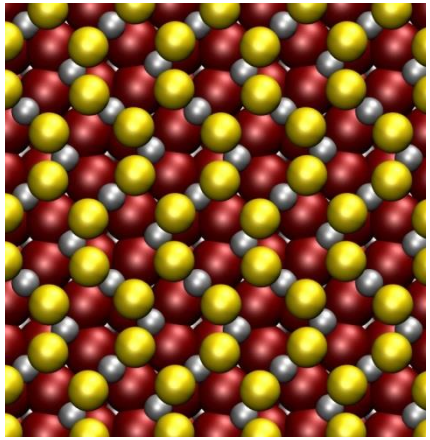
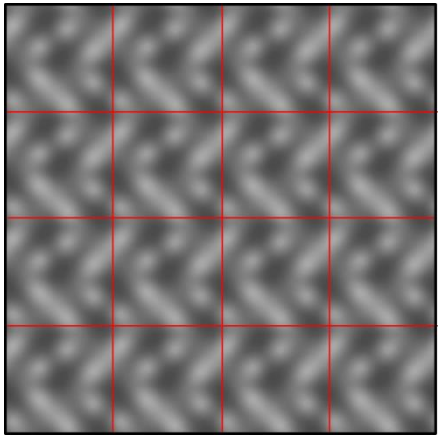
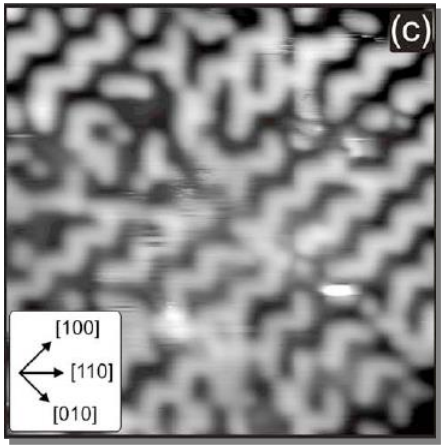

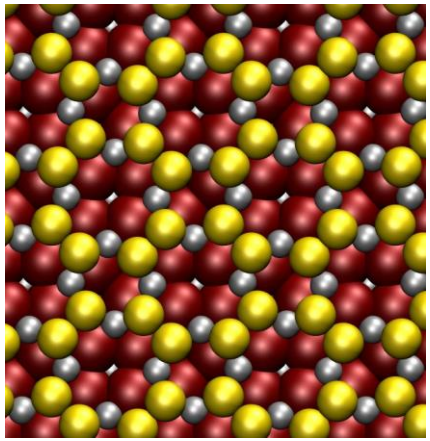
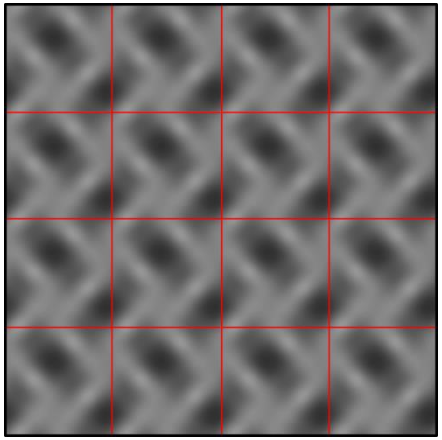
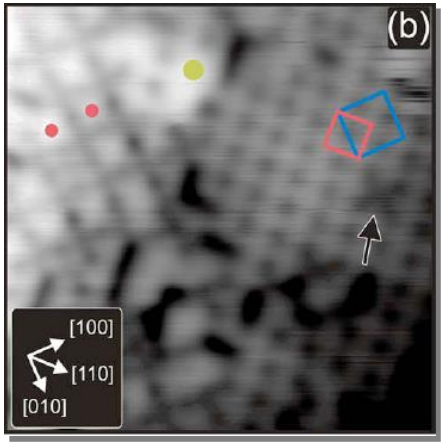

Simulation

Experiment

P. Agoston, K. Albe, Phys. Rev. B **84**, 045311 (2011)

ITO-(001)

Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

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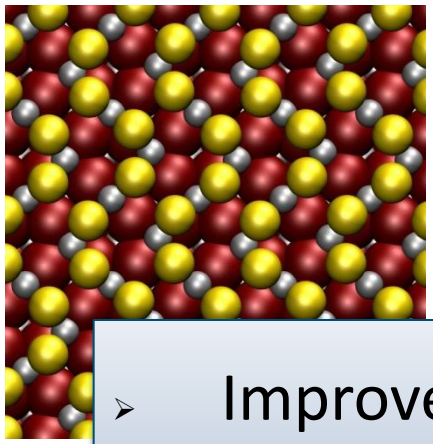

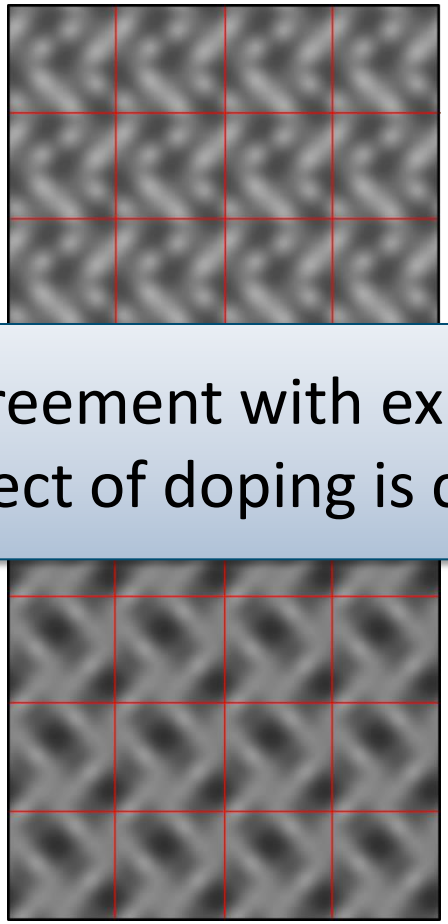

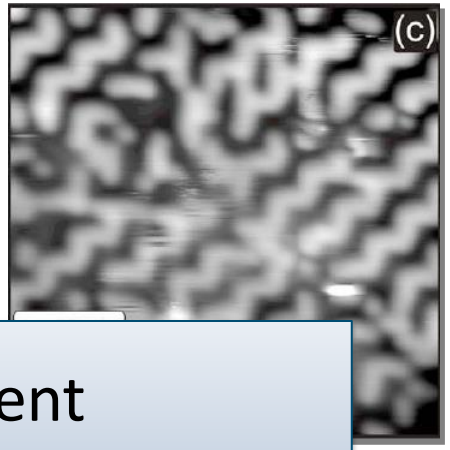

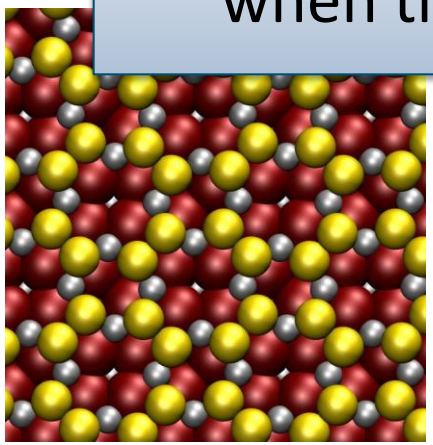

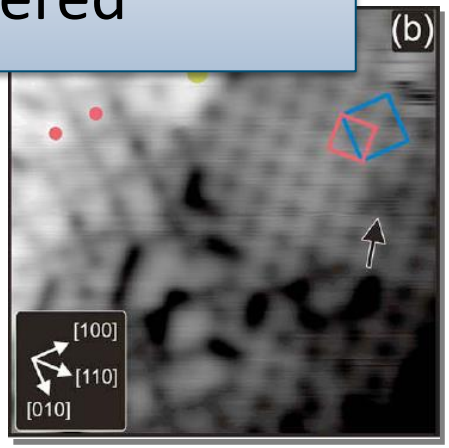

- Improved agreement with experiment when the effect of doping is considered

Thermodynamics of Nanomaterials

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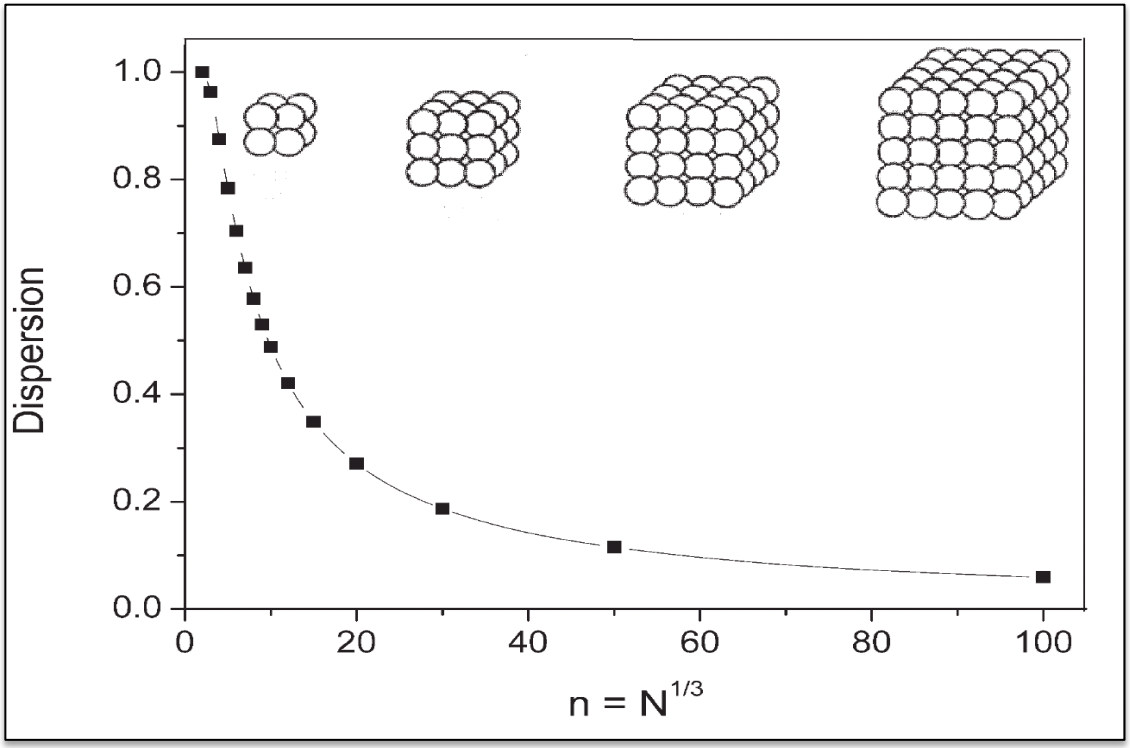
$$F = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{N^{1/3}}\left(1 - \frac{2}{N^{1/3}} + \frac{8}{6N^{2/3}}\right) \approx \frac{6}{N^{1/3}}$$



Materials by Design

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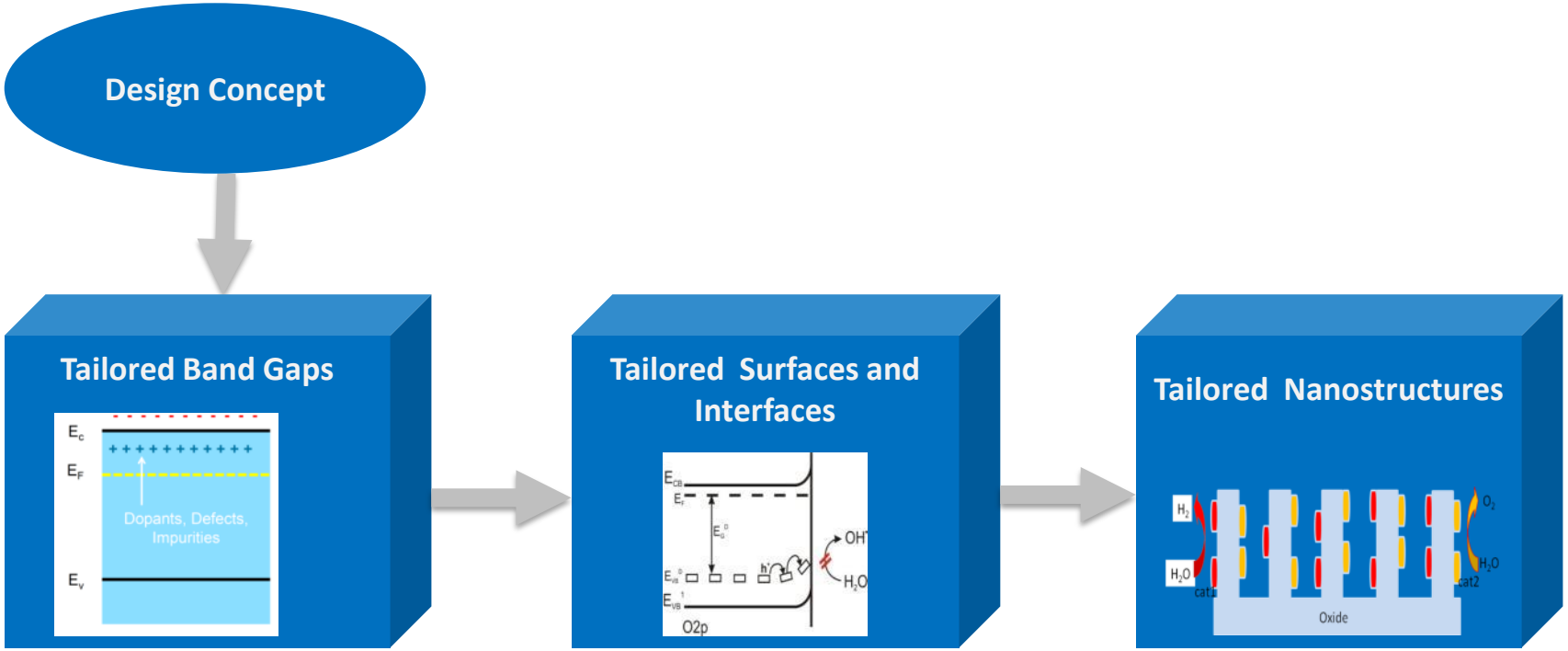

Volume Strain by Surface Stresses

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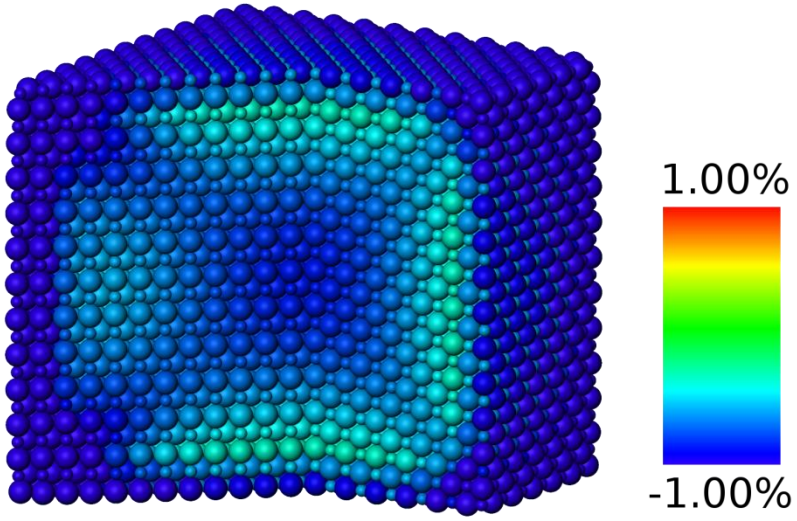
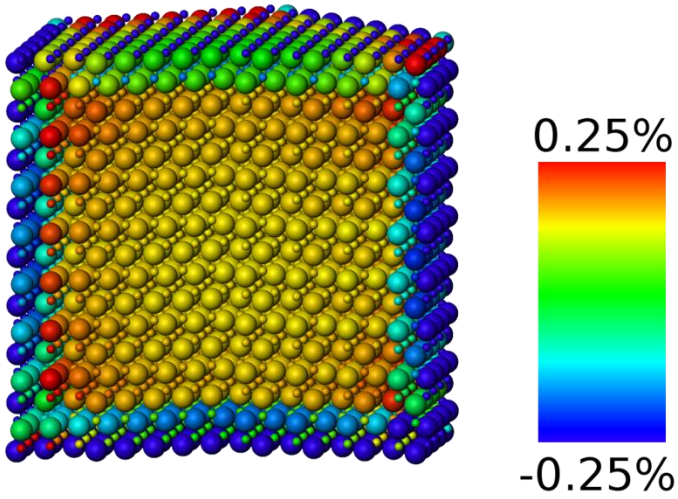
MgO (compressive):



GaN (tensile)

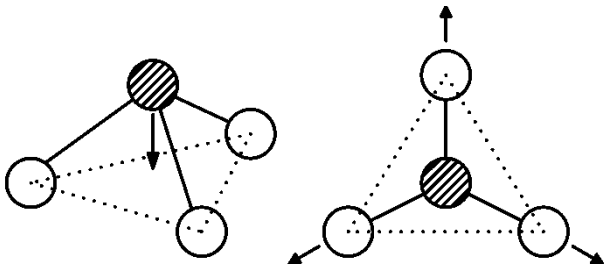


CHEMPHYSCHEM MINIREVIEWS

DOI: 10.1002/cphc.201200257

Size-Dependent Lattice Expansion in Nanoparticles: Reality or Anomaly?

P. Manuel Diehm,* Péter Ágoston, and Karsten Albe[a]



Surface Energy vs. Surface Stress

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Surface Energy γ

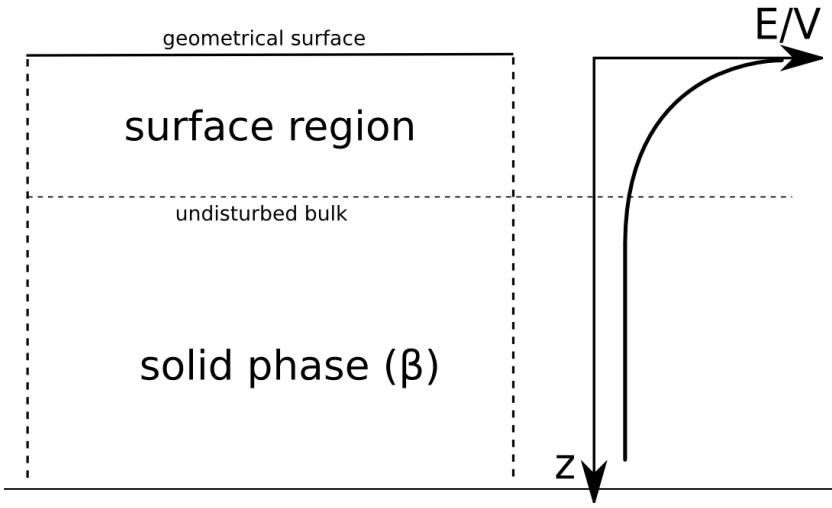
Work required to produce extra surface

$$dW = \gamma dA$$

Surface Stress f_{ij}

Work required to enlarge/minimize existing surface

$$dW = d(\gamma A) = f_{ij} A d\varepsilon_{ij}$$



$$f_{ij} = \frac{1}{A}\frac{d(\gamma A)}{d\varepsilon_{ij}}$$

$$f = \gamma + \frac{d\gamma}{d\varepsilon}$$

Calculated Surface Stresses (DFT)

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Material	Surface	Condition	x-direction	y-direction	γ	f_x	f_y
						(eV Å^{-2})	
hex-Si	(0001)		$\langle 1\bar{1}00 \rangle$	$\langle 1\bar{2}10 \rangle$	0.114	-0.045	-0.039
	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.086	-0.065	-0.032
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.097	-0.043	-0.030
hex-C	(0001)		$\langle 1\bar{1}00 \rangle$	$\langle 1\bar{2}10 \rangle$	0.419	0.003	0.029
	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.184	-0.160	0.056
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.227	-0.337	0.020
GaN	(1100)		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.125	-0.106	-0.055
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.133	-0.031	-0.030
ZnO	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.075	-0.088	-0.059
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.079	-0.011	-0.038
BeO	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.109	-0.089	-0.054
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.113	-0.039	-0.044
MgO	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.073	0.223	0.223
CdO	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.051	0.210	0.210
KF	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.016	0.037	0.037
CsF	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.011	0.033	0.033
CsCl	(110)		$\langle 110 \rangle$	$\langle 100 \rangle$	0.014	0.058	-0.002
c-$SrTiO_3$	(001)	SrO-termination	$\langle 100 \rangle$	$\langle 100 \rangle$	0.166	0.116	0.116

Lattice Expansion

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Material	Max. change (%)	Size (nm)	Method
CeO_2	−0.32	5 - 1200	XRD
	+0.15	5 - 1200	XRD
	+0.33	5 - 60	XRD
	+0.45	6 - 25	XRD
	+1.85	15 - 30	XRD
	+2.6	2.1 - 6.7	ED
	+3.51	3 - 30	XRD
	+3.7	3 - 20	ED
	+6.8	2.2 - 11.8	ED
rutile-TiO_2	$\vec{a}$: +0.50, $\vec{c}$: −0.09	5 - 25	XRD
	V/V_0: +1.40	5 - 20	XRD
anatase-TiO_2	$\vec{a}$: +0.37, $\vec{c}$: −0.53	2 - 65	XRD
	$\vec{a}$: +0.31, $\vec{c}$: −0.34	5 - 40	XRD
	$\vec{a}$: −0.08, $\vec{c}$: −0.29	5 - 35	XRD
MgO	+0.12	10 - 50	XRD
	−0.07	9 - 15	XRD
t-$BaTiO_3$	$\vec{a}$: +2.76, $\vec{c}$: −0.12	100 - 350	ED
t-$BiFeO_3$	$\vec{a}$: +0.23, $\vec{c}$: −0.47	11.0 - 86.4	XRD
t-$PbTiO_3$	$\vec{a}$: +0.46, $\vec{c}$: −1.44	28 - 149	XRD
c-$PbTiO_3$	+0.05	28 - 149	XRD
c-$SrTiO_3$	+0.28	12 - 40	XRD
$MnCr_2O_4$	+0.76	11 - 18	XRD
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	+0.36	10 - 230	XRD
ZnO	$\vec{a}$: +0.47, $\vec{c}$: +0.85	≈ 10	ED
	$\vec{a}$: +0.34, $\vec{c}$: +0.59	11.7	XRD
	$\vec{a}$: +0.04, $\vec{c}$: +0.15	50 - 800	XRD
SnO_2	$\vec{a}$: +0.32, $\vec{c}$: +0.58	2.5 - 9.0	XRD
$LiCoO_2$	$\vec{a}$: +0.46, $\vec{c}$: +0.93	10 - 30	XRD
$CaWO_4$	V/V_0: +0.65	5 - 30	XRD

Material	Max. change (%)	Size (nm)	Method	Source
NaCl	−0.33	4.8 - 15	ED	[40]
KCl	−0.69	1.8 - 15	ED	[40]
NaBr	−0.82	3.5 - 15	ED	[40]
LiF	−0.87	3.2 - 9	ED	[40]
Pt	−0.42	3.8 - 12.2	ED	[13]
Au	−0.69	1.8 - 15	ED	[40]
	−0.27	3.5 - 12.5	ED	[11]
Ag	−3.08	3 - 17.8	ED	[12]
Cu	−2.09	2.4 - 9.2	ED	[13]
Bi	−2.34	3.5 - 10	ED	[40]
Ni	+0.49	18.6 - 51.3	XRD	[41]
Si_xGe_{1-x}	+1.5	7 - 35	ED	[42]

Stress Distribution: MD vs. FEM

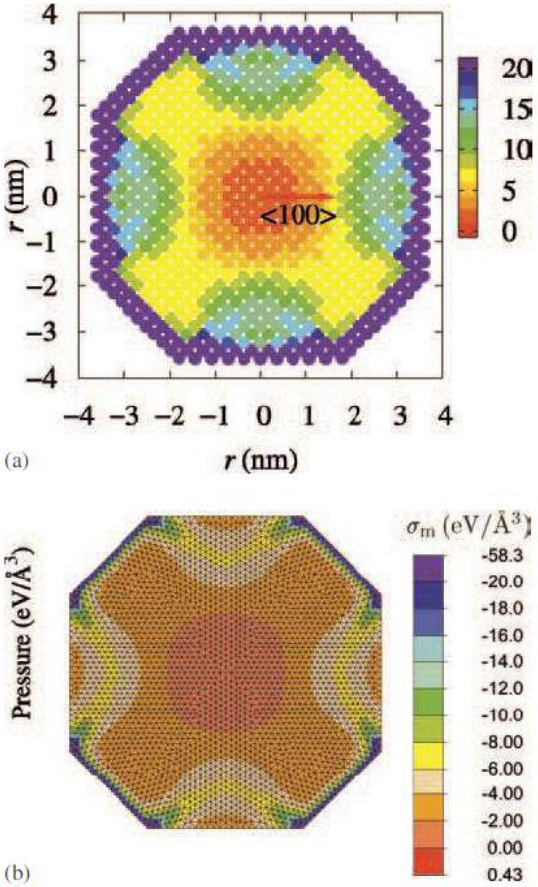

Fig. 3. Hydrostatic stress in a Cu nanoparticle: (a) the atomistic simulation results, (b) the finite element computations.

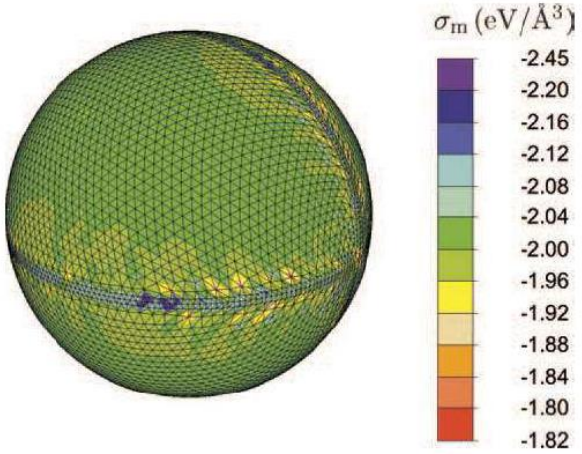

Fig. 2. Hydrostatic stress in a spherical particle.

Int. J. Mat. Res. (formerly Z. Metallkd.) 102 (2011) 6

Ab-initio Phase Diagrams

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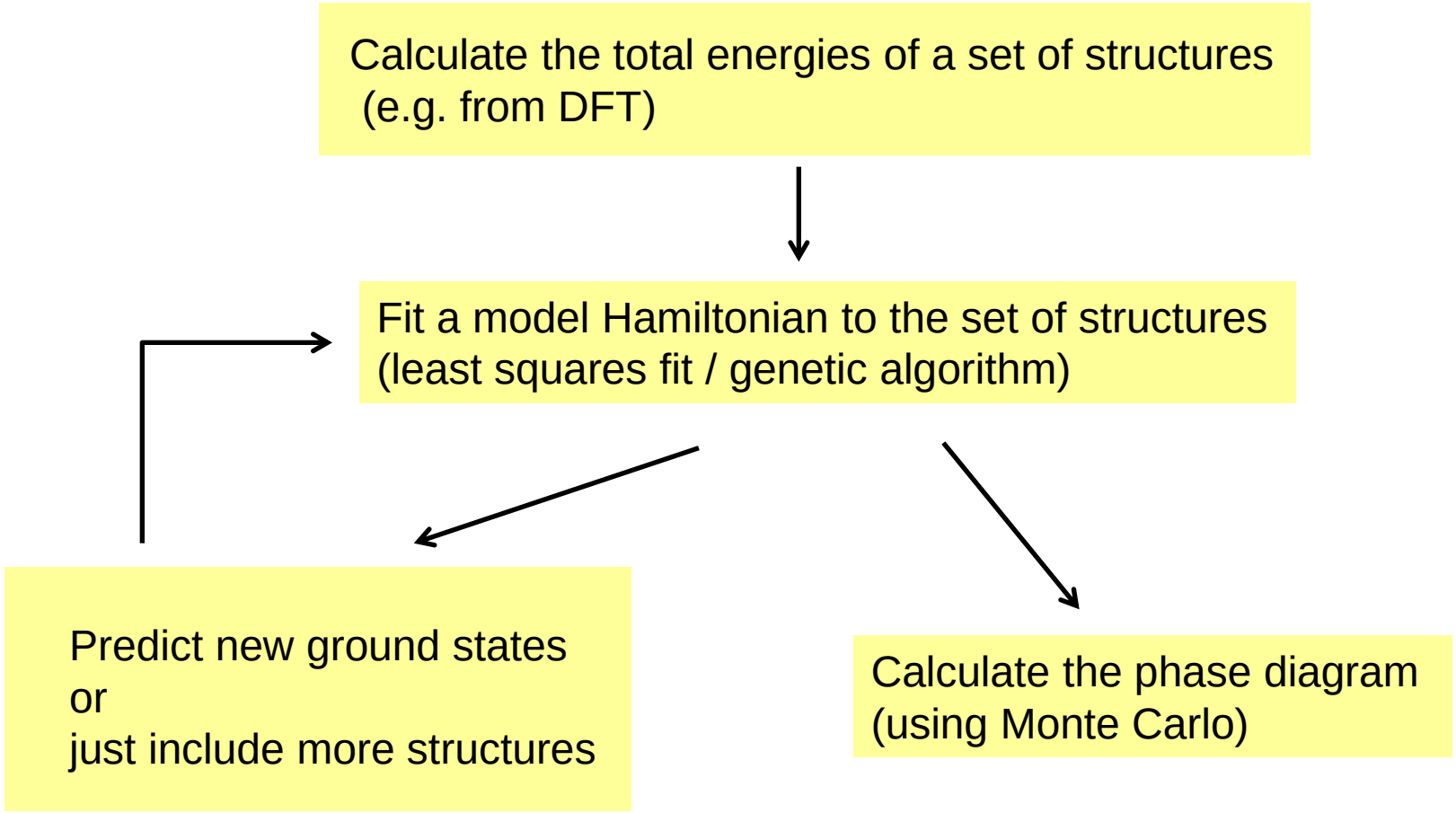

BOS-Model

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How to calculate the energy of a binary alloy system with two species A and B?

Refined Bond Order Simulation Mixing model (BOS: Zhu, dePristo 1995)

$$\epsilon_Z^A(M_n) = \epsilon_Z^A + \frac{1}{2}\sum_{n=1}^{4} M_n \Delta E_n^{AB} + \frac{1}{2} M_1 (M_1 - 1)\lambda_1^A$$

where

ϵ_Z^A is the site energy of an atom of species A with coordination Z

M_n is the number of odd neighbors in the n-th shell

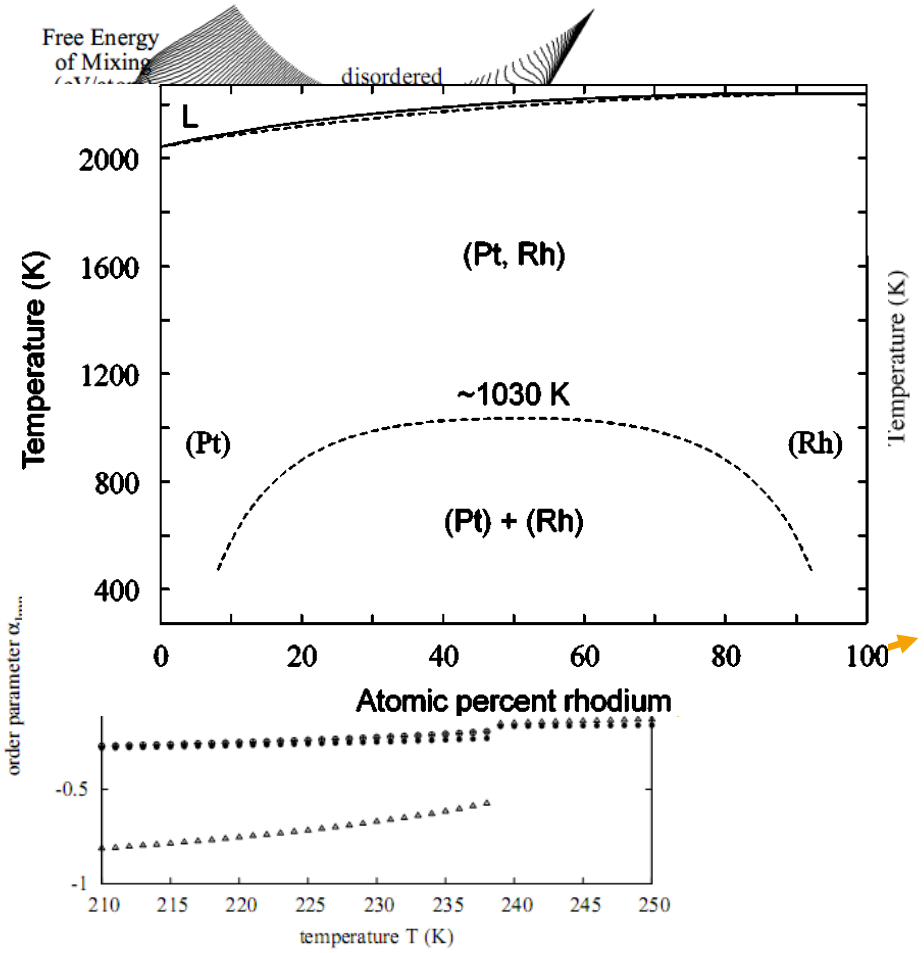
ΔE_n^{AB} is the difference in the site energy when changing a n-th neighbor to odd species

λ_1^A is an asymmetry parameter (asymmetry considered for nearest neighbors only)

(for species B replace $\epsilon_Z^A \rightarrow \epsilon_Z^B$ and $\lambda_1^A \rightarrow \lambda_1^B$)

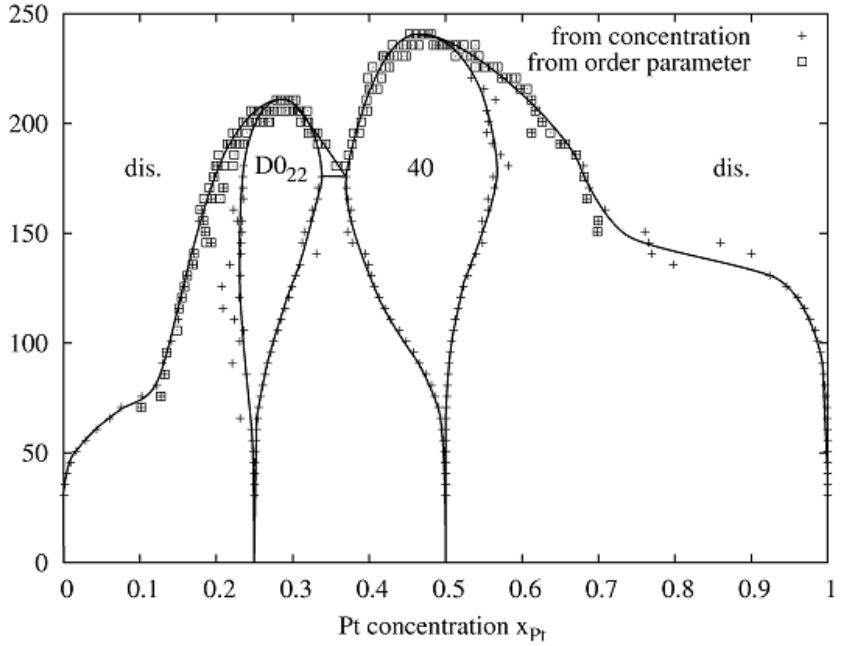
(Pohl, Albe, Acta Materialia **57**, 4140 (2009))

Bulk Phase Diagram Pt-Rh



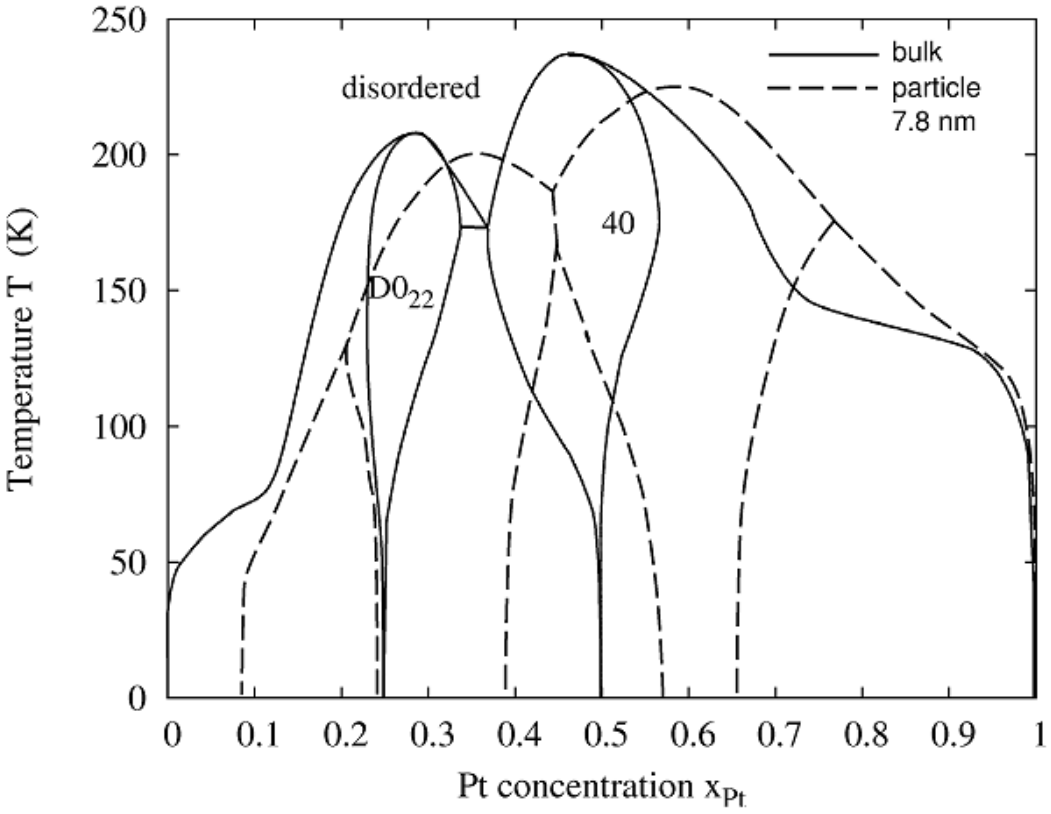
Warren-Cowley Short Range Order Parameters

Theoretical Pt-Rh Bulk phase diagram



(Pohl, Albe, ACTA MAT 57, 4140 (2009))

Nanophase diagram



Effects for shrinking particle size:

- ordering temperature sinks
- concentration stability range of some ordered phases broadens
- stable phases shift towards higher concentrations of segregating species (Pt)
- two-phase regions shrink

Beilstein J. Nanotechnol. **2012,** *3,* 1–11.

2 % Pt, Diameter 7.8 nm

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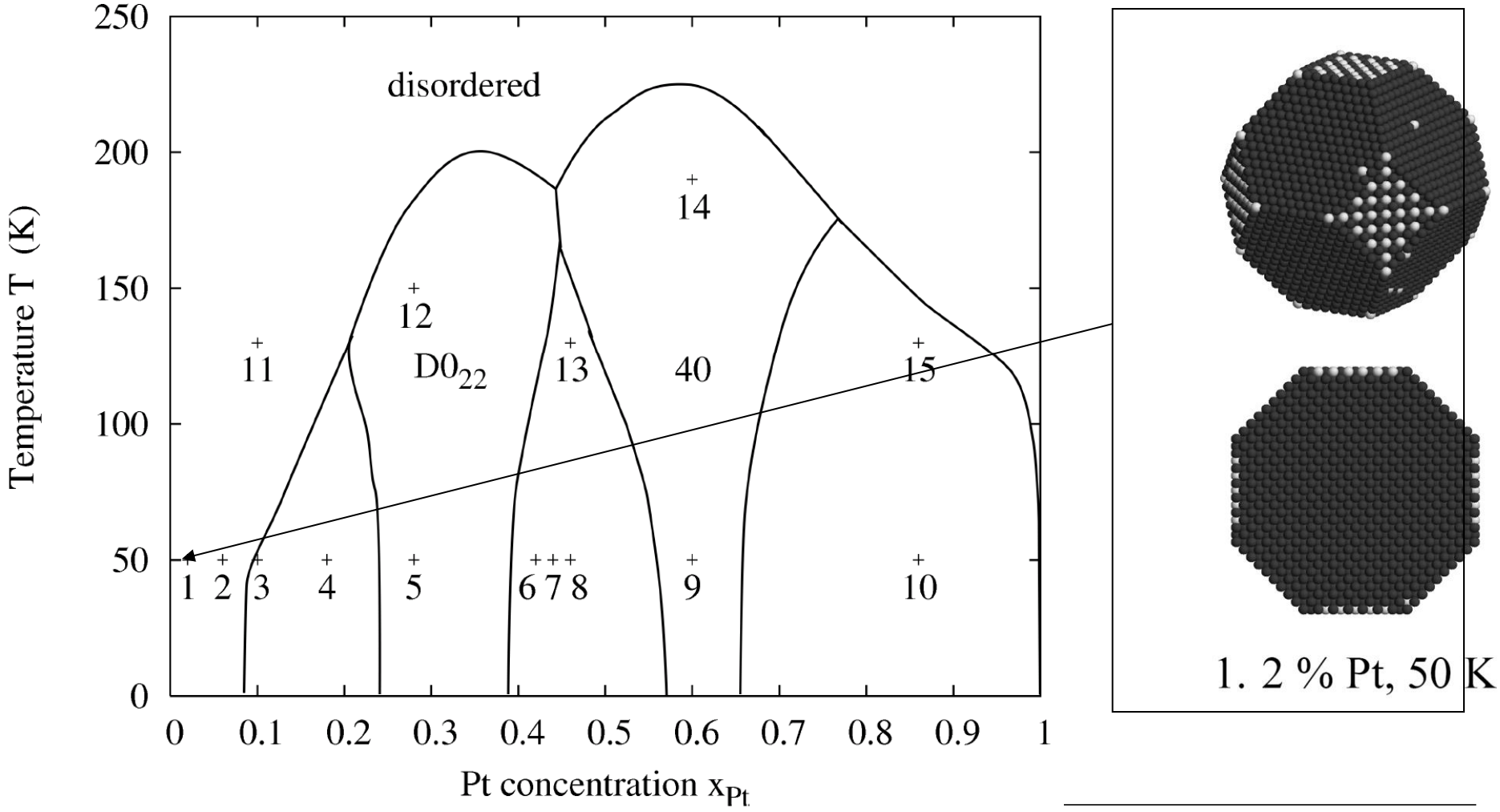

6 % Pt

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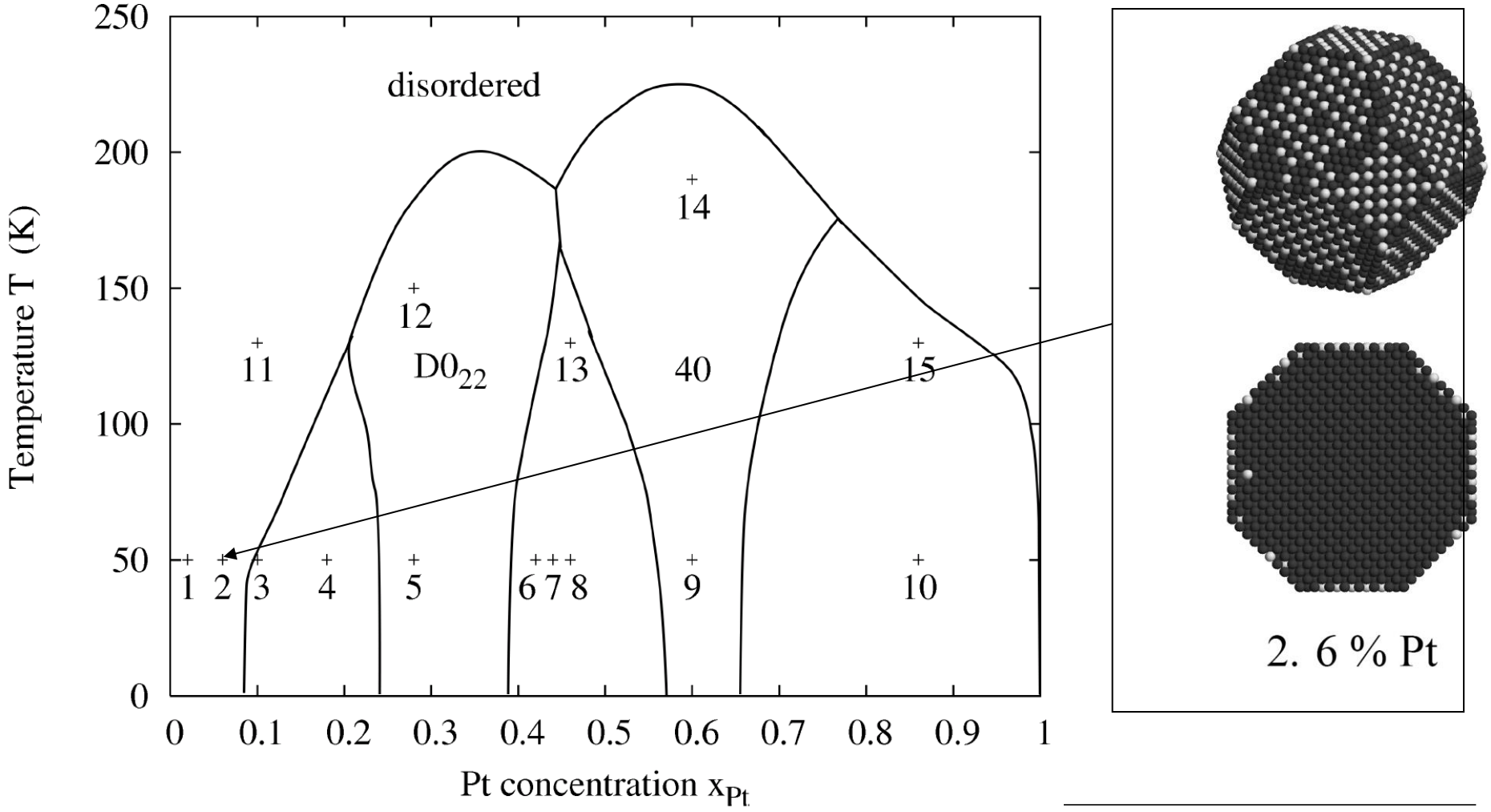

10 % Pt

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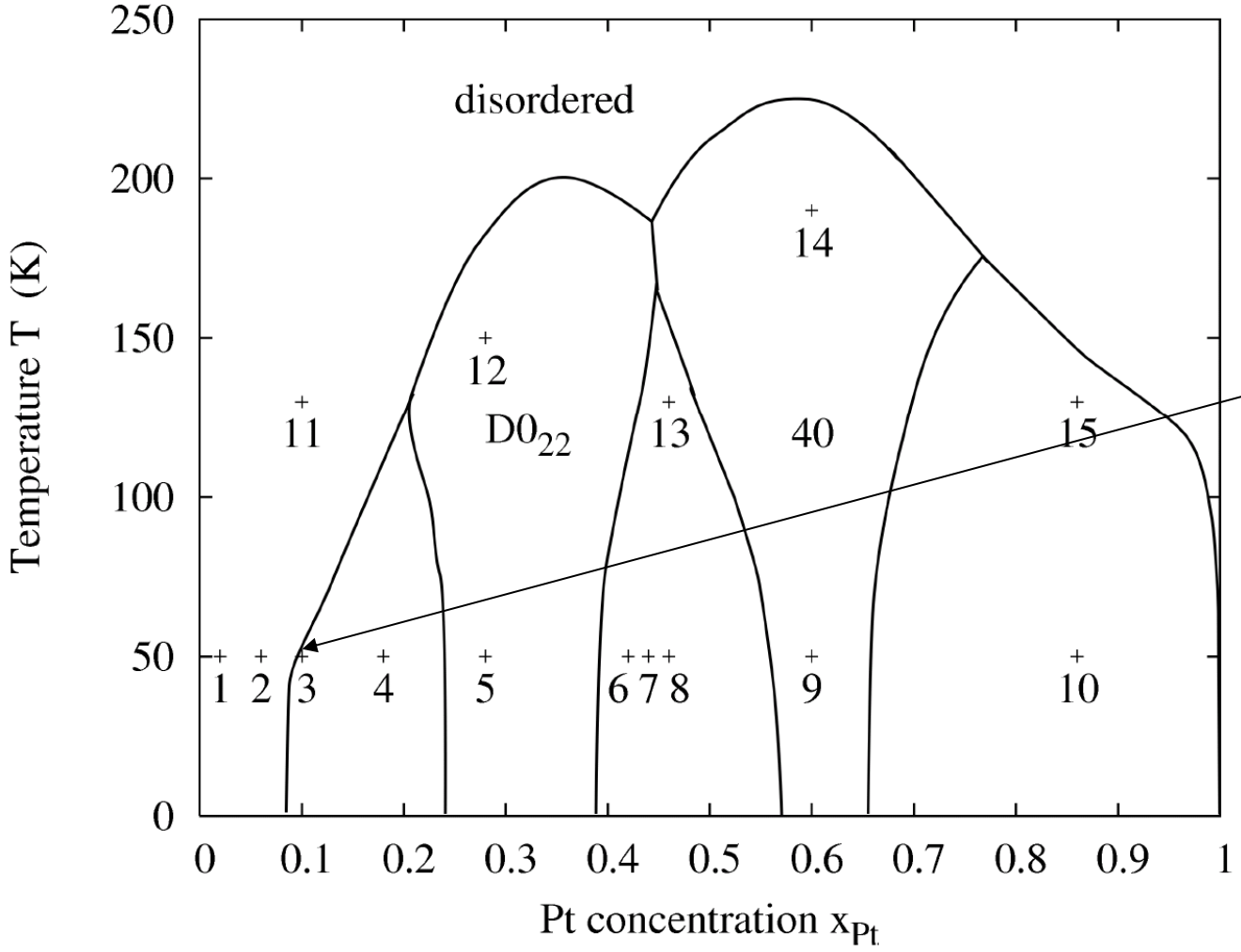

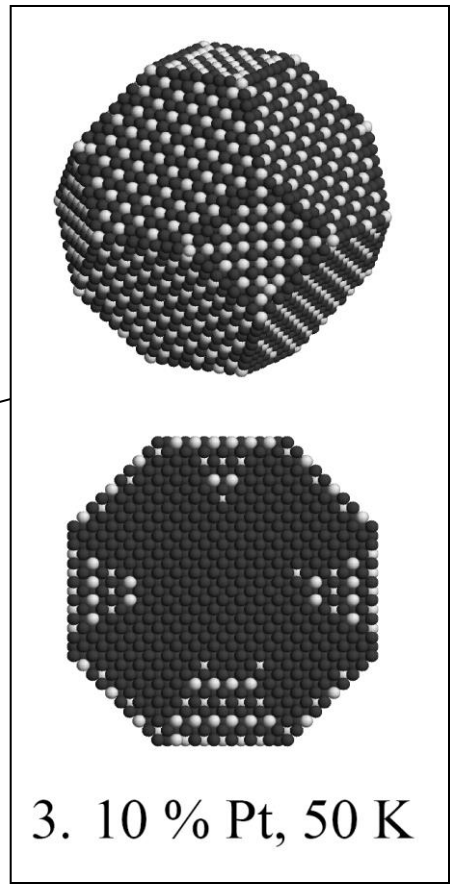

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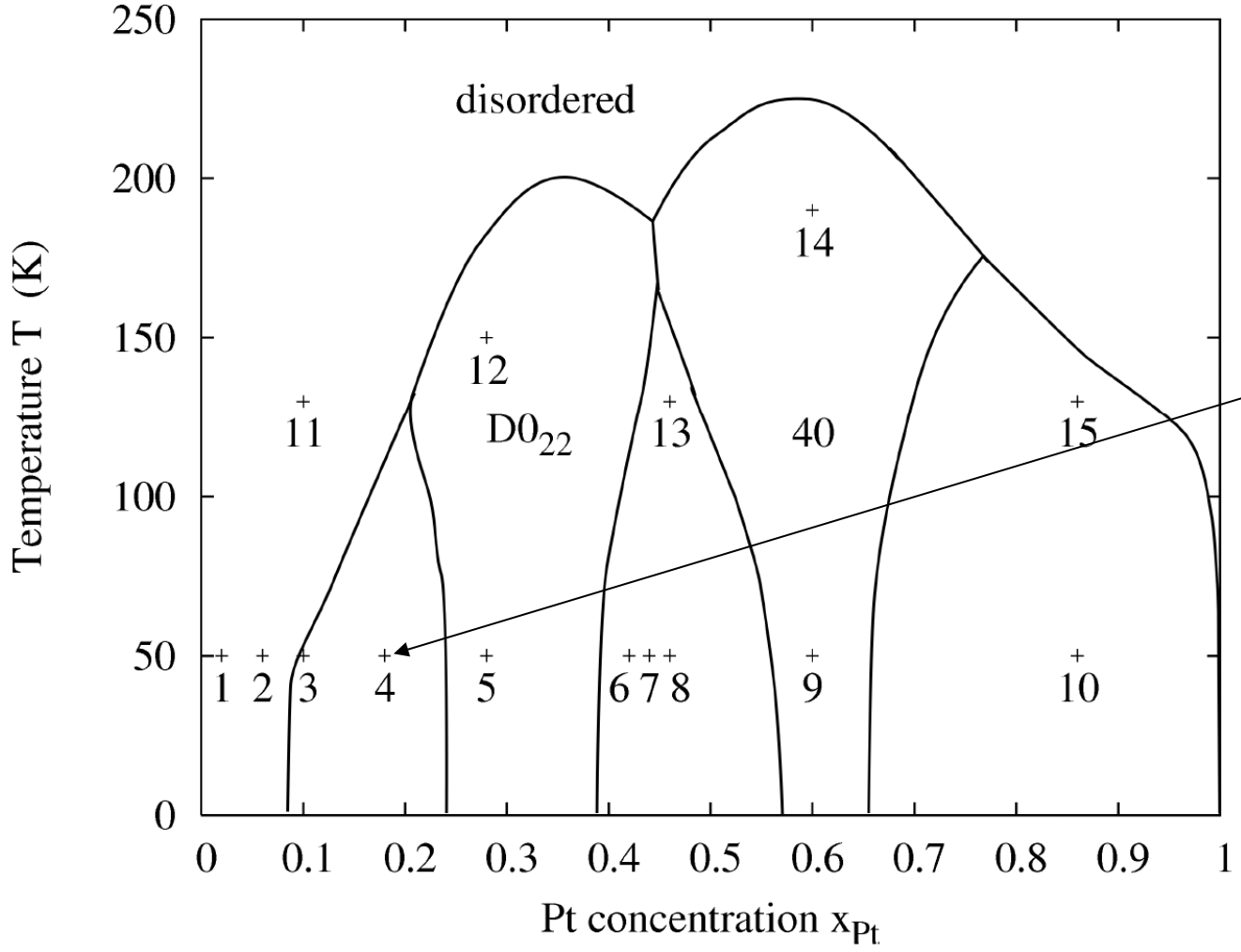

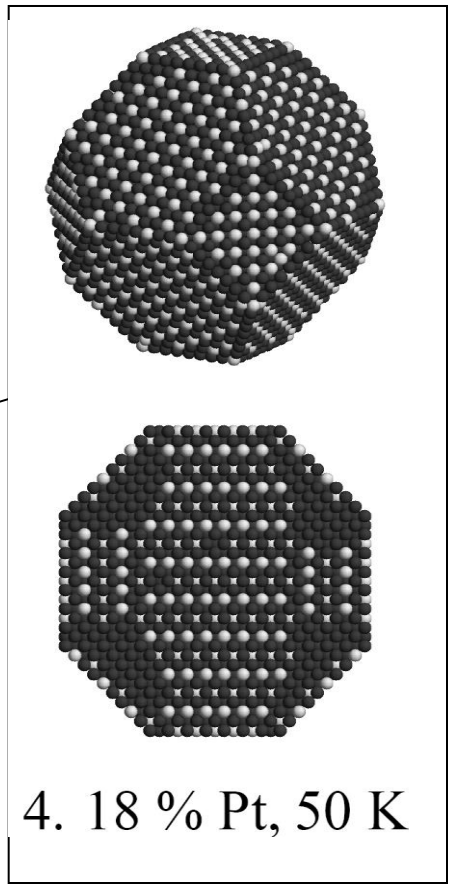

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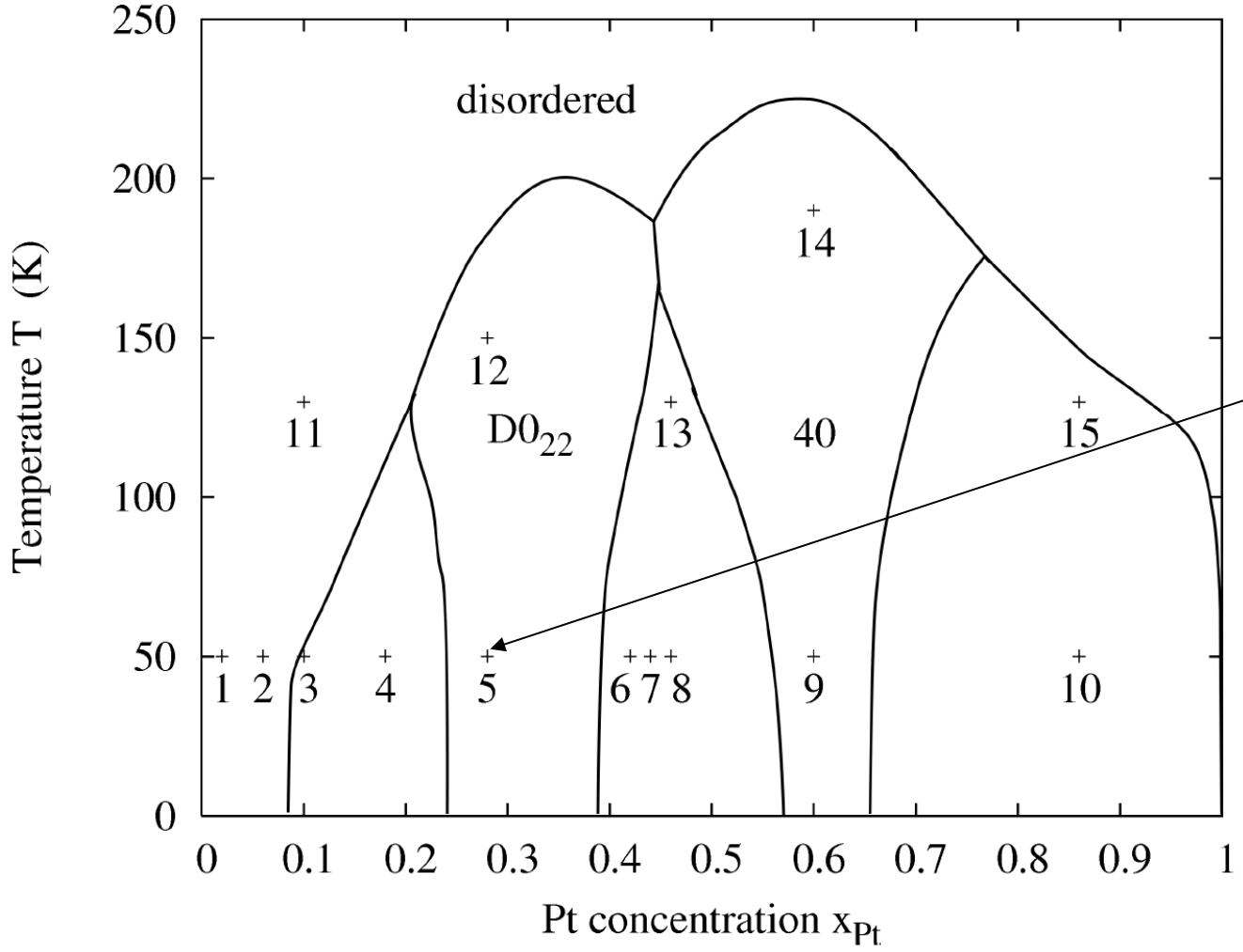

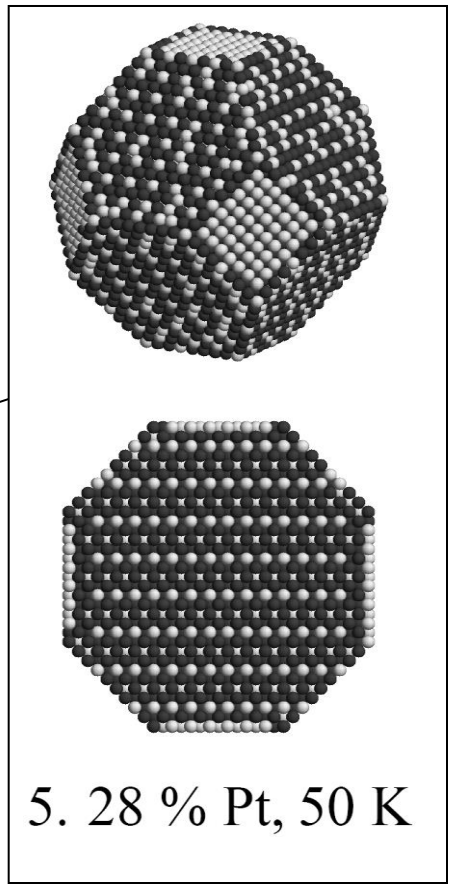

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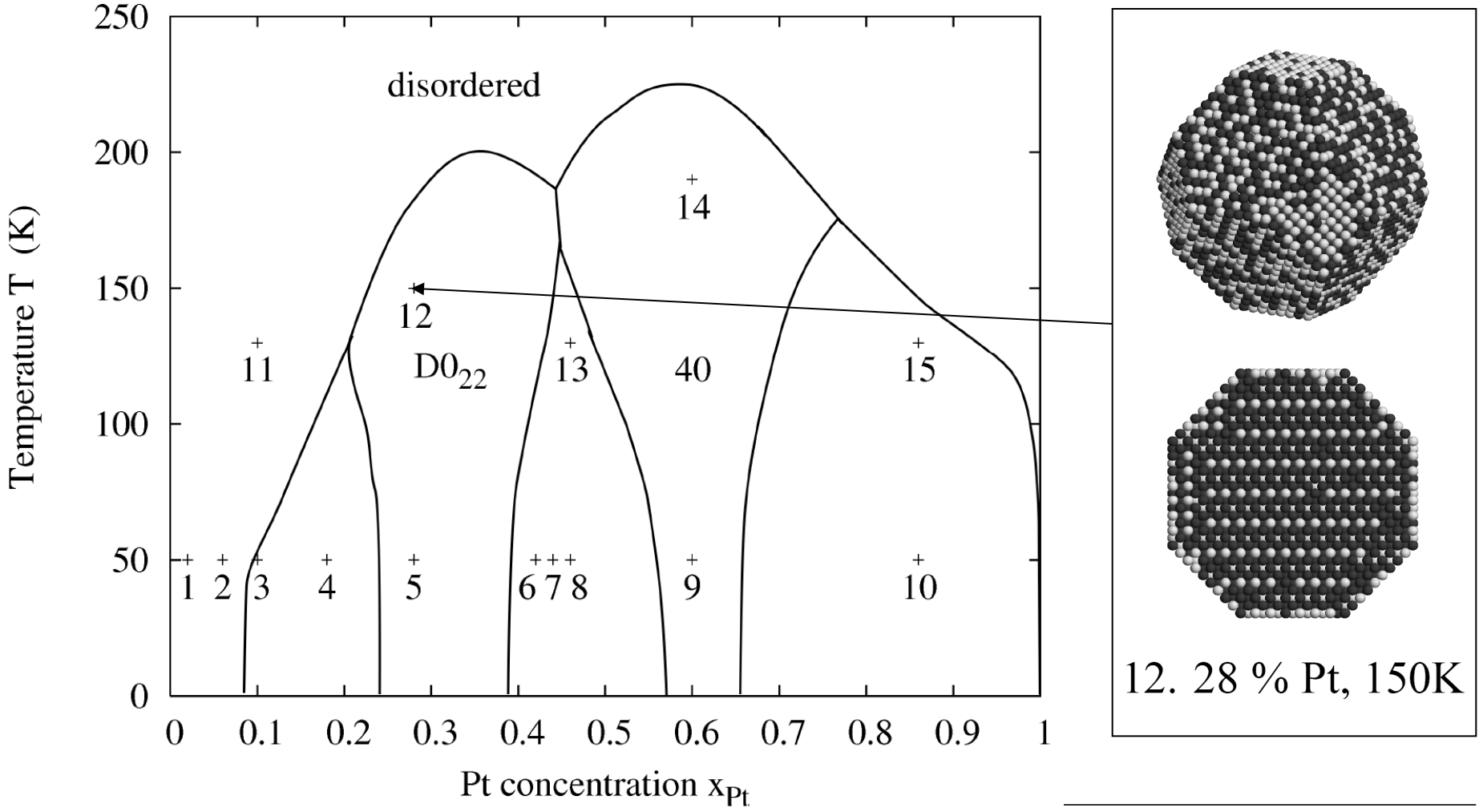

42% Pt

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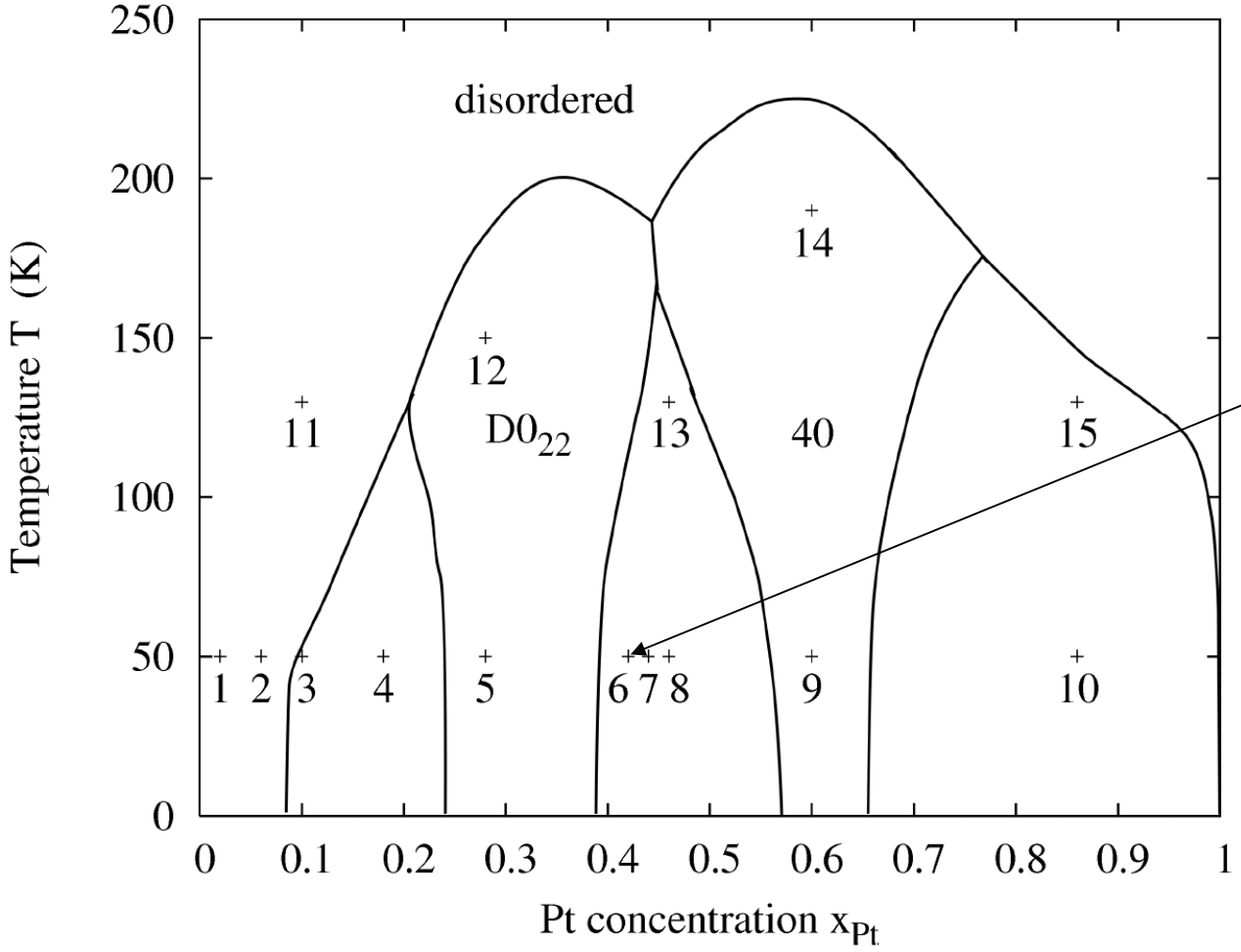

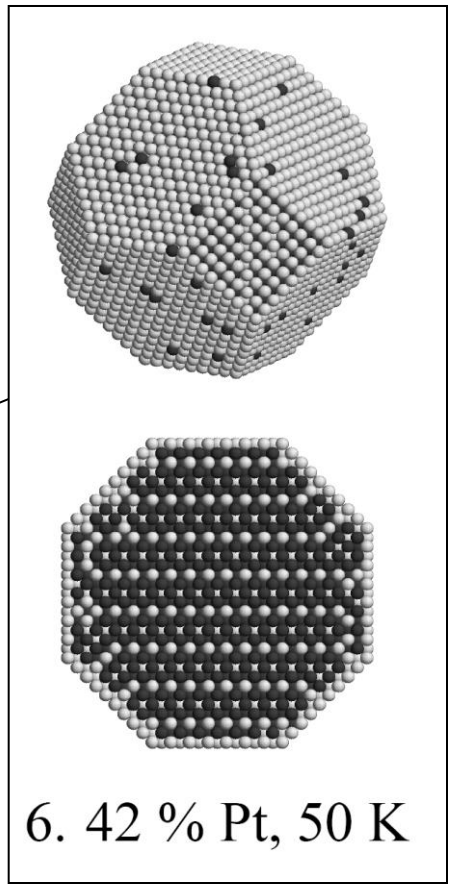

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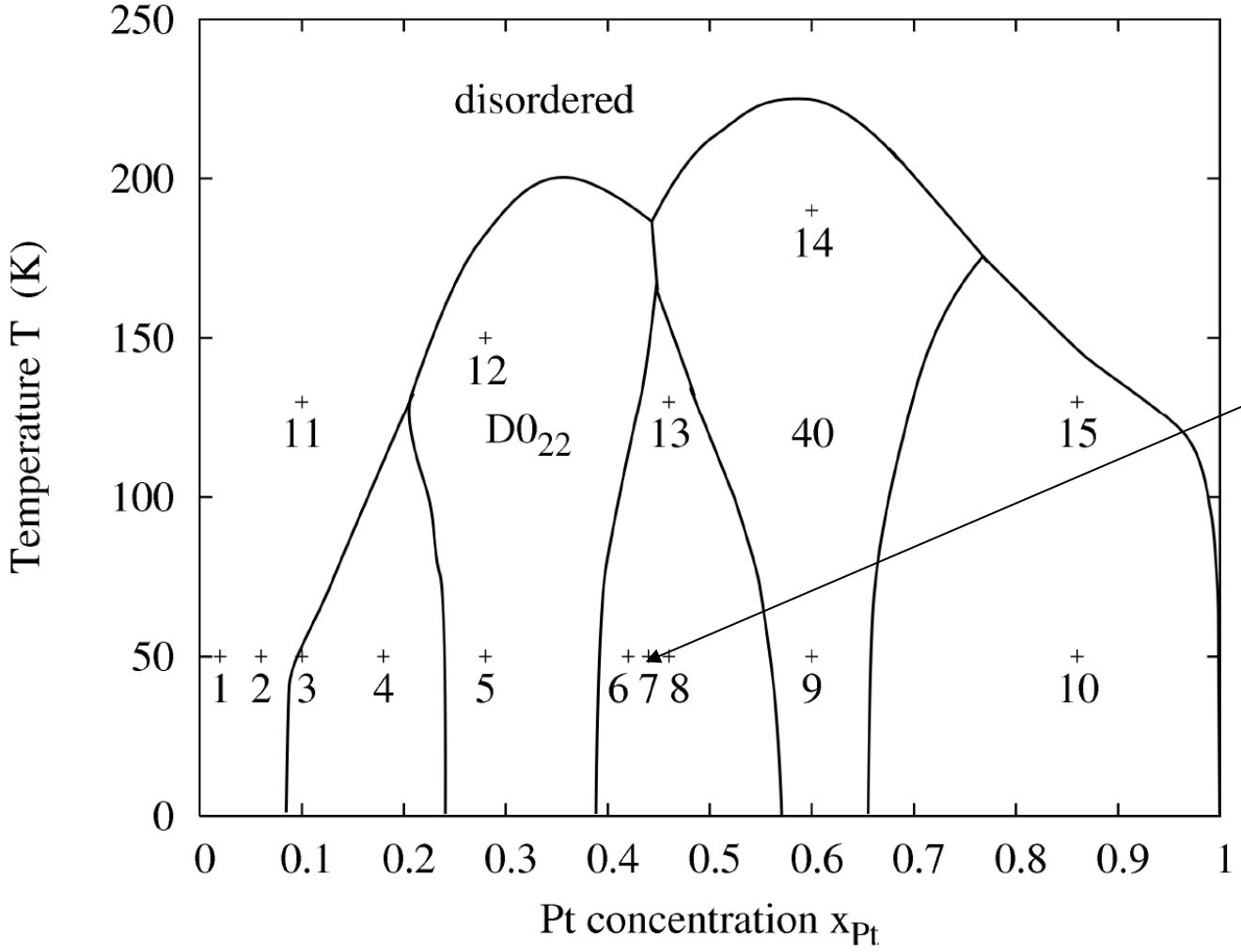

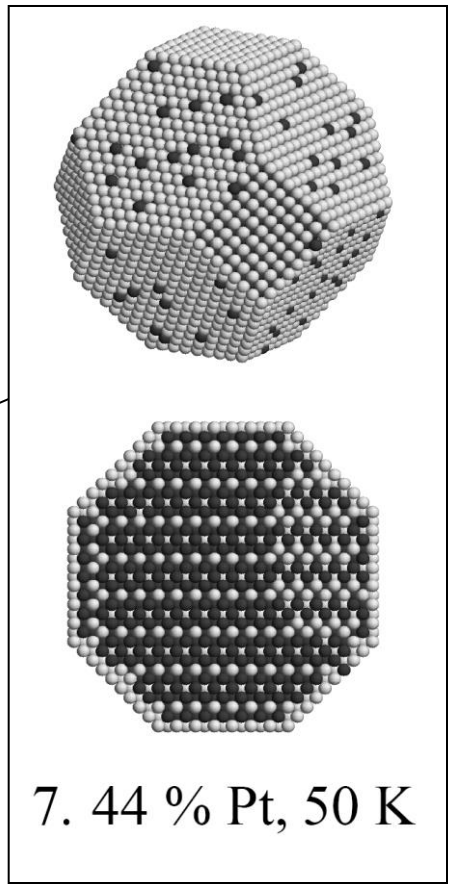

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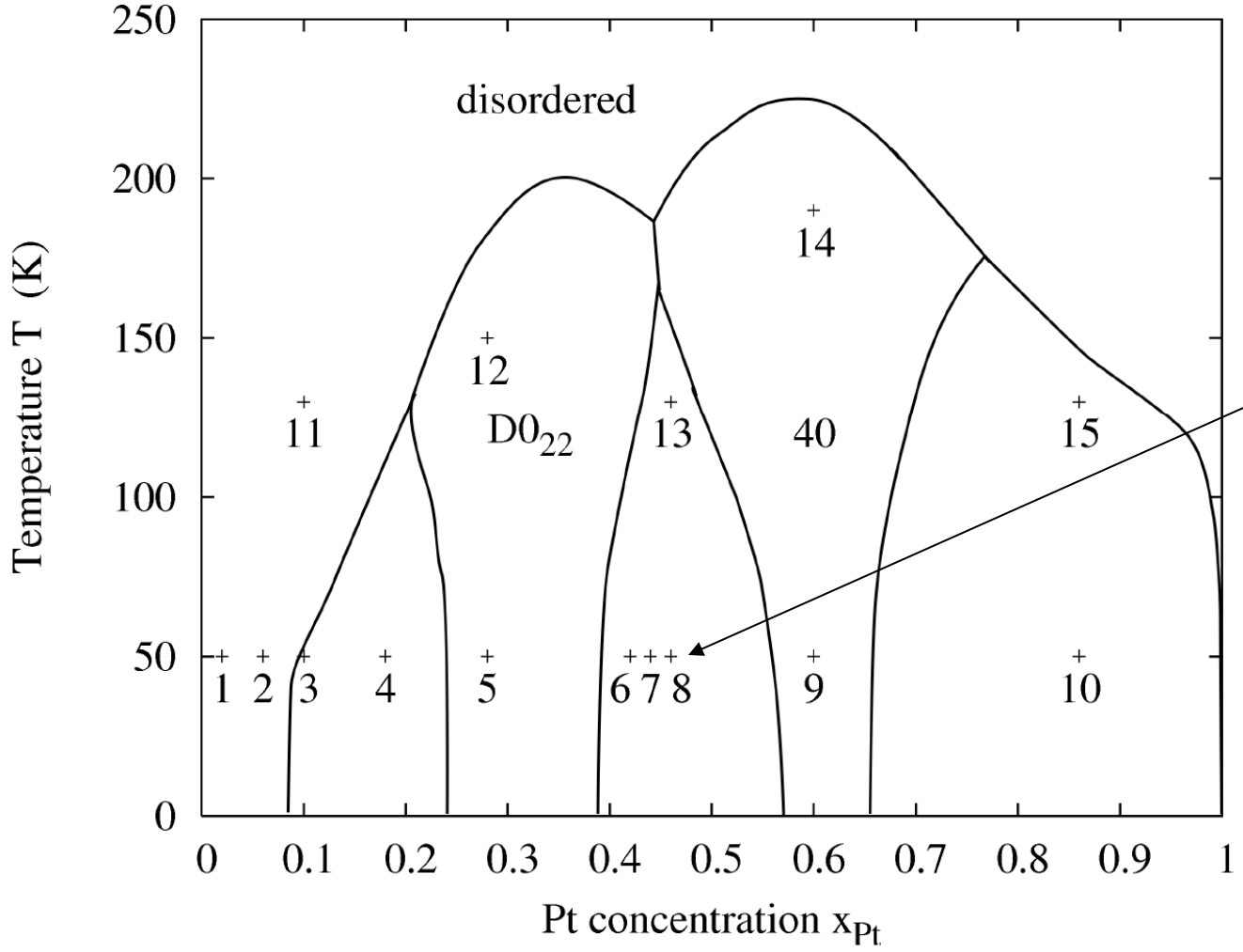

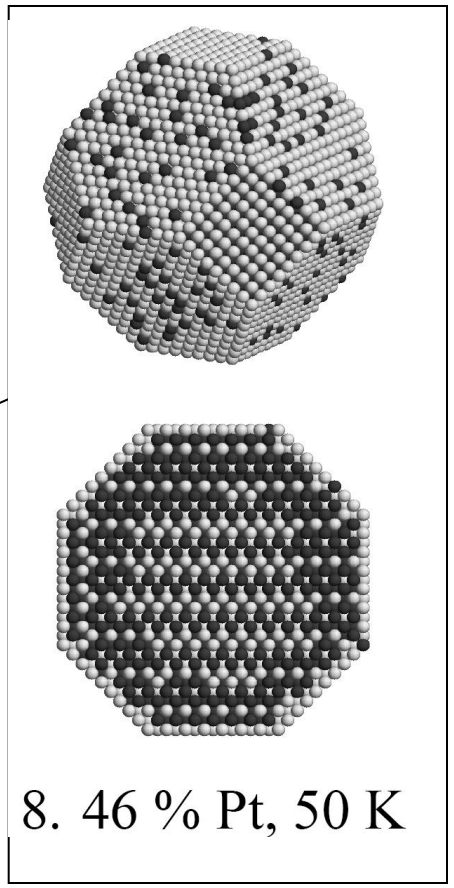

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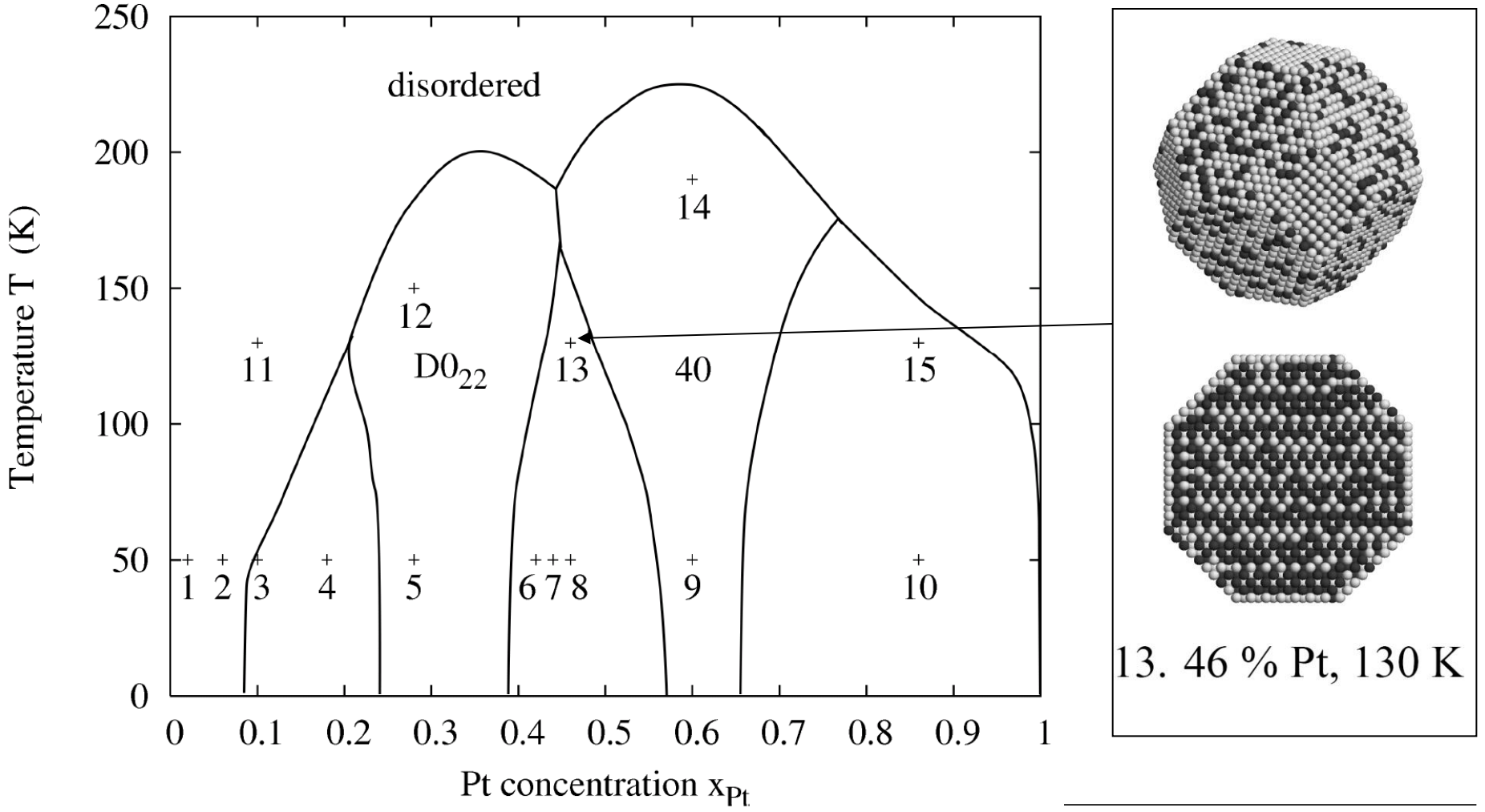
TECHNISCHE UNIVERSITÄT DARMSTADT



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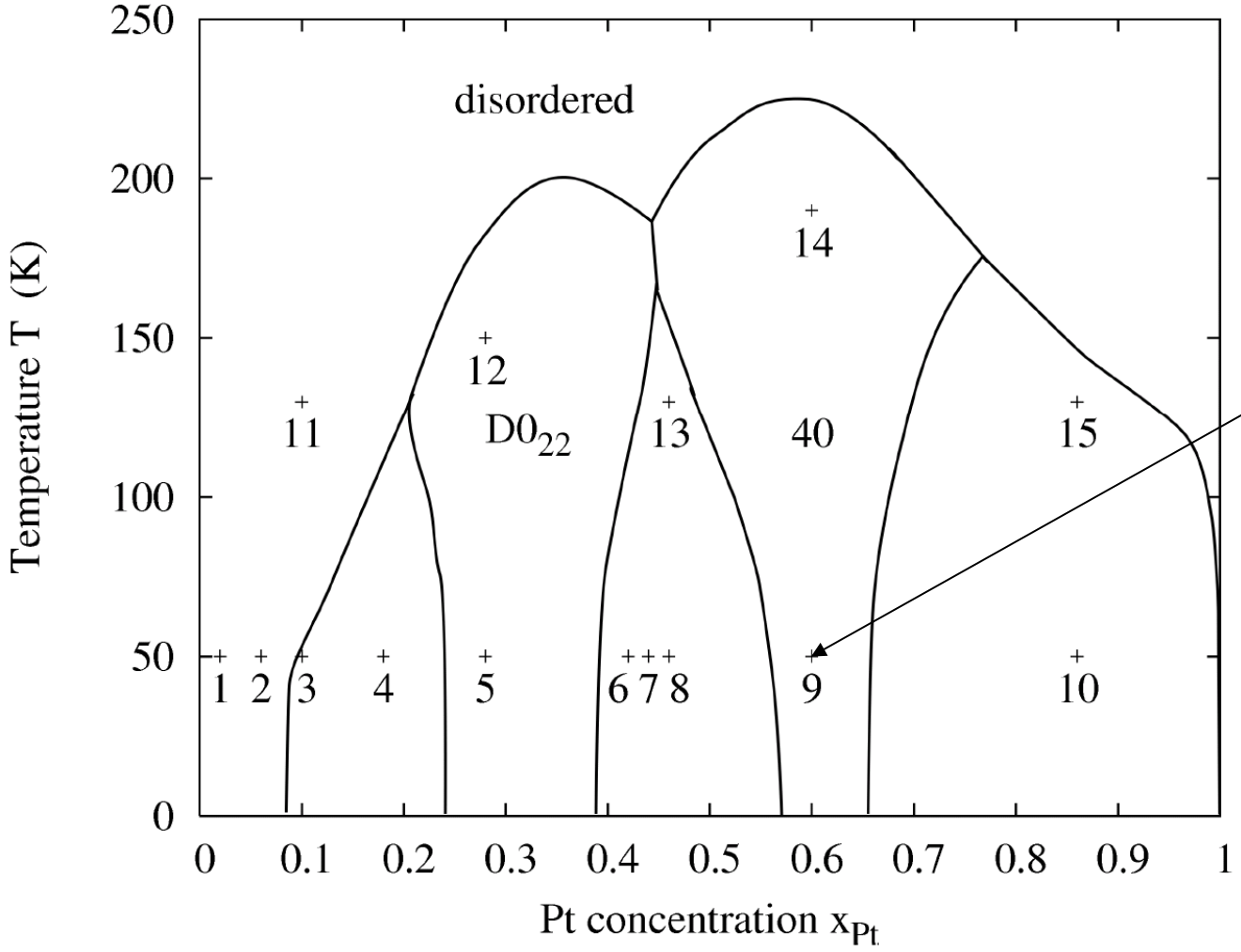
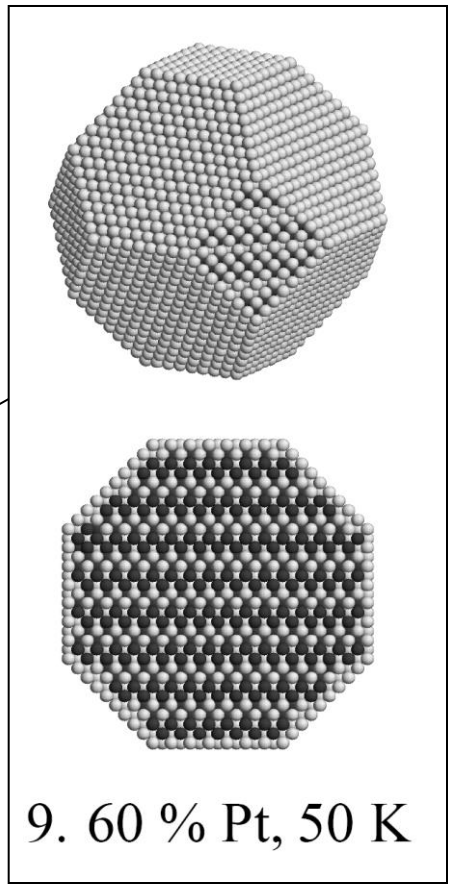
TECHNISCHE UNIVERSITÄT DARMSTADT





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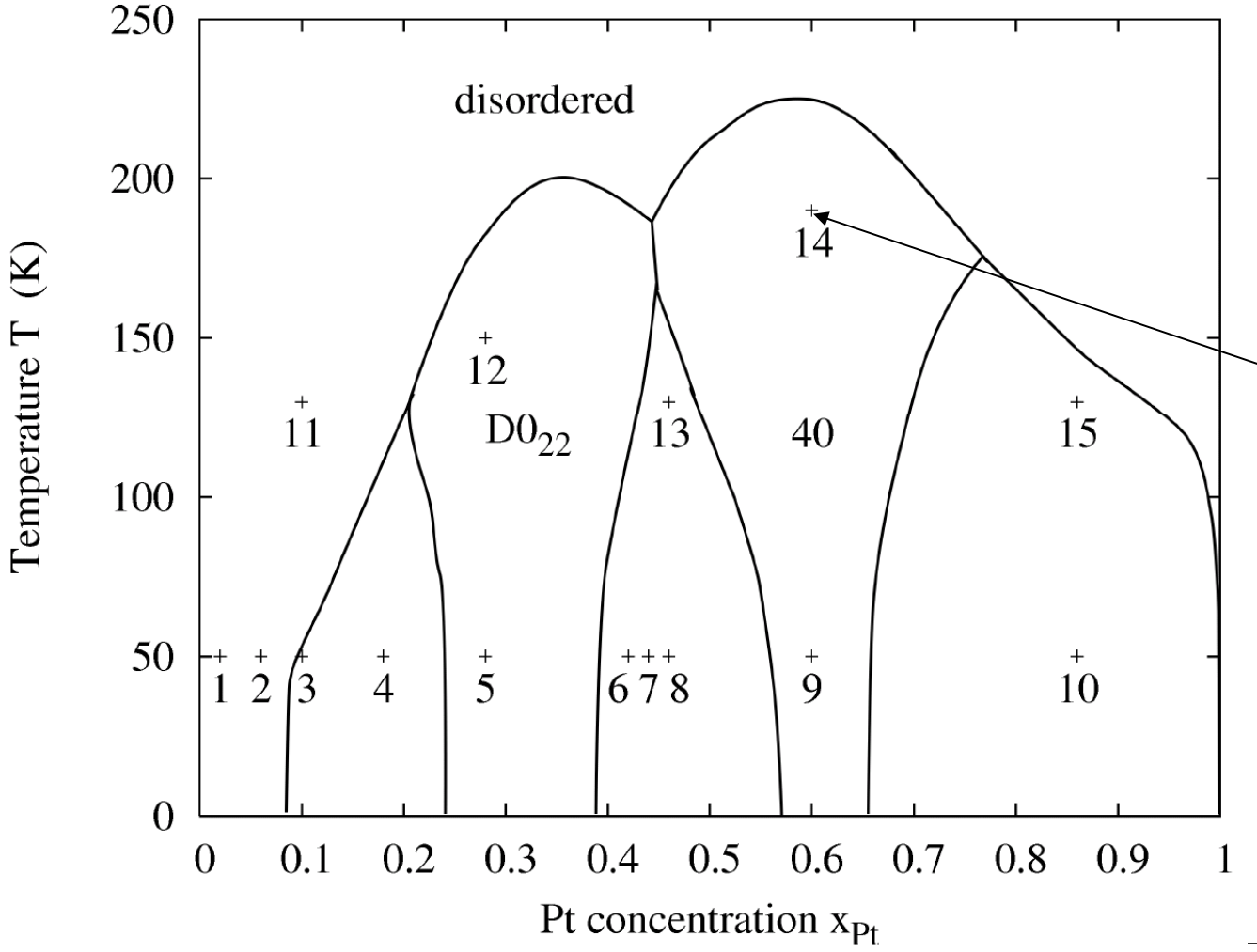
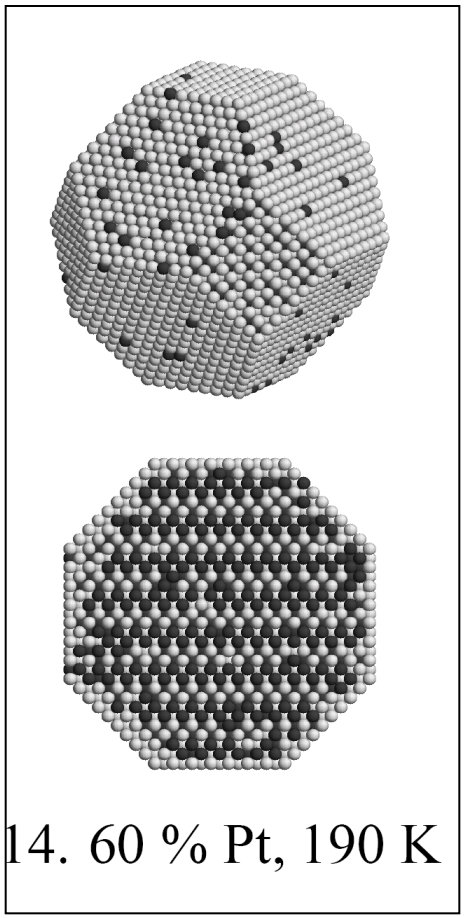
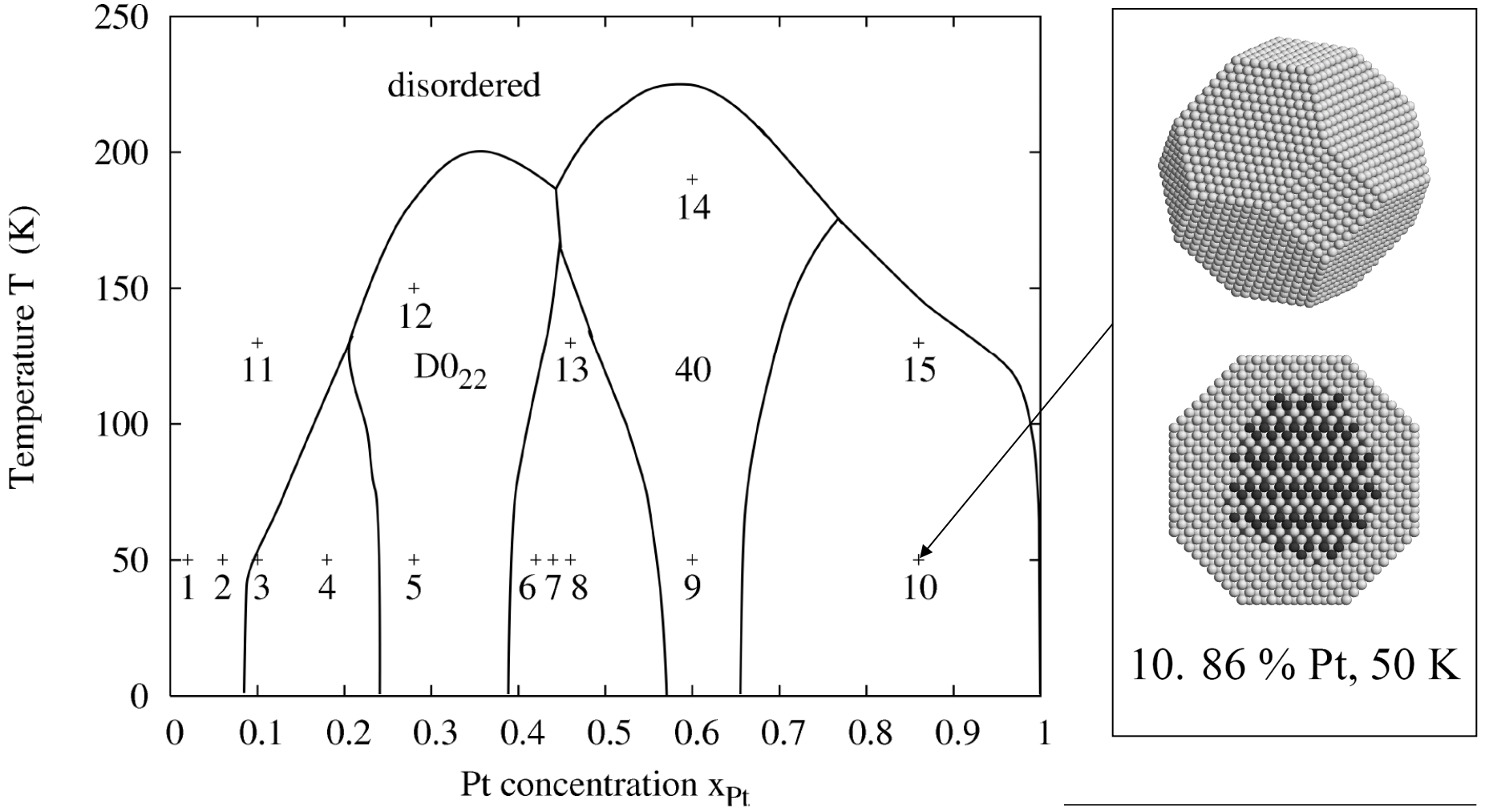




86% Pt

TECHNISCHE UNIVERSITÄT DARMSTADT



86% Pt

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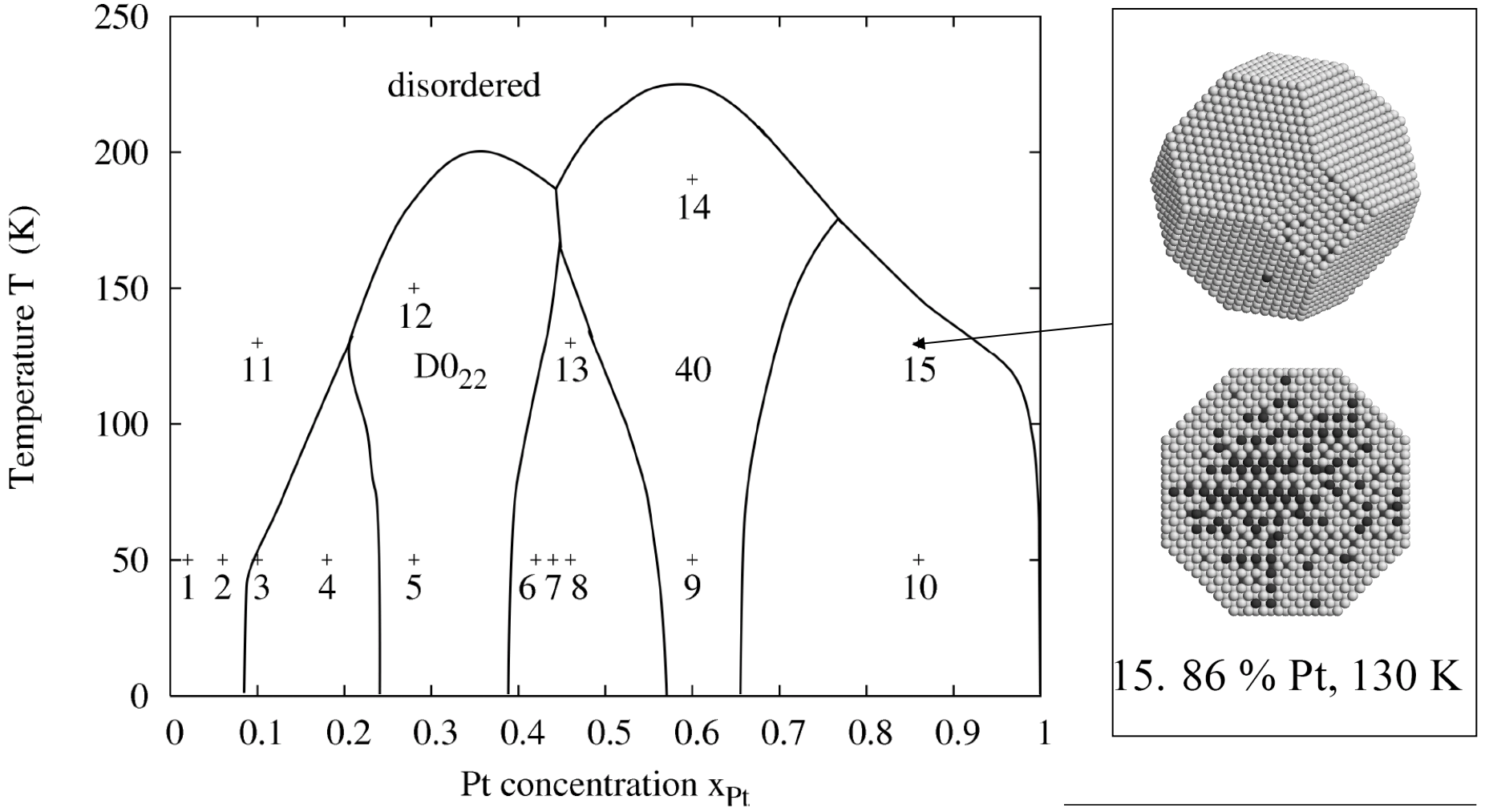

Size-dependent Diffusion ?
Vacancy Mechanism

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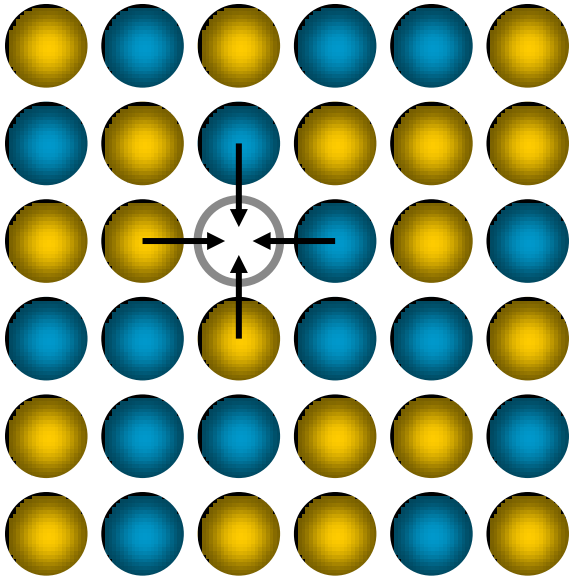

$$D = D_0 \times \exp^{-\frac{E_{\mathrm{mig}}}{k_{\mathrm{B}}T}} \times C_V$$

Vacancies in Lattice Model: KMC

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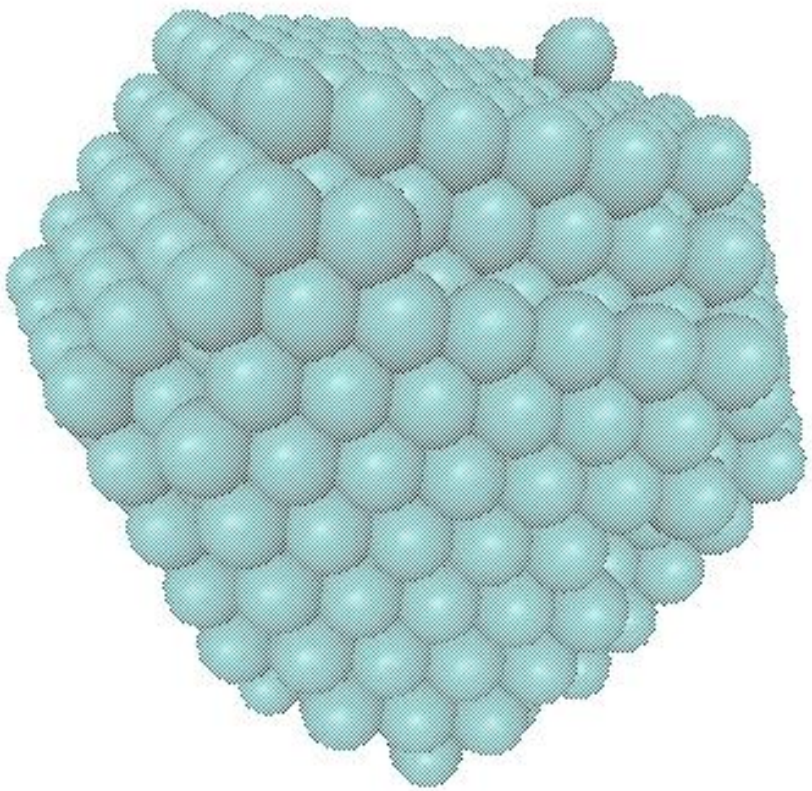

Müller/Albe
Acta Mat. (2007)

Vacancies in Lattice Model: KMC

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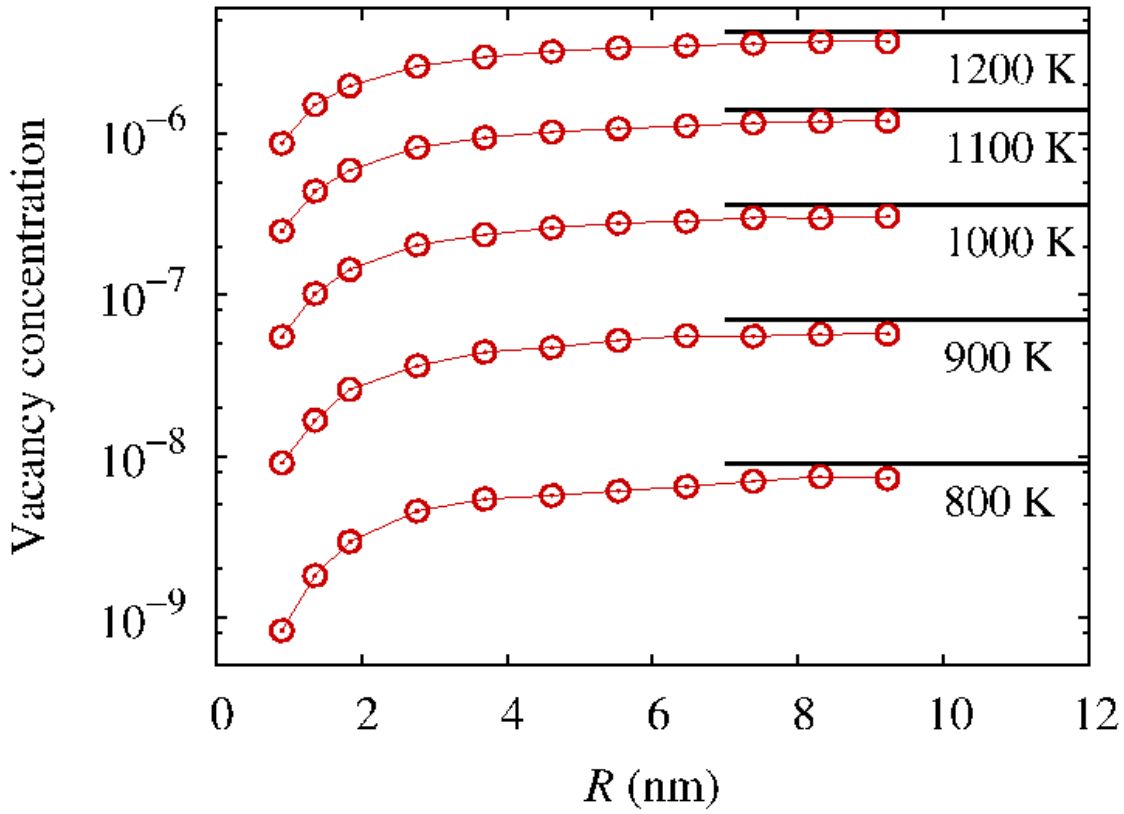
$$E_v^f = 1.28\,\text{eV}$$

Model: Cu



Vacancy Formation Energy: Lattice model

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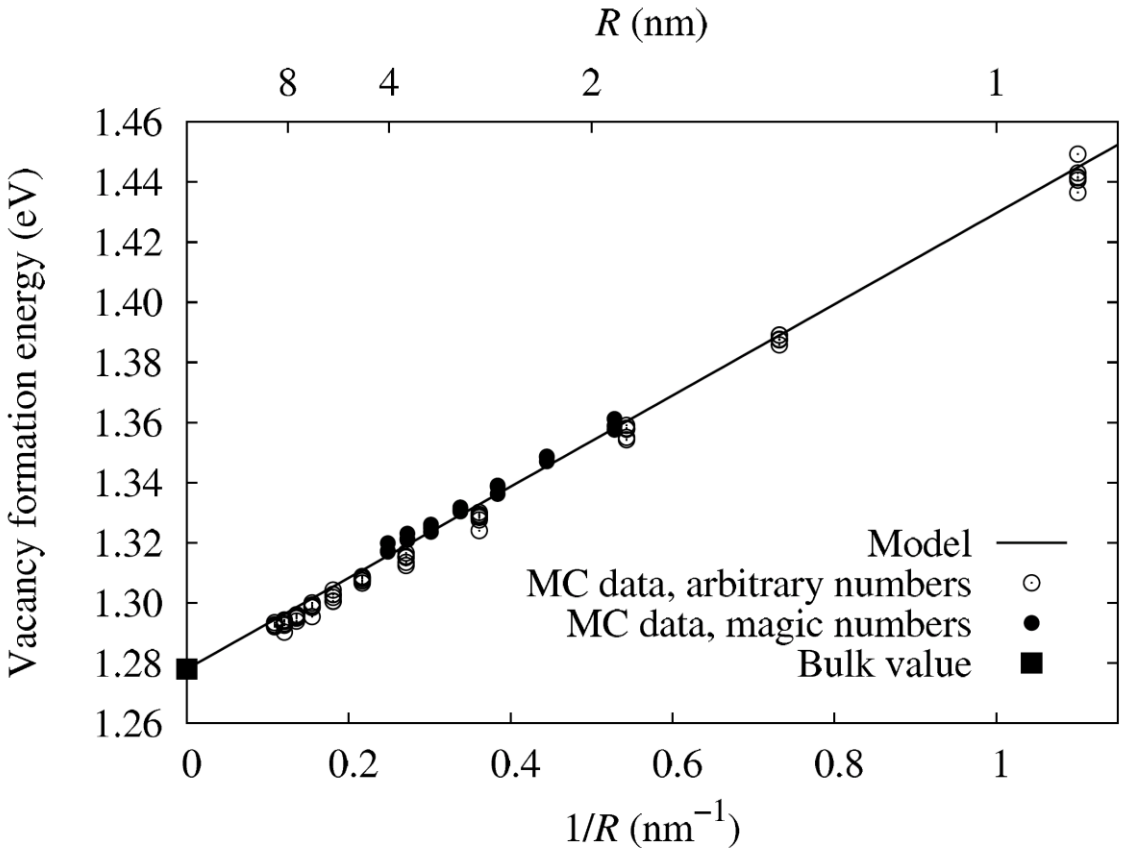

Vacancies in Lattice Model

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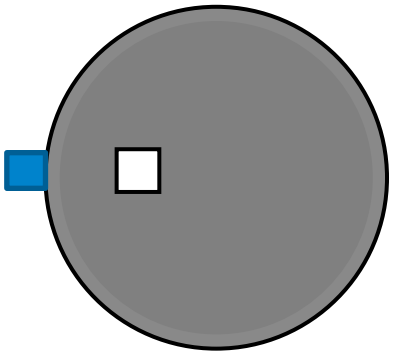
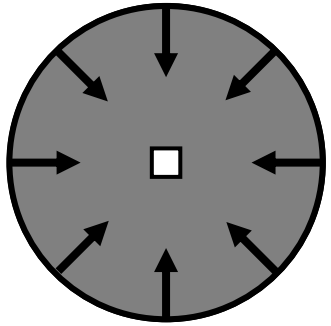
$$E_v^f(R) = E_v^f(R=\infty) + \frac{2\gamma}{R}\Omega$$

Surface energy γ



$2\Omega / R \times \gamma \rightarrow E_v^f$

Surface stress



Vacancies in Nanoparticles

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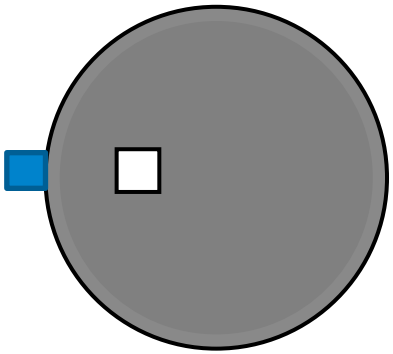
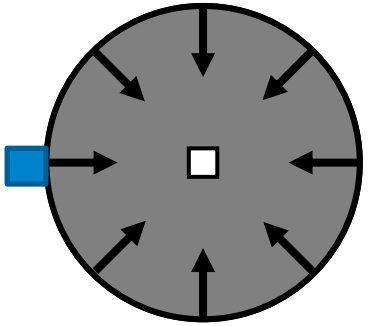
$$E_v^f(R) = E_v^f(R=\infty) + \frac{2(f\,\Delta V)}{R}$$

Surface energy γ



$2\gamma/R \times \Omega \rightarrow E_v^f \uparrow$

Surface stress *f*



$2f / R \times \Delta V \rightarrow E_v^f \downarrow$

Ω: atomic volume

$\Delta V = \Omega - \Delta V_{rel}$ = formation volume

Surface Energy vs. Surface Stress

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Surface Energy γ

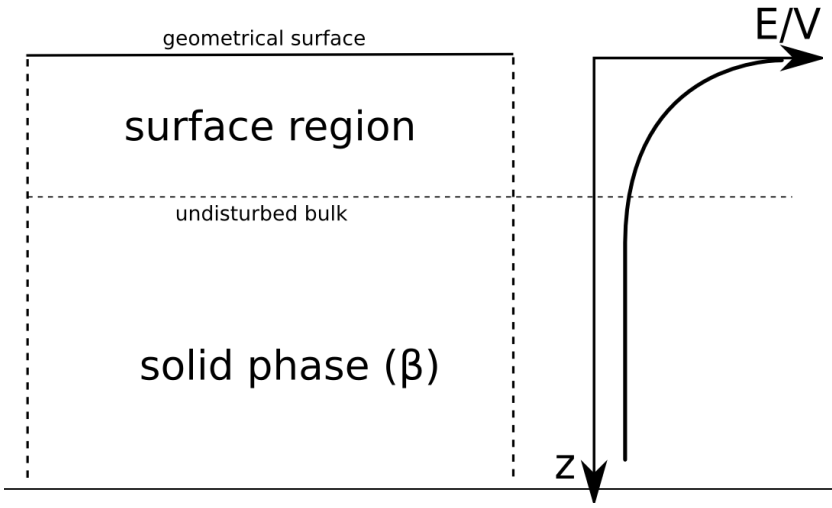
Work required to produce extra surface

$$dW = \gamma dA$$

Surface Stress f_{ij}

Work required to enlarge/minimize existing surface

$$dW = d(\gamma A) = f_{ij} A d\varepsilon_{ij}$$



$$f_{ij} = \frac{1}{A}\frac{d(\gamma A)}{d\varepsilon_{ij}}$$

$$f = \gamma + \frac{d\gamma}{d\varepsilon}$$

Materials by Design

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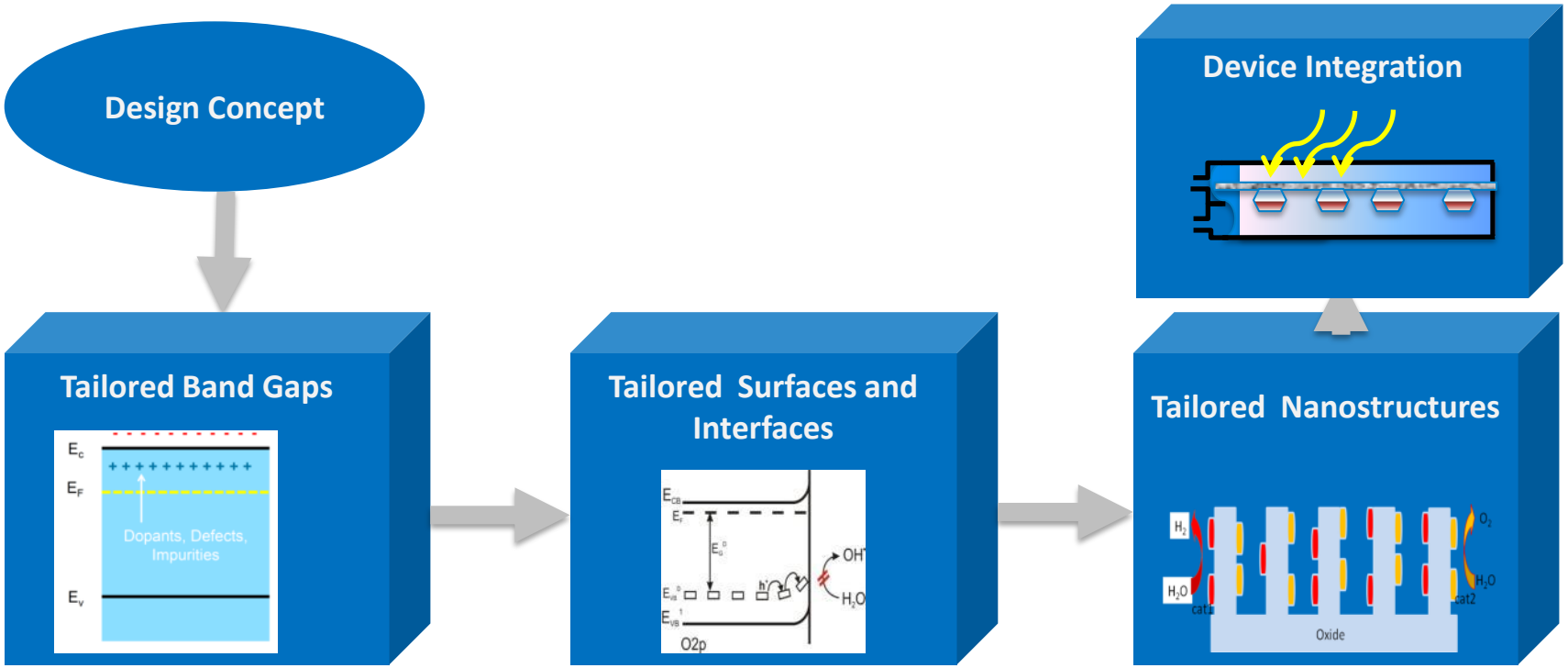

Take home messages

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- The properties of point defects and surfaces in oxides are most sensitive to the Fermi-energy

  → We need Fermi-level engineering

- Defects not only go along with excess energies but also stresses

  → Strain effects due to point, line and planar defects can be significant

- Thermodynamics and kinetics on the nanoscale can be very different

  → We need a better understanding of nanoeffects