# Magnetism, Percolation and Doping in Oxides

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# Outline

1. Basic principles.
2. Theoretical method and examples.
3. Conclusions.

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# Basic principles: fundamental questions

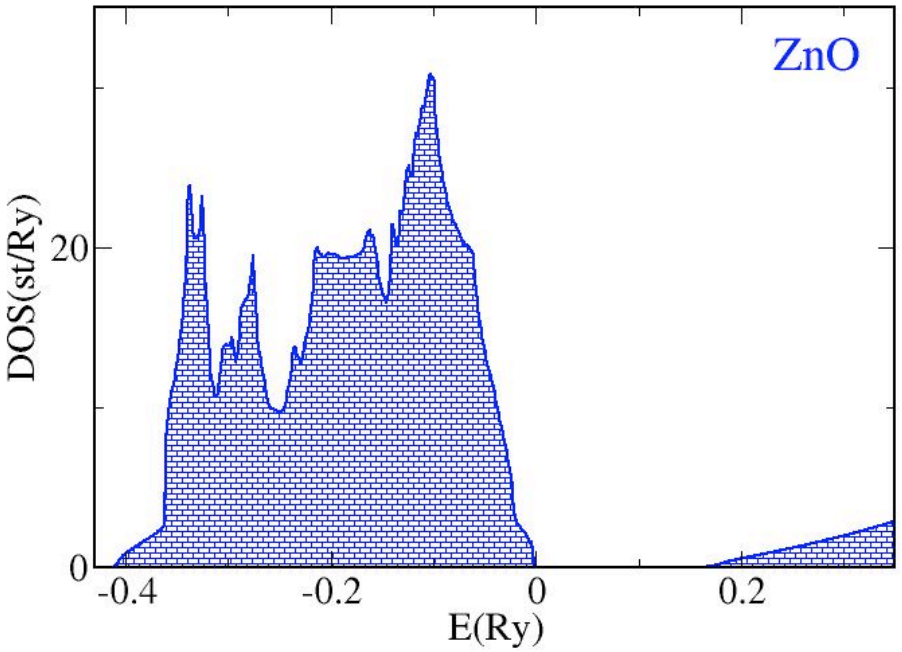
Which are the physical conditions required for the creation of collective ferromagnetism in nonmagnetic oxides by means of intrinsic point defects or dopants?

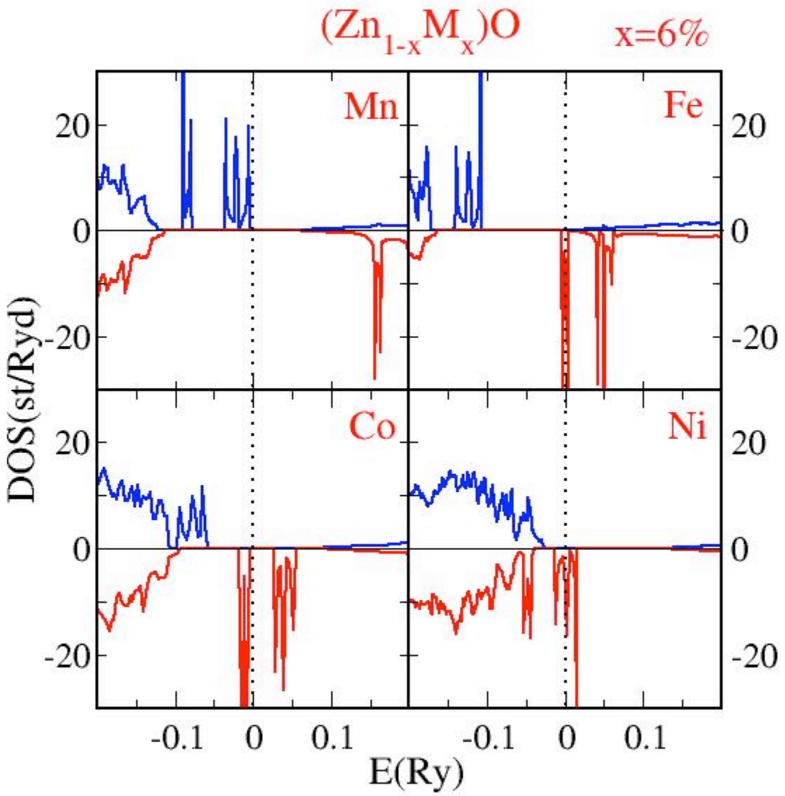
# Basic principles: usual answer

Which are the physical conditions required for the creation of collective ferromagnetism in nonmagnetic oxides by means of intrinsic point defects or dopants?

The most common answer is to identify a defect or dopant with a nonvanishing magnetic moment (usually its neutral charge state) by electronic structure calculations and for those proceed to the calculation of its magnetic properties (magnetic exchange interactions between a pair of them).

# Basic principles: electronic structure

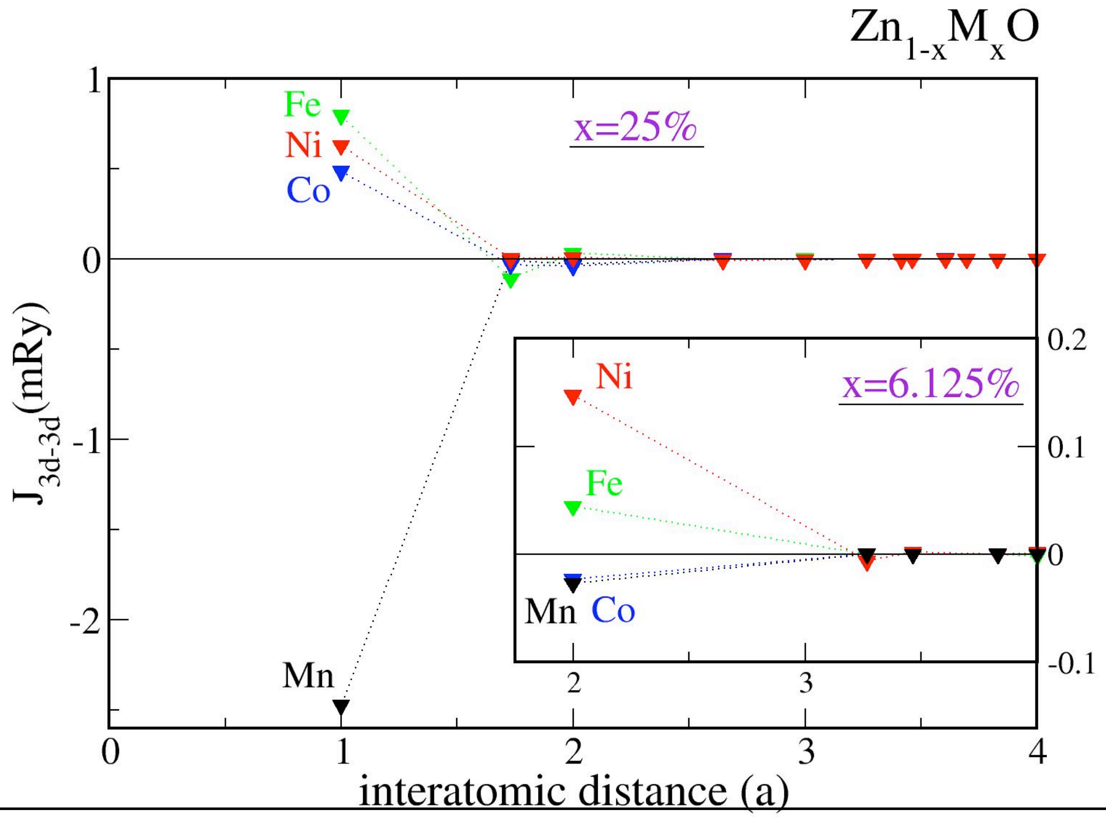




## Properties:

- Impurity-band in the semiconducting gap.
- Spin polarization.
- Half-metallicity.
- Exchange splitting.

# Basic principles: exchange interaction



## Properties:

- Exchange parameters decay quickly (related to wide gap and half-metallicity).
- In the absence of charge carriers the exchange interaction is antiferromagnetic.
- (ZnFe)O and (ZnNi)O are ferromagnetic and (ZnMn)O is antiferromagnetic for both concentrations. (ZnCo)O is ferromagnetic for high and antiferromagnetic for low concentration.

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# Theoretical method: a more complete methodology

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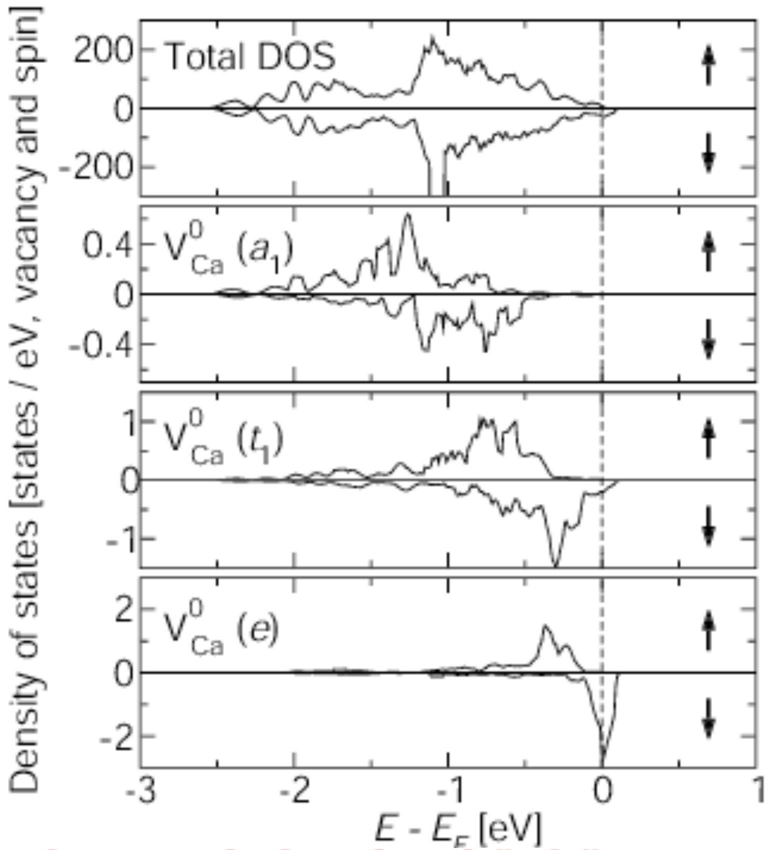
[1] J. Osorio-Guillén et al., Phys. Rev. Lett. **100**, 036601.
[2] J. Osorio-Guillén et al., Phys. Rev. B **75**, 184421.

# First step: electronic structure calculation

CaO

Total and local projected DOS on a empty sphere of 2 Å at the vacancy site

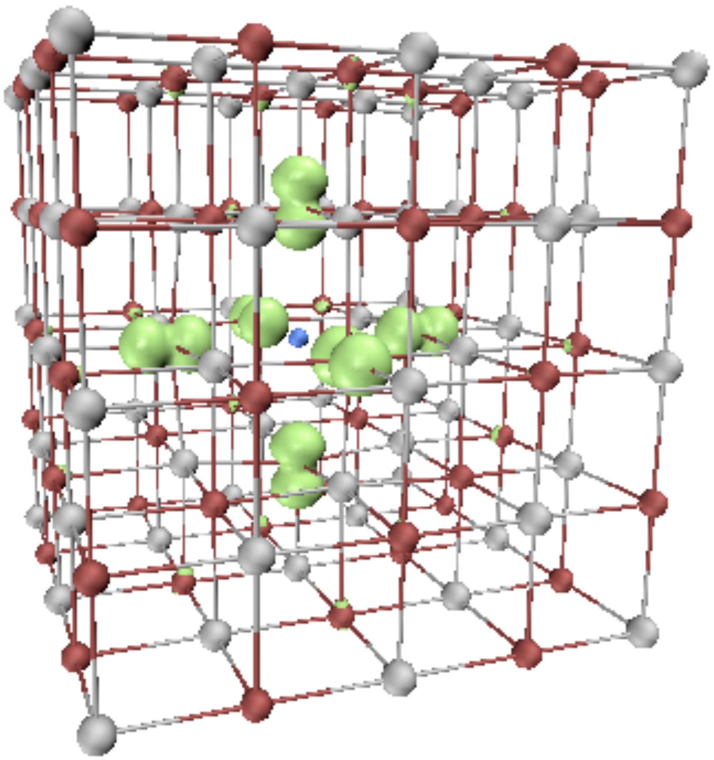


$V^0 \qquad (a_1^2\, t_{1+}^3\, e_+^2\,)\, t_{1-}^{2.5} e_-^{0.5} \qquad \mu = 1.9$

$V^- \qquad \mu = 1$

$V^{2-} \qquad \mu = 0$

Hole density

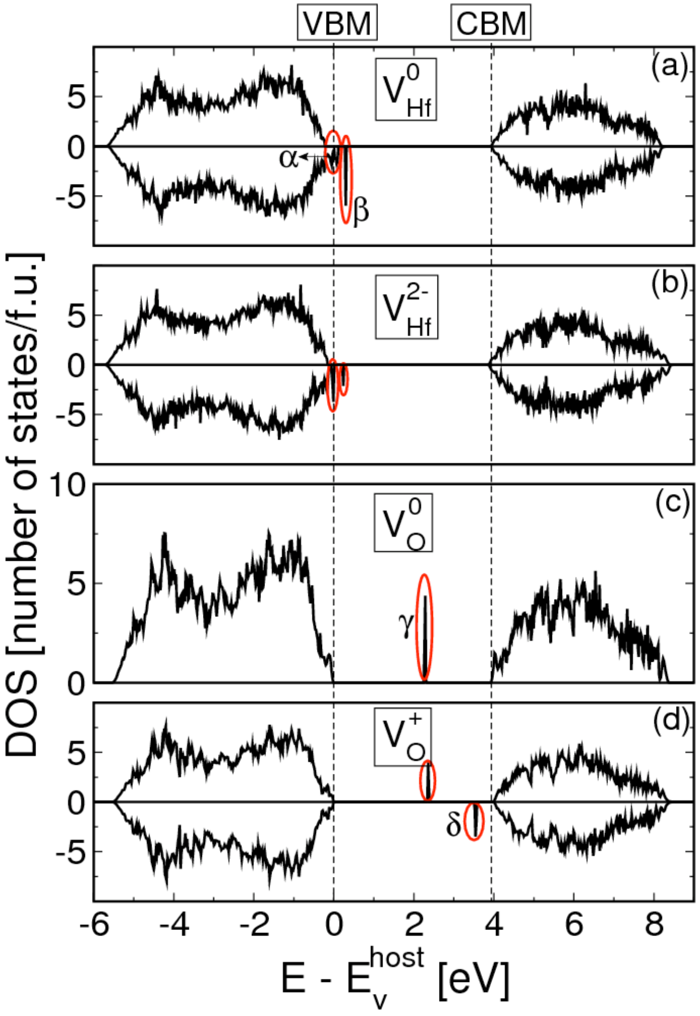


Holes uniformly distributed over the six oxygen ions.

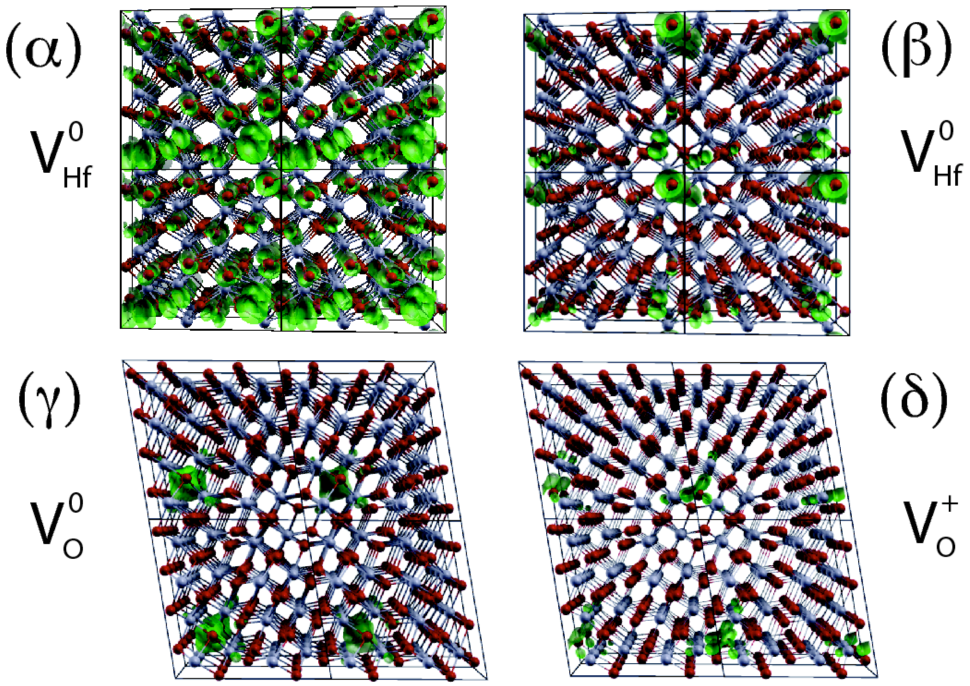
# **First step:** electronic structure calculation

$HfO_2$

Local projected DOS on a empty sphere of 2 Å at the vacancy sites

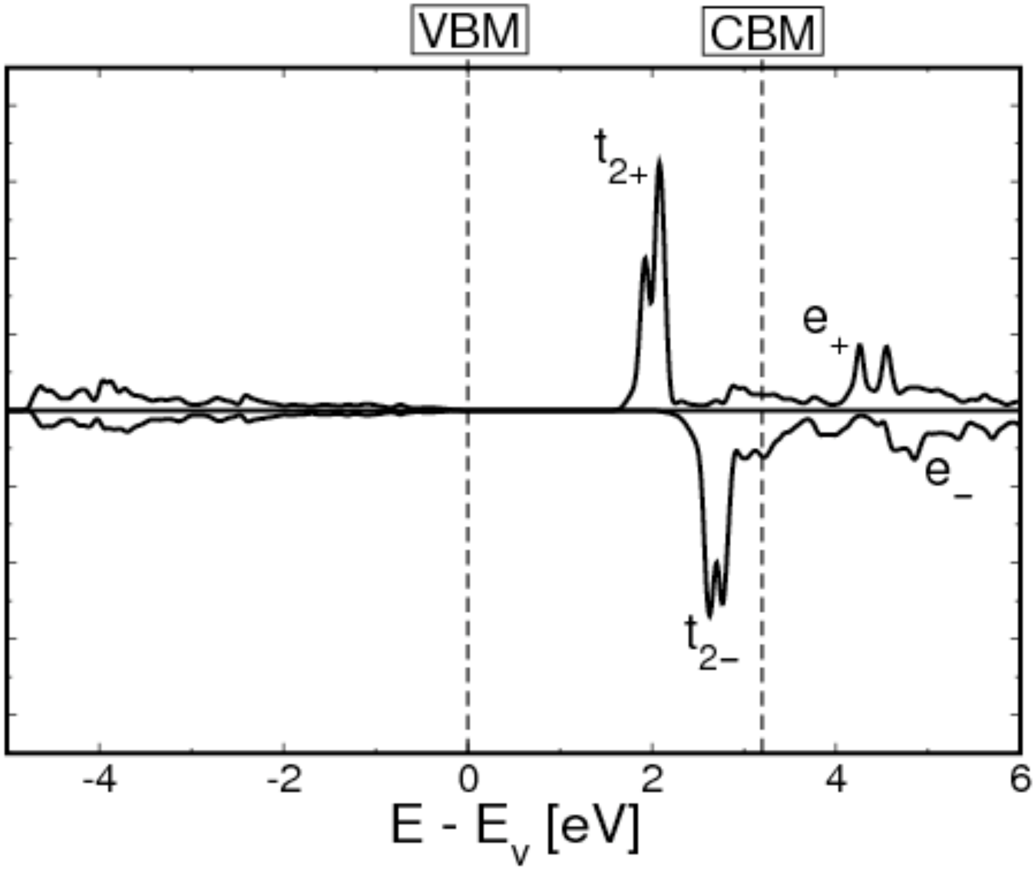


$|\Psi|^2$



# First step: electronic structure calculation

$TiO_2$



$V_{Ti}$ introduce deep, spin-polarized levels in the gap, due to its low 3*d*-orbital energy relative to Ti. $\mu = 1\ \mu_B$.

# Theoretical method: a more complete methodology

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# Second step: (a) LDA/GGA supercell calculations of defect formation energy $\Delta H$

$$\Delta H_{\mathrm{D},q}(\mu, E_{\mathrm{F}}) = [E_{\mathrm{D},q} - E_{\mathrm{host}}] + [\mu_{\mathrm{host}} - \mu_{\mathrm{D}}] + q \cdot E_{\mathrm{F}}$$

Supercell total energies

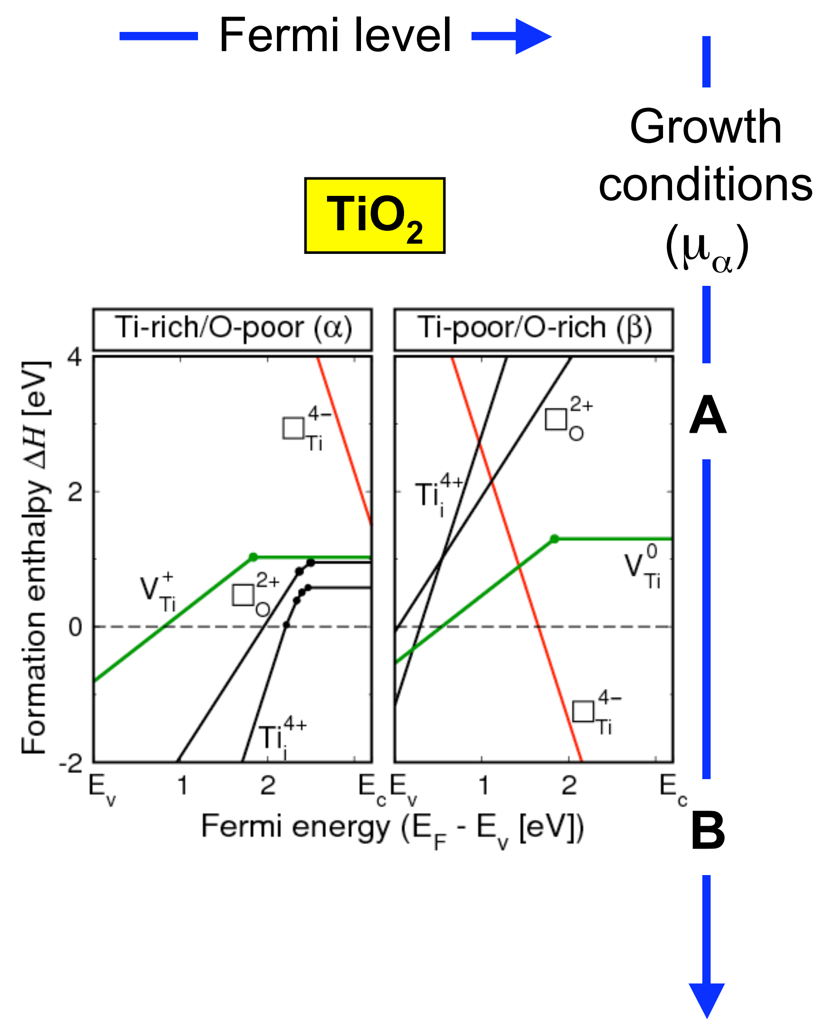
Atomic chemical potentials

Electron chem. potential

| **Corrections to LDA-supercell calculations [1]** | **due to** |
|---|---|
| • Band gap correction $\Delta E_{VBM}$, $\Delta E_{CBM}$ | LDA |
| • Shallow donor/acceptor correction | LDA |
| • Band-filling (Moss-Burstein shift) of shallow defects | supercell |
| • Potential alignment for charged defects | supercell |
| • Image charge correction for charged defects | supercell |

[1] C. Persson et al., Phys. Rev. B **72**, 035211.

# Second step: given the calculated $\Delta H$, what can we learn?



- Equilibrium **defect/dopant densities** as function of $T_{growth}$, $\mu_\alpha$ (sample all possible growth conditions)

- Calculate, not assume equilibrium **Fermi level**

- Which growth conditions **optimize** desired **doping**?

- Which growth conditions **minimize compensation**?

- **Compound properties** (e.g. TiO$_2$)
  "Natural" non-stoichiometry
  "Natural" Fermi level

# Second step: Le Chatelier’s principle for doping

*A perturbation of a system at equilibrium shifts the thermodynamic variables into a direction that counteracts the perturbation*

Dope *n*-type (add donors)

↓

$E_F$ rises in the band gap and $n$ increases

↓

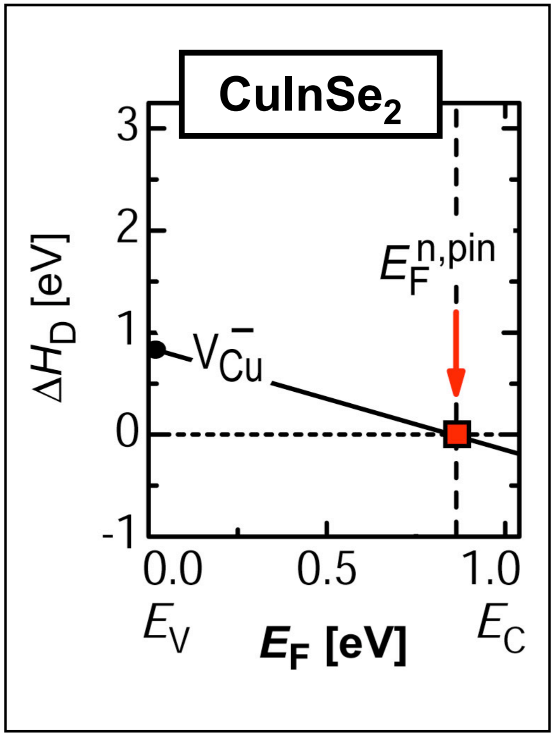
$\Delta H$ of charged acceptors (electron killers) is lowered

↓

Concentration of electron killers rises

↓

$E_F$ is lowered and $n$ is reduced



**How to deal with the feedback due to Le Chatelier’s principle?**

**→ Find equilibrium $E_F$ and a self-consistent solution!**

# Second step: defect – carrier charge feedback method

| | |
|---|---|
| Defect formation energy | $\Delta H = \Delta H_{D,q}(\mu, E_F)$ |
| Defect concentration | $c_D = N \times \exp(-\Delta H/kT)$ |
| Electron/hole density | $c_e = \int f_{FD}(E - E_F)\, g(E)\, dE$ |
| Charge neutrality | $-c_e + c_h + S\, [q \times c(D^q)] = 0$ |

Self-consistent solution

$$\begin{tikzcd} \Delta H(E_F) \arrow[r] & c_D(\Delta H) \arrow[r] & E_F \arrow[ll, bend left] \end{tikzcd}$$

$T_{growth} \rightarrow RT$

“freeze” defect densities of $T_{growth}$,

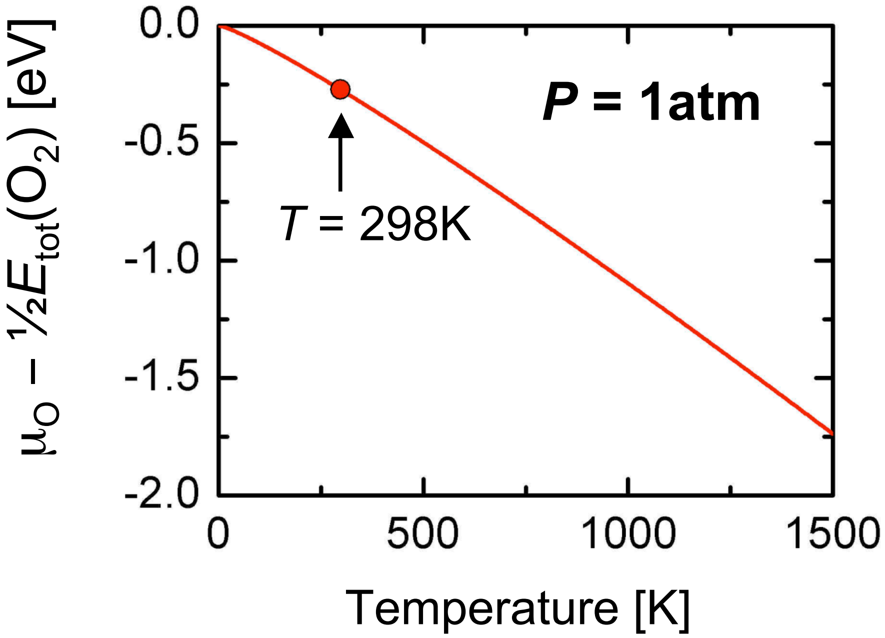
recalculate $E_F$ for room temperature

# **Second step:** temperature and pressure dependent gas phase chemical potentials, e.g. $O_2$: $\mu_O = \mu_O(T,P)$

**Solid phase** (e.g., Ti-metal): $\mu_{Ti}^{elem} = E_{tot}(\text{hex-Ti})/N$

**Gas phase** (e.g., $O_2$):

$$\mu_O(T,P) = \tfrac{1}{2}[E_{tot}(O_2) + (H_0^{298K} + \Delta H) - T(S_0^{298K} + \Delta S) + kT\ln(P/P_0)]$$



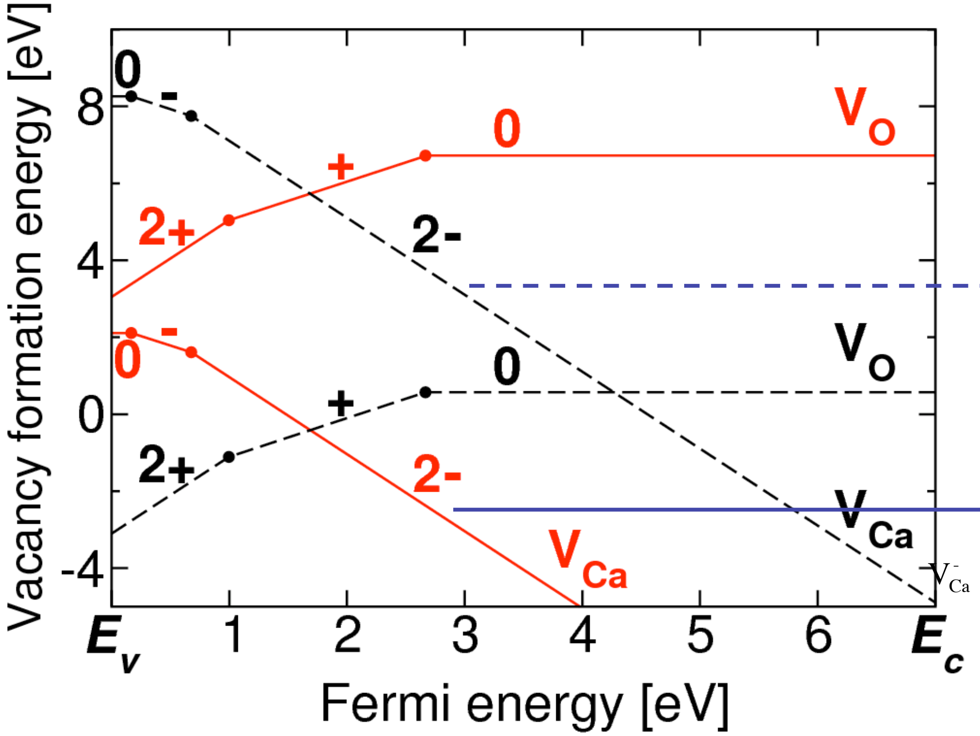
Use $H_0^{298K}$, $S_0^{298K}$, and ideal gas law for $T > 298K$

$C_p = 3.5k_B$

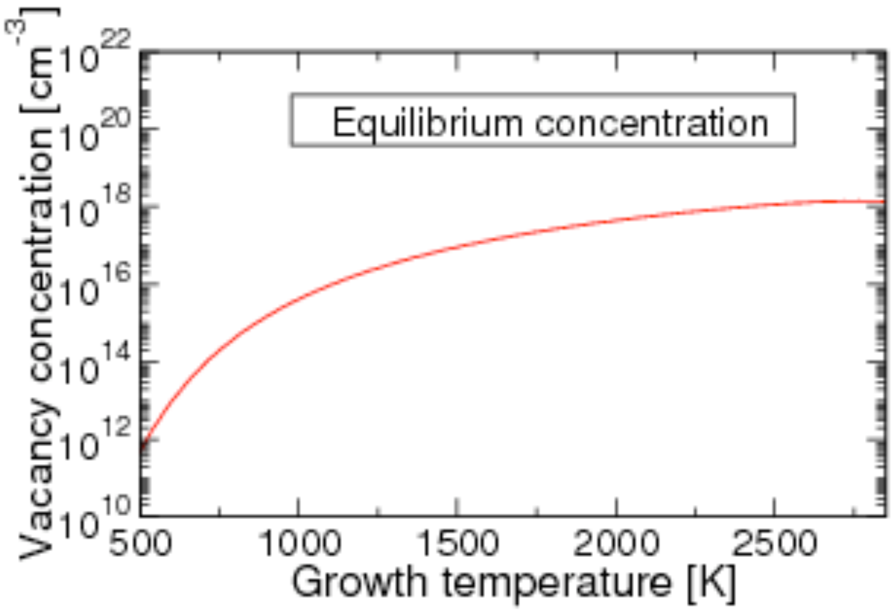
$\Delta H = C_p(T - T_0)$

$\Delta S = C_p \ln(T/T_0)$

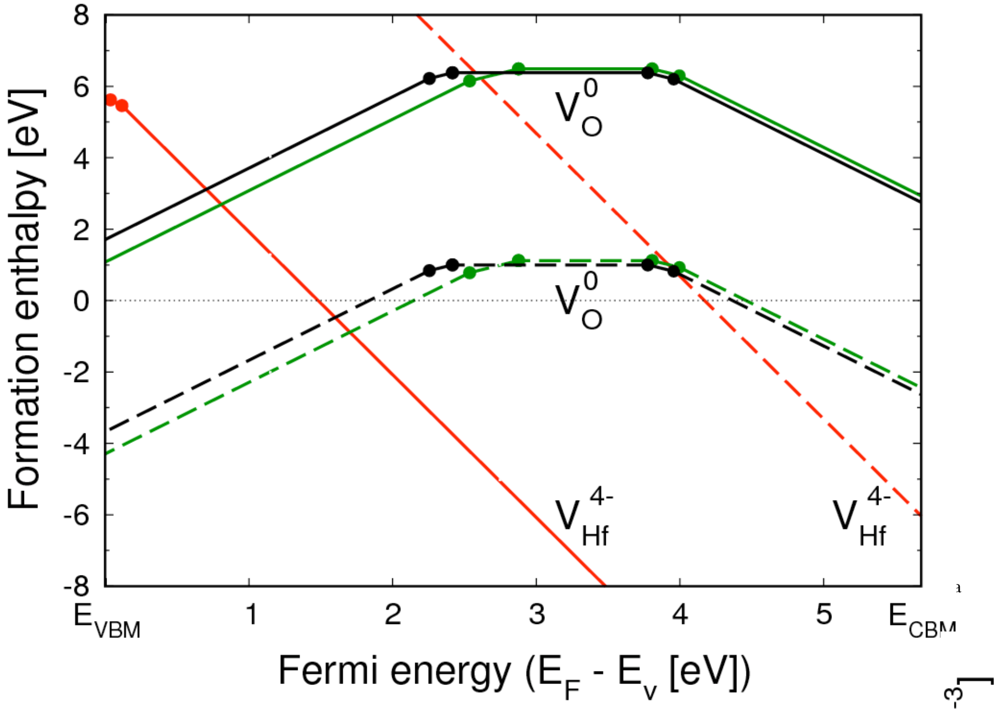
# Second step: CaO

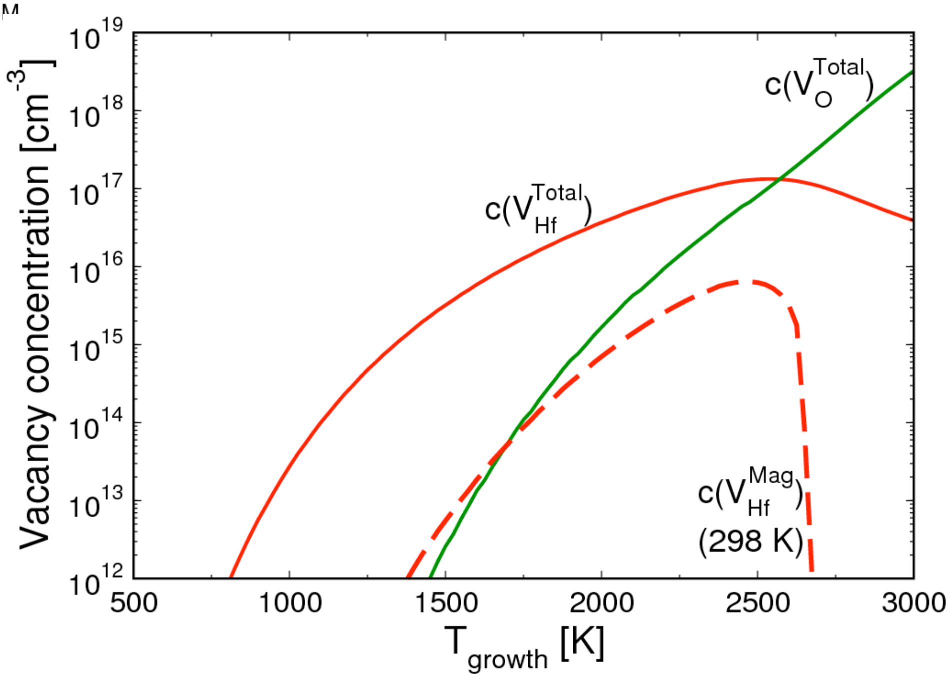


Concentration of moment-carrying $V_{Ca}$ states for the best growth conditions is up to $10^{18}$ cm$^{-3}$ ($10^{-3}$%).



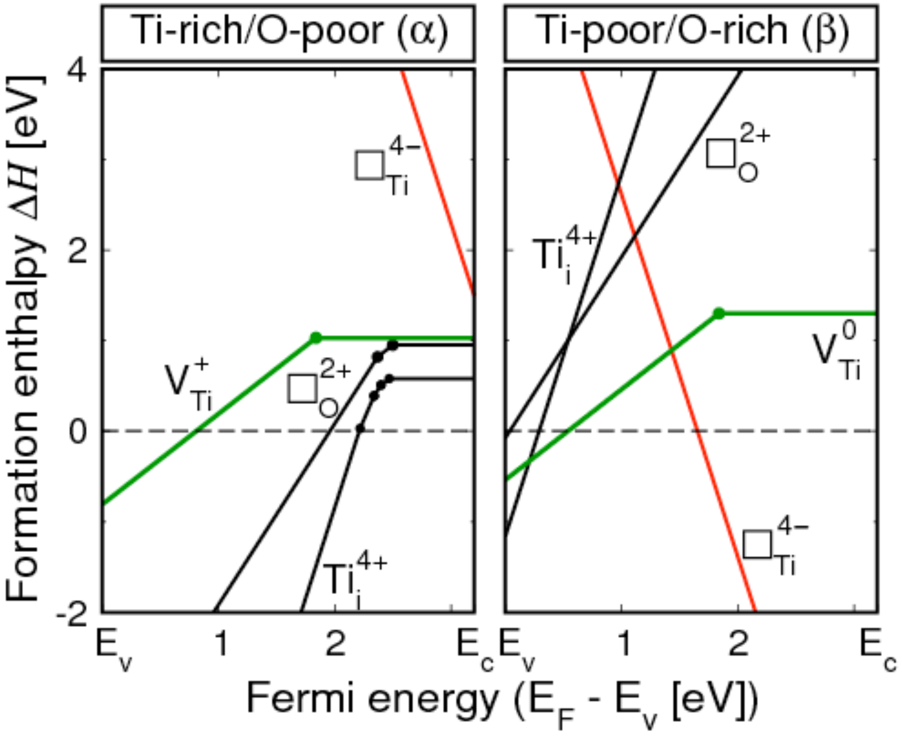
# Second step: $HfO_2$

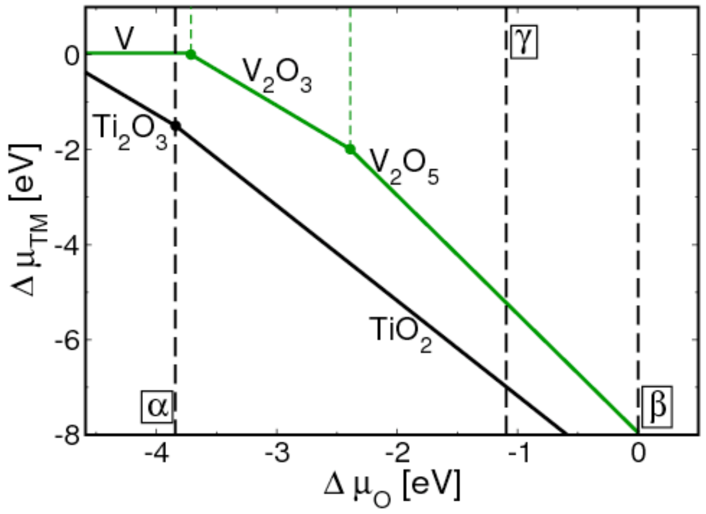


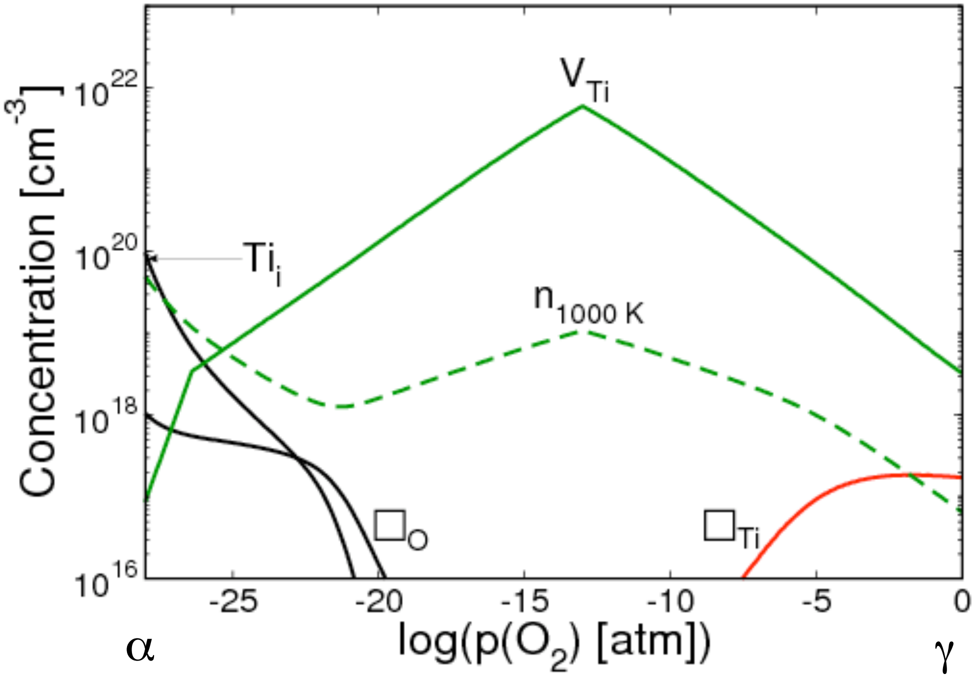


Concentration of moment-carrying $V_{Hf}$ states for the best growth conditions is up to $6.4 \times 10^{15}$ $cm^{-3}$ ($10^{-7}$%).

# Second step: $TiO_2$







$V_{Ti}$ is soluble up to $10^{21}$ $cm^{-3}$ (21%).

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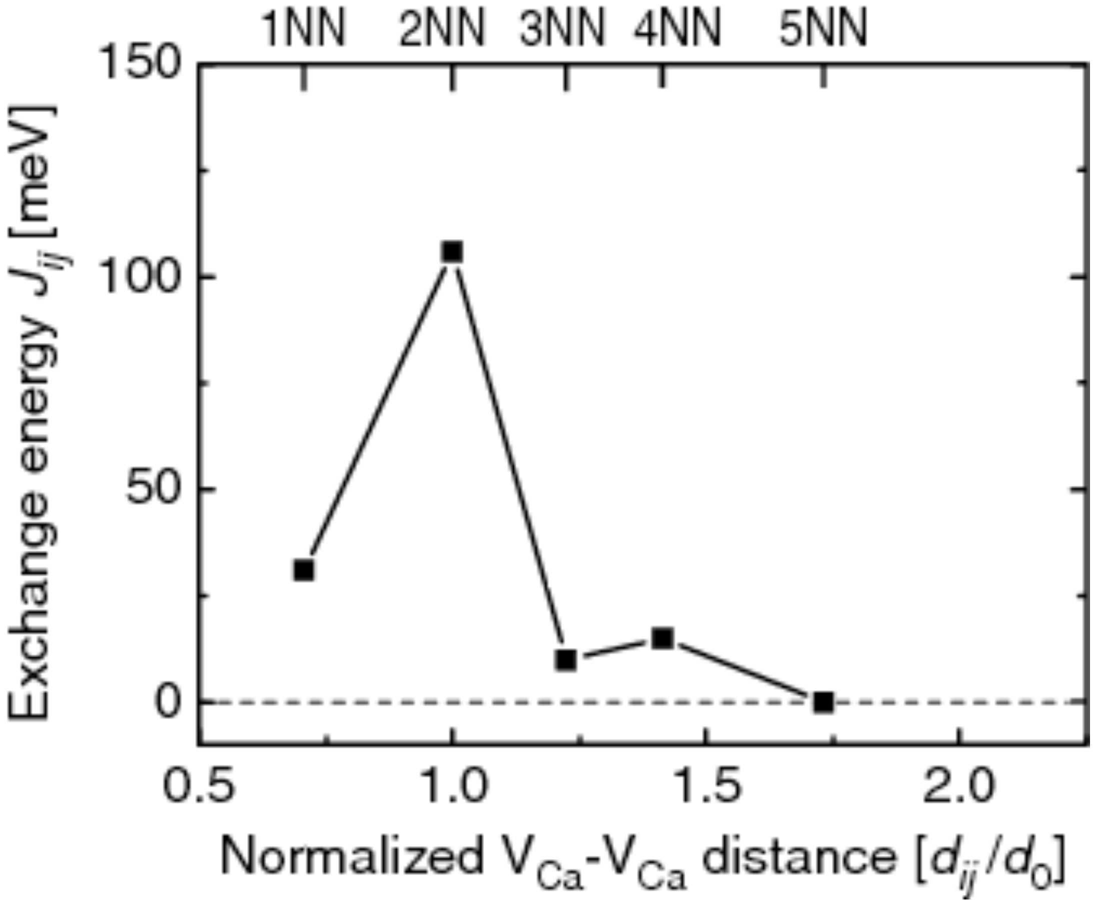
[2] J. Osorio-Guillén et al., Phys. Rev. B **75**, 184421.

# Third step: range of interaction of two $V_{Ca}$-$V_{Ca}$ in CaO

$$J_{ij}(d) = \frac{1}{\lambda}(E_{\mathrm{AFM}} - E_{\mathrm{FM}})$$



Range of interaction is ≤ 4 NN

# Third step: range of interaction of two $V_{Hf}$-$V_{Hf}$ in $HfO_2$

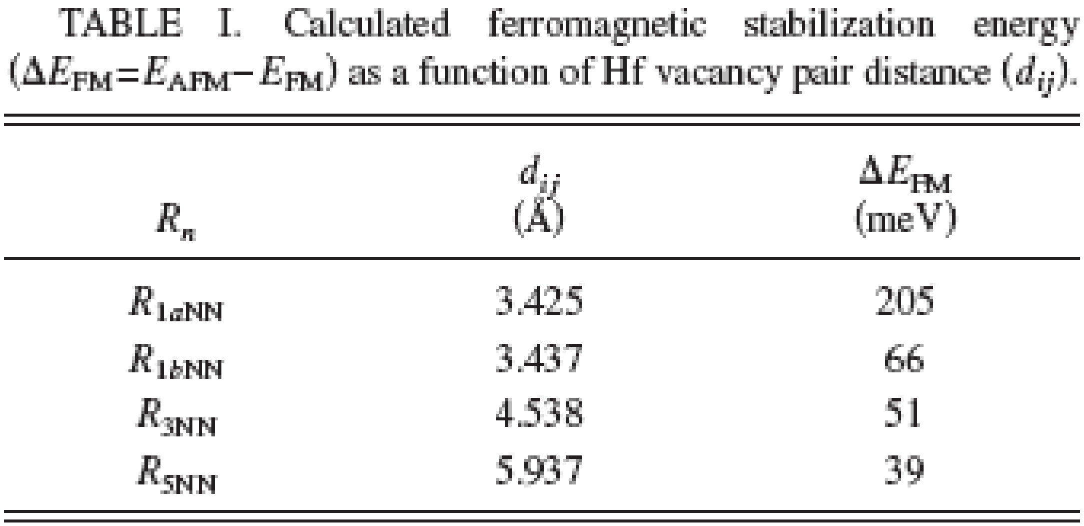
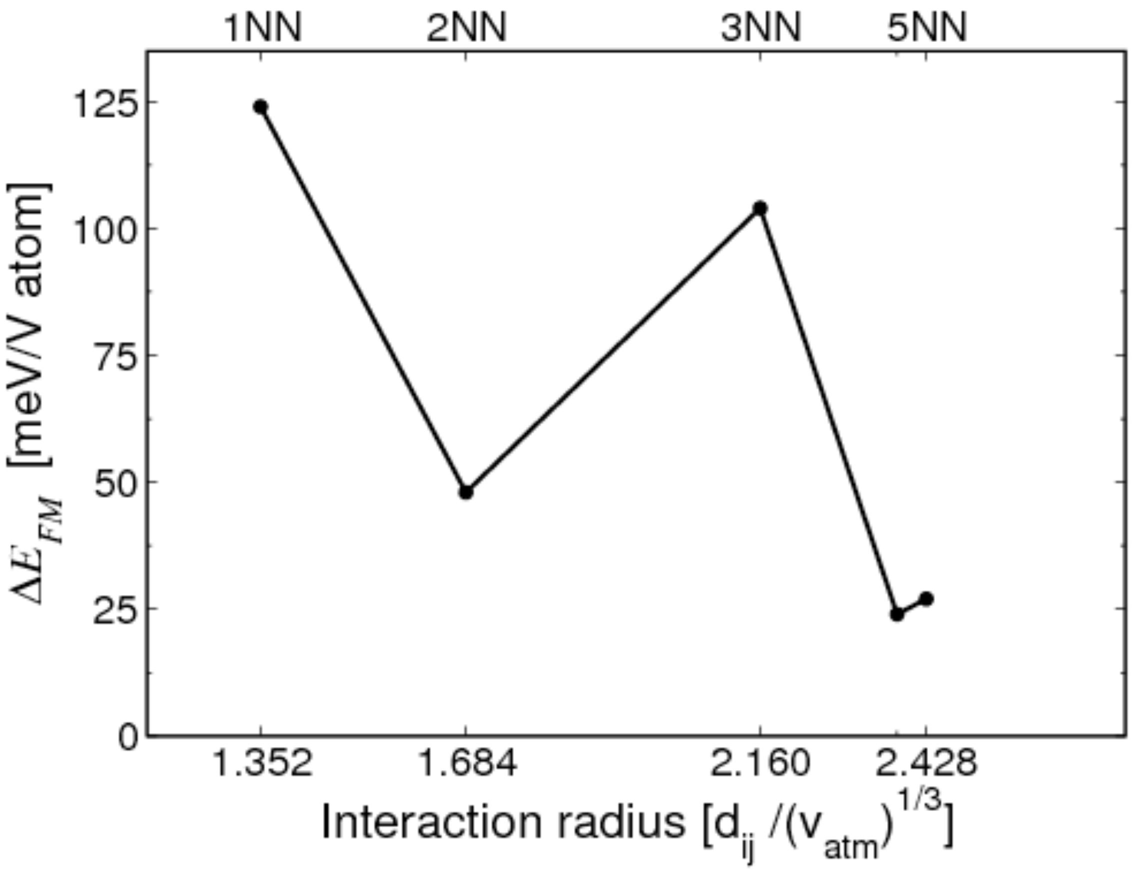


TABLE I. Calculated ferromagnetic stabilization energy ($\Delta E_{FM}=E_{AFM}-E_{FM}$) as a function of Hf vacancy pair distance ($d_{ij}$).

| $R_n$ | $d_{ij}$ (Å) | $\Delta E_{FM}$ (meV) |
|---|---|---|
| $R_{1a\mathrm{NN}}$ | 3.425 | 205 |
| $R_{1b\mathrm{NN}}$ | 3.437 | 66 |
| $R_{3\mathrm{NN}}$ | 4.538 | 51 |
| $R_{5\mathrm{NN}}$ | 5.937 | 39 |

Range of interaction is ≤ 5 NN

# Third step: range of interaction of two $V_{Hf}$-$V_{Hf}$ in $TiO_2$



- GGA predicts a range of interaction ≤ 5 NN.
- GGA+U predicts a shorter range of interaction.

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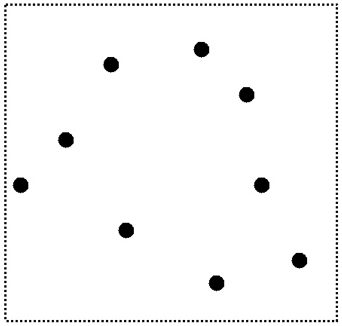
# **Fourth step:** minimal percolation concentration

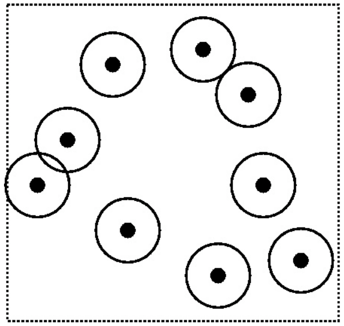
For each structure, we find the smallest radius $R_P$ around a sublattice site that causes percolation in 3D:

sample configuration of cation sites in $M_xO_y$



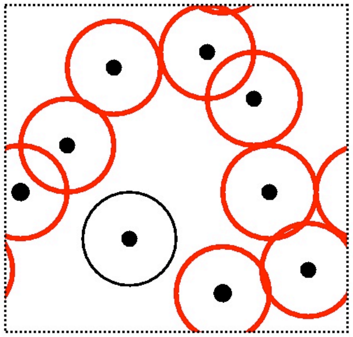
sphere of radius $R$ around each cation site

$R<R_P$



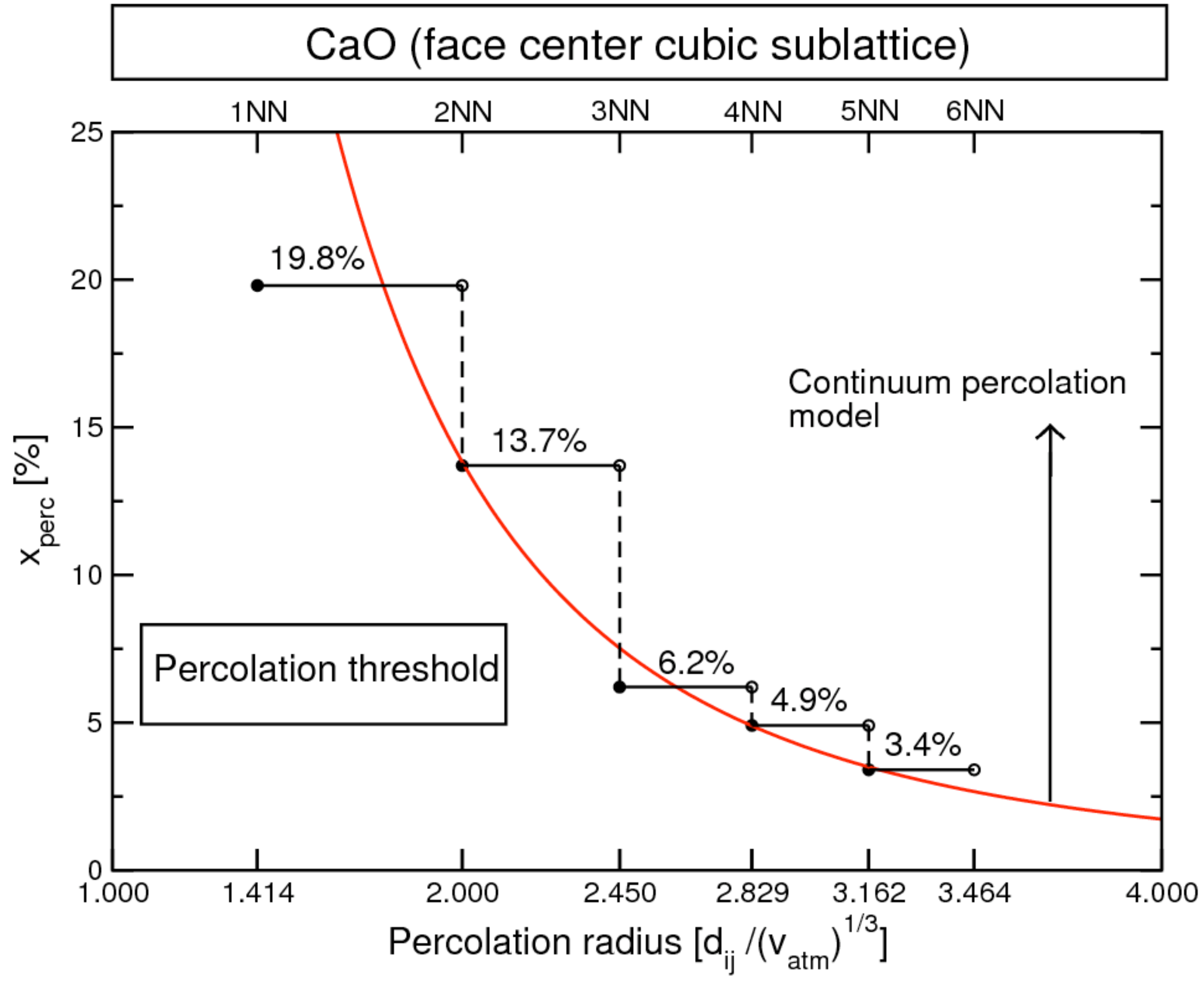
increase $R$ until spheres form an infinite cluster

$R=R_P$



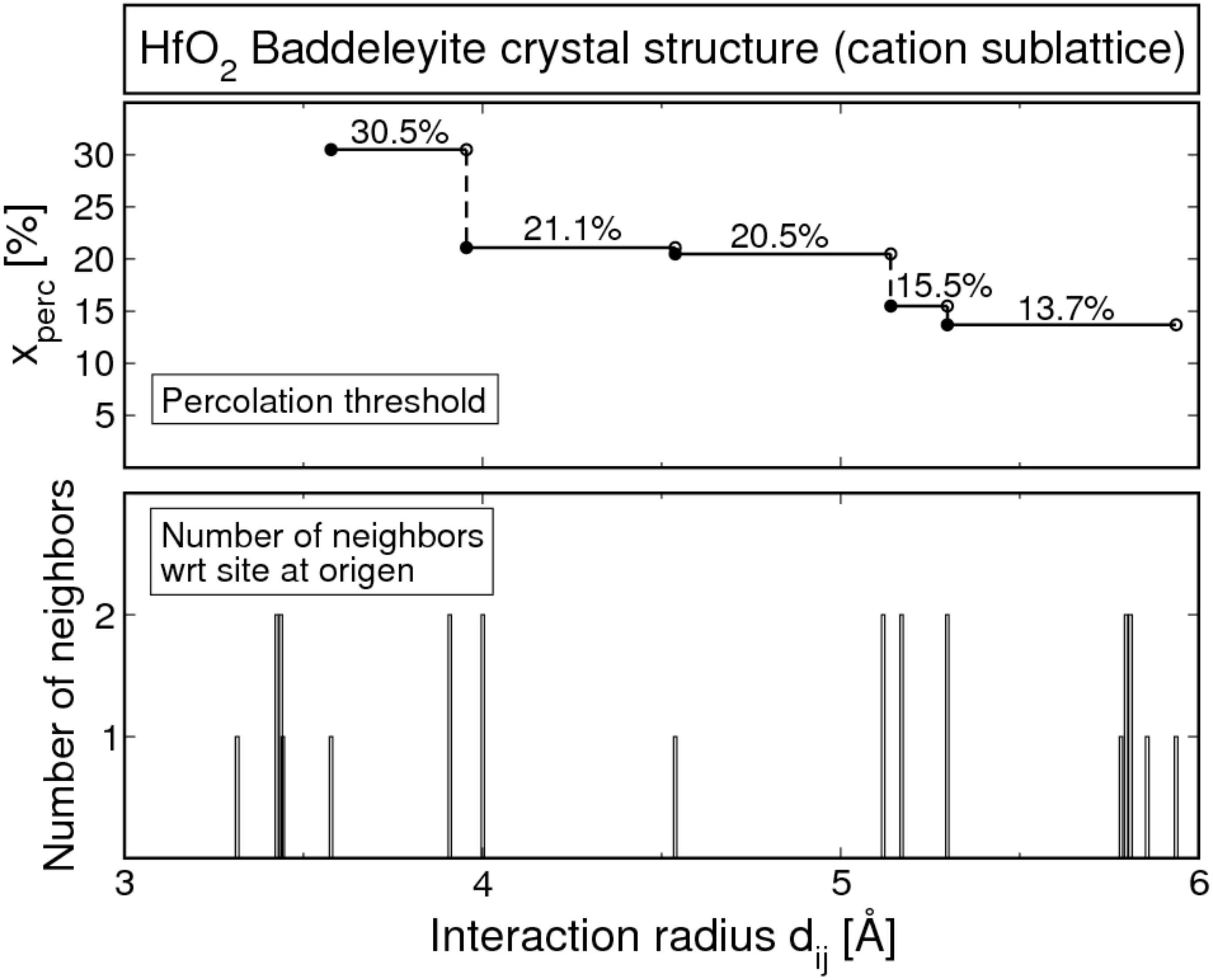
Finite-size analysis of Monte Carlo simulations

# Fourth step: minimal percolation concentration for CaO



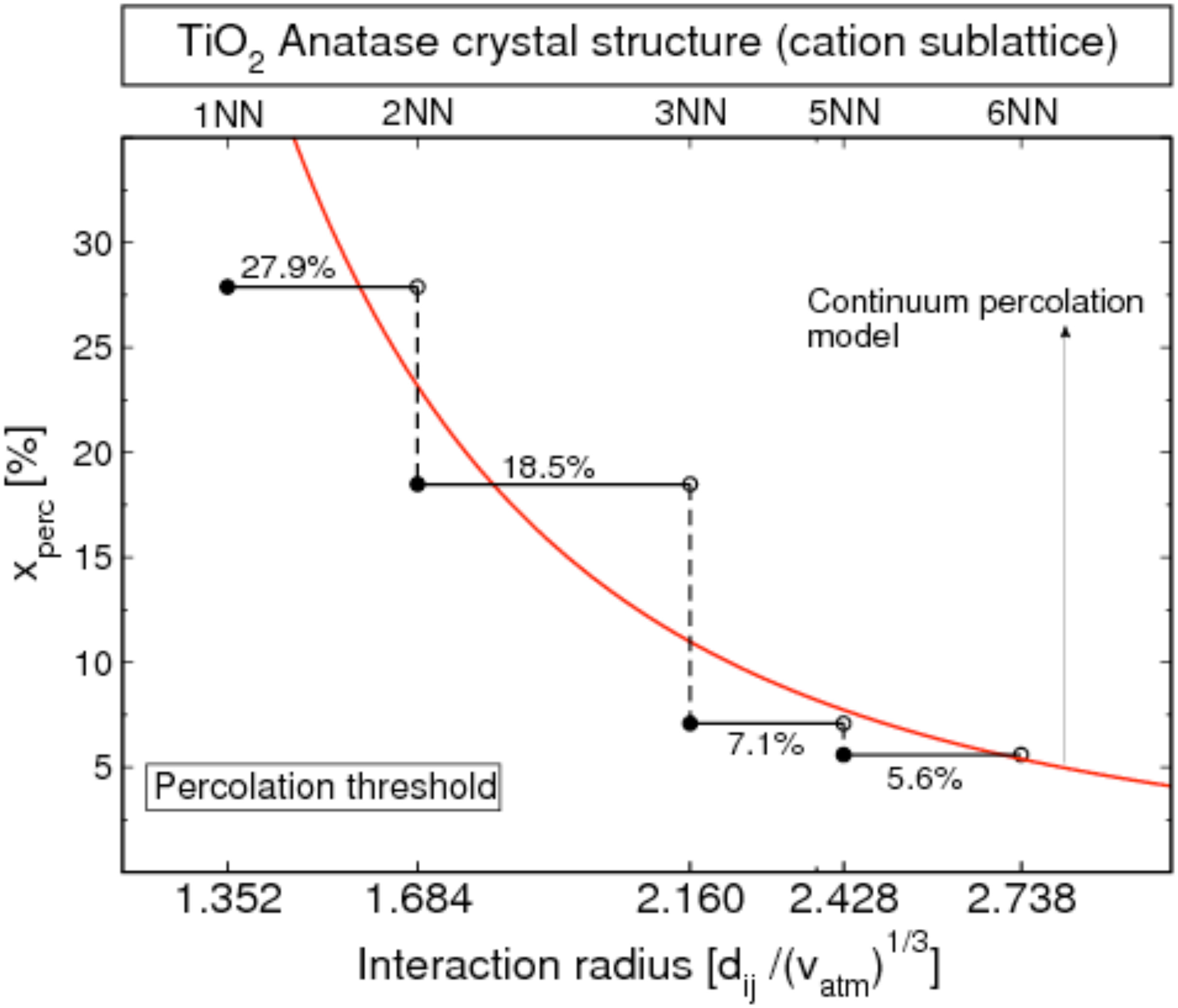
For 4NN, $x_{per}$ = 4.9 %

# Fourth step: minimal percolation concentration for $HfO_2$



For 5NN, $x_{per}$ = 13.5 %

# Fourth step: minimal percolation concentration for $TiO_2$



For 5NN, $x_{per}$ = 5.6 %

# Conclusions

1. Cation vacancies introduce spin-polarized gap states in CaO and $HfO_2$, leading to FM V-V coupling with interaction range ≤ 4NN and 5NN, respectively. However, the moment-carrying vacancy concentration falls very short to promote collective ferromagnetism.

2. V introduces spin-polarized gap state in $TiO_2$, leading to FM V-V coupling with interaction range  5NN.

3. V solubility in $TiO_2$ is above the magnetic percolation threshold.