Defect thermochemistry: Spinney

18-04-24. 27th Wien2k Workshop. Trieste.

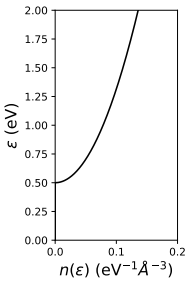
TECHNISCHE UNIVERSITÄT WIEN

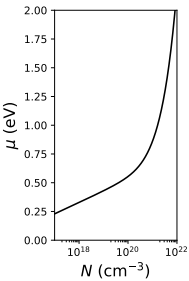
Overview

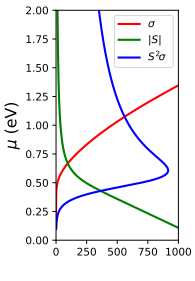
1. Defects
2. Defect tehrmochemistry
3. Examples

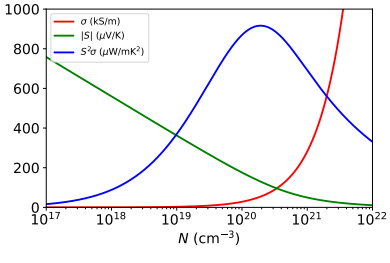
Parabolic band. DOS, transport and doping

$$\varepsilon(k) = \varepsilon_{\mathrm{CBM}} + \frac{\hbar^2 k^2}{2m^*} \quad , \quad n(\varepsilon) = \frac{m^{3/2}}{\pi^2\hbar^3}\sqrt{\frac{\varepsilon}{2}} \quad , \quad \sigma(\varepsilon) = \frac{\sqrt{8m^*}}{\pi^2\hbar^3}\tau\varepsilon^{\frac{3}{2}}$$









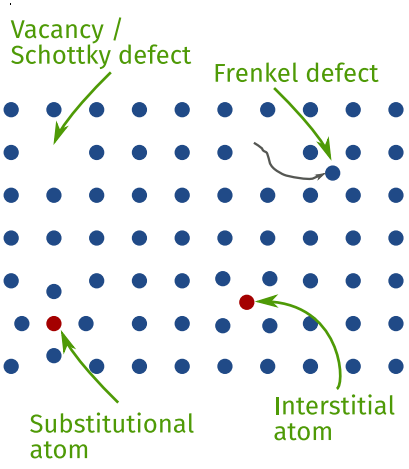
Defects according to their dimensionality

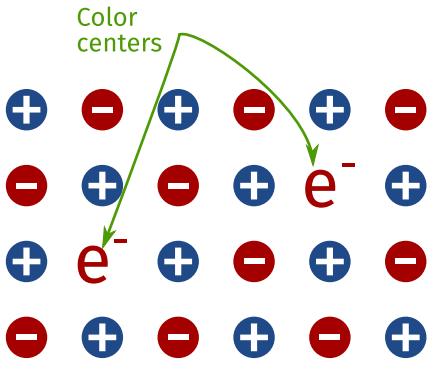
Defects are breakdowns of periodicity. Along each dimension, they can be:

Localized: size $\lesssim$ a few lattice parameters
Extended: size $\gg$ a few lattice parameters

Name	Localized/extended along	Examples
Point defects	3D/0D	Vacancies Interstitial atoms Substitutions Frenkel defects Small clusters of the above
Line defects	2D/1D	Dislocations Chains of point defects
Planar defects	1D/2D	Grain boundaries Twinning External boundaries
Bulk defects	0D/3D	Pores Inclusions Precipitates

Some point defects





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Equilibrium concentration of defects

Model:

- Crystal with N sites
- Cost in energy by formation of isolated point defect: E_d

Competition between energetic cost and entropy advantage when forming defects:

- Increase in energy due to n defects: nE_d
- $\Omega = \binom{N}{n} = \frac{N!}{(N-n)!n!}$ ways to arrange them
- Configurational entropy $S = k_B \log \Omega$
  $S \simeq k_B[N \log N - n \log n - (N-n) \log (N-n)]$

Defect concentration that minimizes F at constant T:

$$\frac{\partial F}{\partial n} = \frac{\partial (nE_d - TS)}{\partial n} = 0 \implies n/N \simeq e^{-\frac{E_d}{k_B T}}$$

$V/atom \approx 10$ Å$\rightarrow 10^{23}$ atoms/cm^3

E_D	n/N	c_D
1.0 eV	$\approx 10^{-5}$	$\approx 10^{-18}$ cm^{-3}
0.6 eV	$\approx 10^{-3}$	$\approx 10^{-20}$ cm^{-3}
0.4 eV	$\approx 10^{-2}$	$\approx 10^{-21}$ cm^{-3}

Defect formation energy

$$E_{D^{(q)}}(\{\mu\}) = E_{f,D^{(q)}} - \sum_{\alpha} n_\alpha \Delta\mu_\alpha + q\mu_e$$

Example: $\square_A$ in AB.

A rich environment

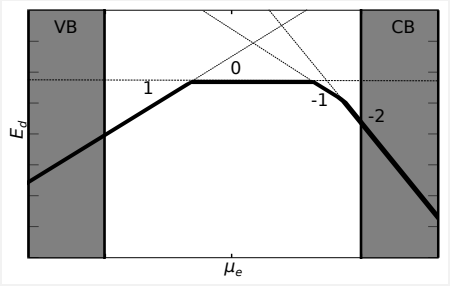
$$AB \rightarrow A_{1-x}B + xB$$

B rich environment

$$A_{1-x}B_{1-x} + xB \rightarrow A_{1-x}B$$

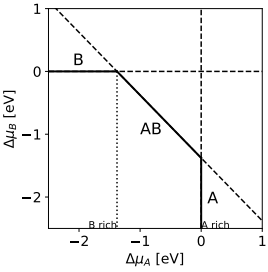
$$2\Delta H_f(\mathrm{AB}) \leq \mu_A \leq 0$$

Charge chemical potential



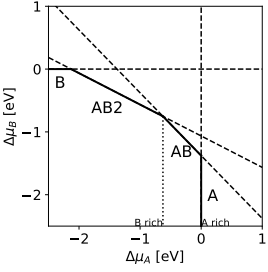
Chemical potentials of the constituents

$$\Delta\mu_A + \Delta\mu_B = 2\Delta H_{f,AB} \Delta\mu_A \leq 0 \quad , \quad \Delta\mu_B \leq 0$$



Competing phase: AB_2

$$\Delta\mu_A + 2\Delta\mu_B = 3\Delta H_{f,AB_2}$$



Supercell approach to $E_{f,d}$

$$E_{f,\mathrm{D}^{(q)}} = E_{\mathrm{D}^{(q)}} - n_\alpha \mu_{\alpha,ref} + q\varepsilon_{VBM} + E_{corr} - E_{bulk}$$

Correction scheme: Point charge at defect position embedded in dielectric constant of crystal (Kumagai, Oba 2014 and refs therein)

$$E_{corr} = E_{PC,q} - q\Delta V_{PC,q}$$

$E_{PC,q}$: Lattice of supercells with point charge at defect position
$\Delta V_{PC,q/b}$: Difference between defect induced potential and the point charge potential averaged over positions “far” from the defect

$$\Delta V_{PC,q/b} = V_{\mathrm{D}^{(q)}} - V_{bulk} - V_{PC,q}$$

Exercise: $\square_B^{(-3)}$:c-BN

- `pip install spinney`
- Download `Spinney_VacB.tgz` from W2K deposit
- Unpack and run script
- Reproduce the results
  - Setup supercells
  - Make defect and break symmetry in pristine cell
  - Initialize calculations. Note the need for a precise calculation of the Coulomb potential. `lvns, gmax` and `R2V`
- Compare your `case.struct`, `case.in0` and `case.in2` to the ones from the deposit
- Run the calculation and compare your `case.scf`
- Modify the script to work on your calculation

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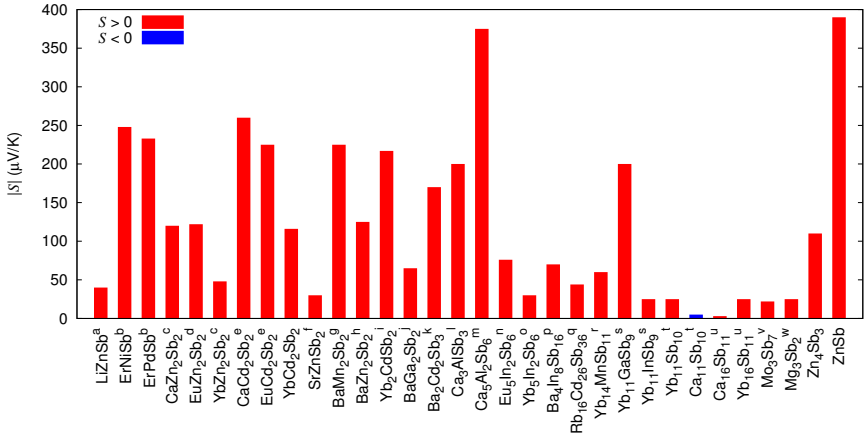
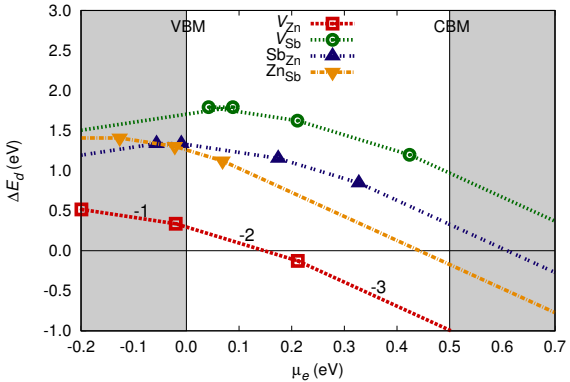
Zintl Antimonides. Seebeck Coefficient



- Always positive Seebeck coefficient
- Binary and ternary Zintl antimonides always *p*-type

Bjerg, GKHM, Iversen *Chem Mat* 24 p2111 (2012)

Intrinsic Defects. ZnSb



- Low formation energy of Zn vacancy pins chemical potential of the electrons to lower half of band gap
- Small stability window of ZnSb limits μ_α
- Always positive Seebeck coefficient

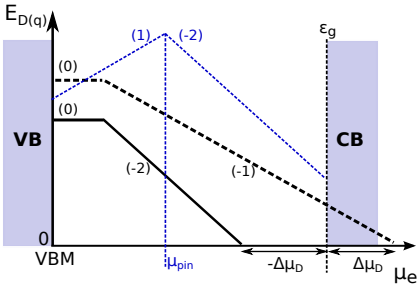
Automated search strategy

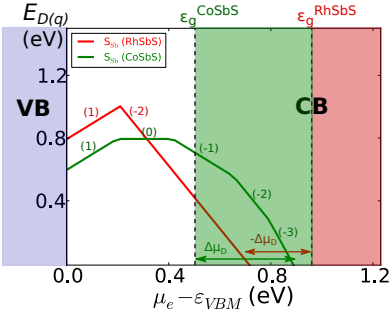
- Goal: Low-cost high-performance thermoelectric
- Computationally screen transport properties of innocuos, abundant sulfides
- Calculate bulk energy of competing phases
- Screen intrinsic defects, vacancies, antisites and interstitials, for potential doping limits
- Screen potential extrinsic potential defects, if no doping limits

Find ternary ***n***-type sulfide to be used with ***p***-type tetrahedrites

Ternary sulfides: Doping limits ?

Likelihood of intrinsic limit to ***n***-doping given by stable hole producing killer defect

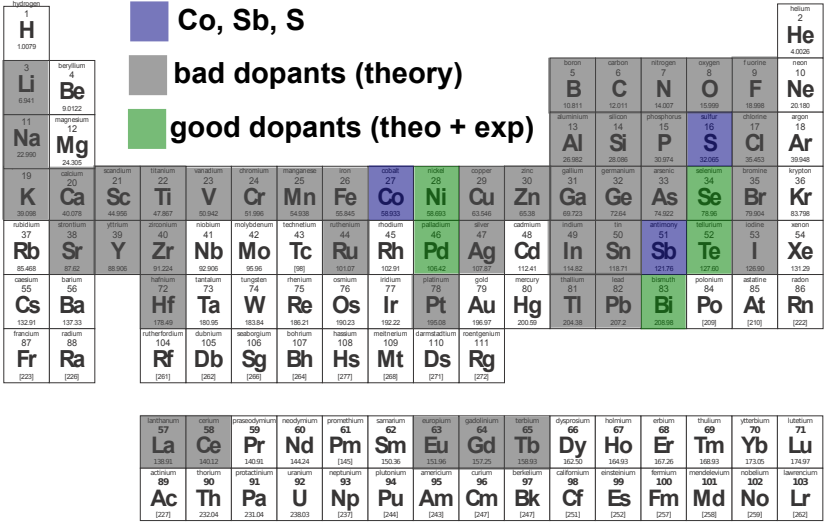




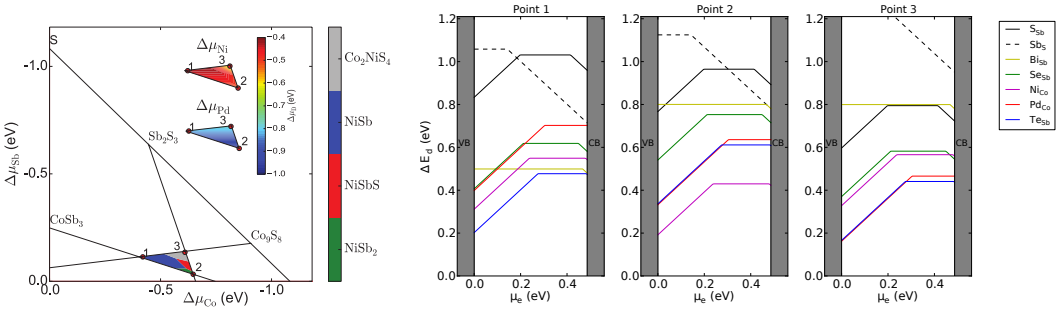
Compound	*D*	$\Delta\mu_D$ (eV)	ε_g (eV)
$Ca_2Sb_2S_5$	Vac_{Sb}	-0.33	2.11
RhSbS	S_{Sb}	-0.25	0.96
$NaSbS_2$	Na_{Sb}	-0.86	1.58
$CuSbS_2$	Vac_{Cu}	-0.80	1.05
CoSbS	S_{Sb}	0.38	0.50

Bhattacharya et al. *J. Mater. Chem. A* 4 (2016) p11086

CoSbS: Extrinsic doping



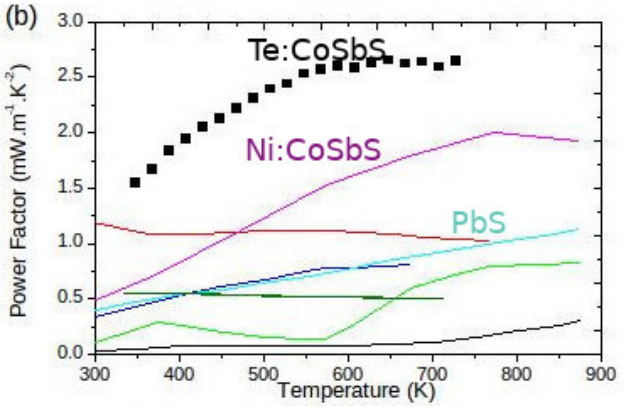
CoSbS defects



- $PdSb_2$ limiting competing phase in entire stability region when Pd doping
  - Work in Co AND Sb poor (sulfur rich) environment
- Ni-S phases set strict limits for Ni doping
- Te doping attractive in several limits

Chmielowsky, et al. *J. Mater. Chem. C* 4, p3094 (2016)

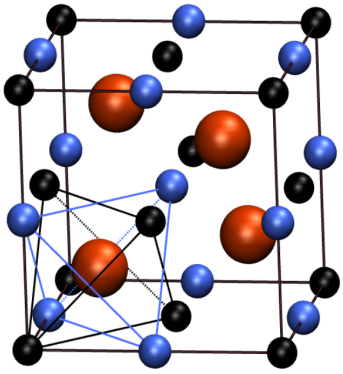
CoSbS powerfactor

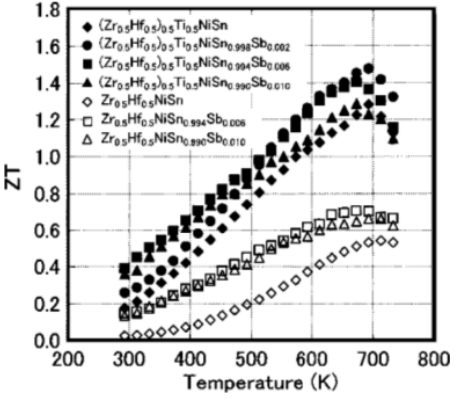


- 150% increase in PF over best known sulfide
- Te doping: 50% increase in PF over Ni doped CoSbS

Chmielowsky, et al. *J. Mater. Chem. C* 4, p3094 (2016)
For Se alloying see: Chmielowsky, et al. *Sci. Rep.* 7, p46630 (2017)

Half-Heusler thermoelectrics

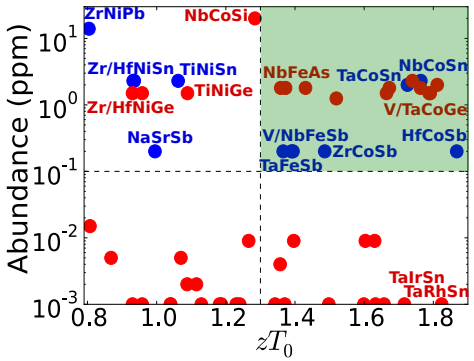




Sakurada, Shutoh *Appl. Phys. Lett.* **86**, p082105 (2005)

- 18 electron rule
- High intrinsic thermal conductivity
- Large chemical tunability

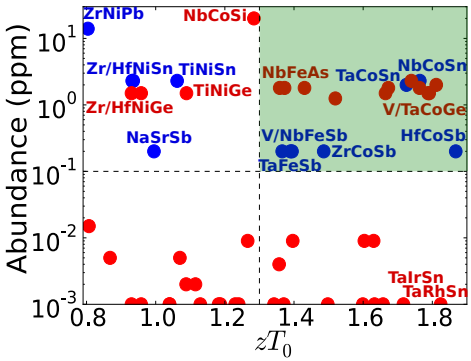
Screening: Band structure, abundance and stability.



Compound	ΔE_{hull} (meV/atom)	orth phase
TaFeAs	33.03	yes
TaFeSb	0.00	no
NbFeAs	125.81	yes
NbFeSb	0.00	no
VFeSb	0.00	no
ZrCoAs	0.00	yes
ZrCoSb	0.00	no
WFeGe	64.34	no
NbCoGe	0.00	yes
HfCoAs	0.00	yes
TaCoSn	0.00	no
VCoSn	90.77	no
TiCoAs	0.00	yes
NbCoSn	0.00	no
TaCoGe	0.00	yes
VCoGe	0.00	yes
TaCoSi	91.47	yes
HfCoSb	0.00	no

Bhattacharya, GKHM *J. Mater. Chem. C*, **4**, p11261 (2016)

Screening: Band structure, abundance and stability.



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VFeSb	0.00	no
ZrCoAs	0.00	yes
ZrCoSb	0.00	no
WFeGe	64.34	no
NbCoGe	0.00	yes
HfCoAs	0.00	yes
TaCoSn	0.00	no
VCoSn	90.77	no
TiCoAs	0.00	yes
NbCoSn	0.00	no
TaCoGe	0.00	yes
VCoGe	0.00	yes
TaCoSi	91.47	yes
HfCoSb	0.00	no

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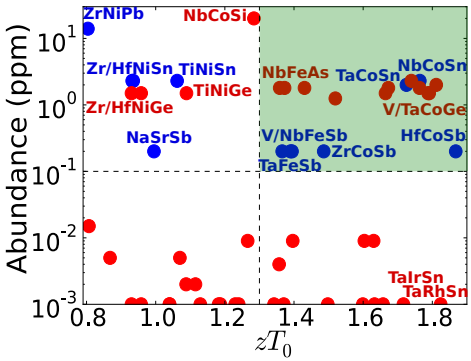

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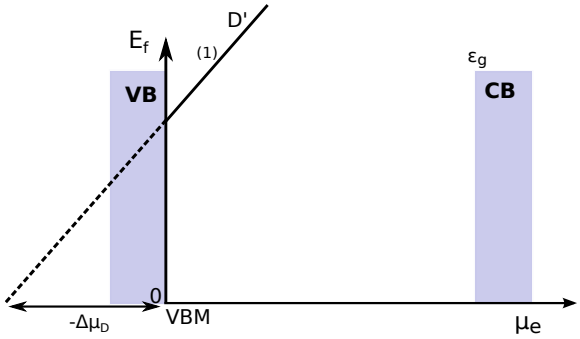
Intrinsic defects



	$\Delta\mu_{D'}$ (eV)	$D'^{(q)}$
NbCoSn	-0.27	$Co_{Int}^{(3)}$
VFeSb	-0.18	$Fe_{Int}^{(2)}$
ZrCoSb	-0.51	$Sb_{Zr}^{(1)}$
TaCoSn	-0.26	$Co_{Int}^{(2)}$
NbFeSb	-0.60	$Fe_{Int}^{(2)}$
HfCoSb	-0.37	$Co_{Int}^{(2)}$

No intrinsic doping limits

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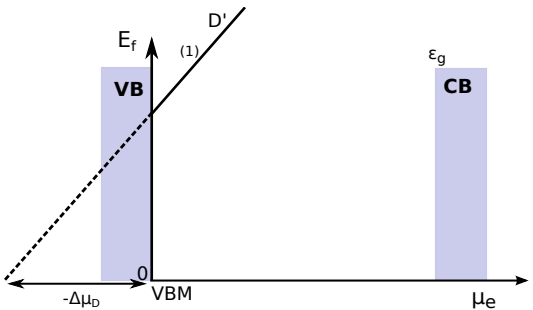
Extrinsic doping



	$E_f^D(\mu_{VB})$ (eV)	D(q)	$\Delta E^{D'-D}$ (eV)	D'(q)
NbFeSb	-0.01	$Hf_{Nb}^{(-1)}$	1.20	$Fe_{Int}^{(2)}$
	0.09	$Ti_{Nb}^{(-1)}$	1.10	$Fe_{Int}^{(2)}$
	0.21	$Mn_{Fe}^{(-1)}$	0.72	$Vac_{Fe}^{(2)}$
	0.41	$Zr_{Nb}^{(-1)}$	0.78	$Fe_{Int}^{(2)}$
	0.55	$Sn_{Sb}^{(-1)}$	0.70	$Fe_{Int}^{(2)}$
ZrCoSb	0.17	$Sc_{Zr}^{(-1)}$	0.60	$Sb_{Zr}^{(1)}$
	0.61	$Sn_{Sb}^{(-1)}$	0.35	$Vac_{Co}^{(1)}$
	0.61	$Fe_{Co}^{(-1)}$	-0.48	$Vac_{Co}^{(1)}$
NbCoSn	0.32	$Hf_{Nb}^{(-1)}$	0.50	$Co_{Int}^{(3)}$
	0.62	$Fe_{Co}^{(-1)}$	-0.15	$Fe_{Int}^{(2)}$
	0.68	$Ti_{Nb}^{(-1)}$	0.14	$Co_{Int}^{(3)}$
	0.72	$Zr_{Nb}^{(-1)}$	0.10	$Co_{Int}^{(3)}$
TaCoSn	0.44	$Hf_{Ta}^{(-1)}$	0.33	$Co_{Int}^{(2)}$
	0.87	$Fe_{Co}^{(-1)}$	-0.10	$Fe_{Int}^{(2)}$

- Known carrier inducing defects reproduced in NbFeSb and ZrCoSb
- A new system with favorable extrinsic dopants identified

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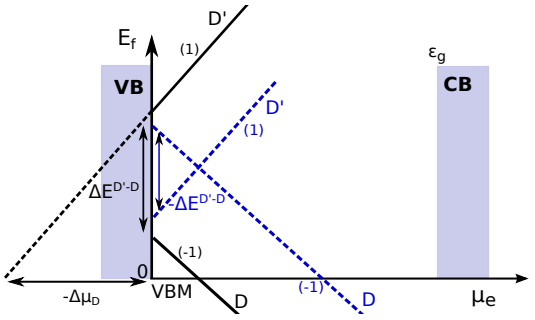
Extrinsic doping



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