

Defect thermochemistry: Spinney

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

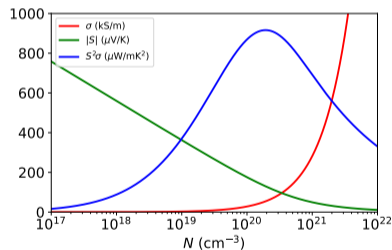
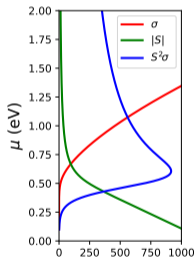
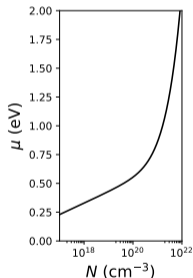
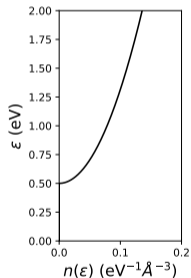


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1. Defects
2. Defect thermochemistry
3. Examples

Parabolic band. DOS, transport and doping

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



Defects according to their dimensionality

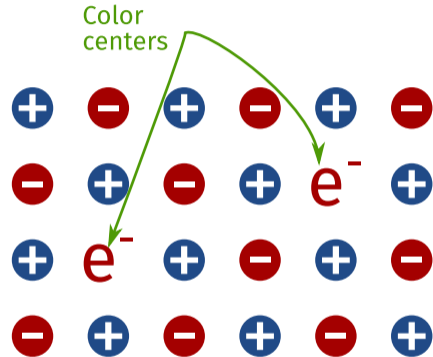
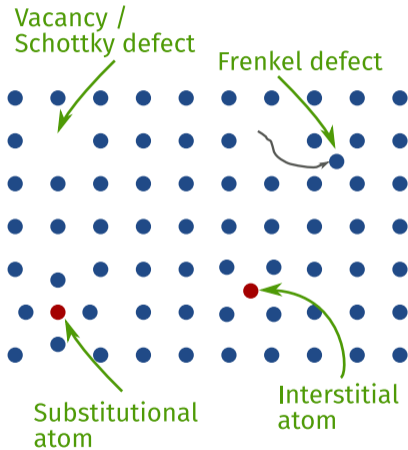
Defects are breakdowns of periodicity. Along each dimension, they can be:

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 $S = k_B \log \Omega$
 $S \approx k_B [N \log N - n \log n - (N - n) \log (N - n)]$

Defect concentration that minimizes F at constant T :

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

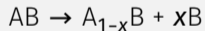
$$V/\text{atom} \approx 10 \text{ \AA} \rightarrow 10^{23} \text{ atoms/cm}^3$$

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

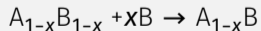
$$E_{D^{(q)}}(\{\mu\}) = E_{f,D^{(q)}} - \sum_{\alpha} n_{\alpha} \Delta\mu_{\alpha} + q\mu_e$$

Example: \square_A in AB.

A rich environment

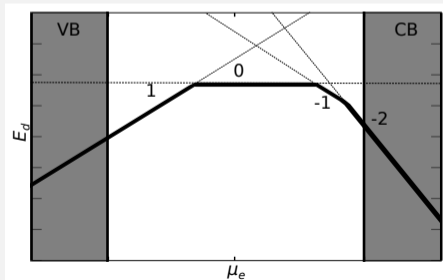


B rich environment



$$2\Delta H_f(AB) \leq \mu_A \leq 0$$

Charge chemical potential

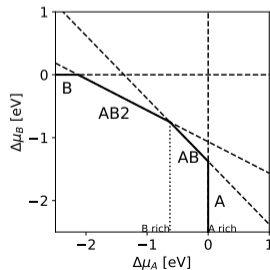
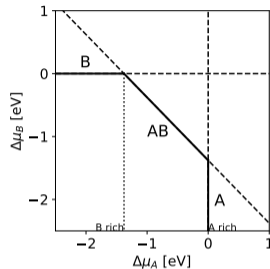


Chemical potentials of the constituents

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

Competing phase: AB₂

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



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

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

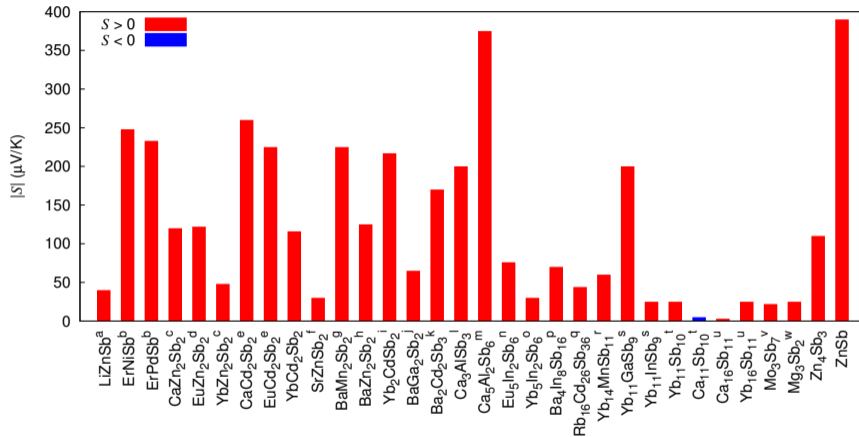
$$\Delta V_{PC,q/b} = V_{D(q)} - V_{bulk} - V_{PC,q}$$

Exercise: $\square_{\text{B}}^{(-3)}\text{:c-BN}$

- `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

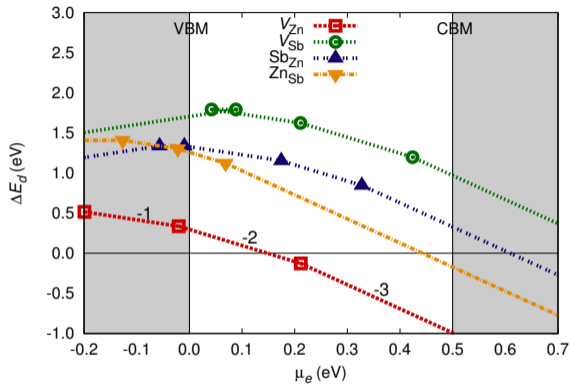
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Zintl Antimonides. Seebeck Coefficient



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

Intrinsic Defects. ZnSb



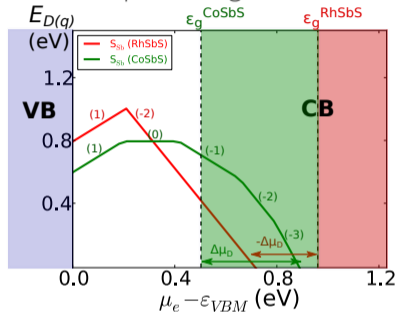
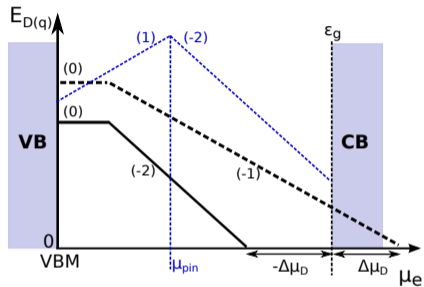
- Low formation energy of Zn vacancy pins chemical potential of the electrons to lower half of band gap
- Small stability window of ZnSb limits μ_α
- Always positive Seebeck coefficient

- Goal: Low-cost high-performance thermoelectric
- Computationally screen transport properties of innocuous, 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)
$\text{Ca}_2\text{Sb}_2\text{S}_5$	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

CoSbS: Extrinsic doping

hydrogen																				helium															
1 H 1.0079																				2 He 4.0026															
beryllium																				neon															
3 Li 6.941	4 Be 9.0122																	9 F 18.998	10 Ne 20.180																
magnesium																				argon															
11 Na 22.990	12 Mg 24.305																	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948														
scandium		titanium		vanadium		chromium		manganese		iron		cobalt		nickel		copper		zinc		gallium		germanium		arsenic		selenium		bromine		krypton					
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798																		
rubidium		strontium		yttrium		zirconium		niobium		molybdenum		technetium		ruthenium		rhodium		palladium		silver		cadmium		indium		tin		antimony		tellurium		iodine		xenon	
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29																		
caesium		barium		hafnium		tantalum		tungsten		rhenium		osmium		iridium		platinum		gold		mercury		thallium		lead		bismuth		polonium		astatine		radon			
55 Cs 132.91	56 Ba 137.33	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]																			
francium		radium		rutherfordium		dubnium		seaborgium		bohrium		hassium		meitnerium		darmstadtium		roentgenium																	
87 Fr [223]	88 Ra [226]	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [277]	109 Mt [268]	110 Ds [271]	111 Rg [272]																										



Co, Sb, S



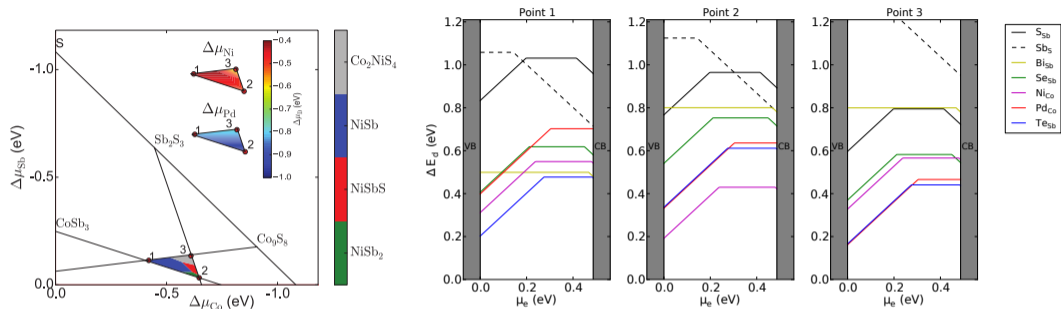
bad dopants (theory)



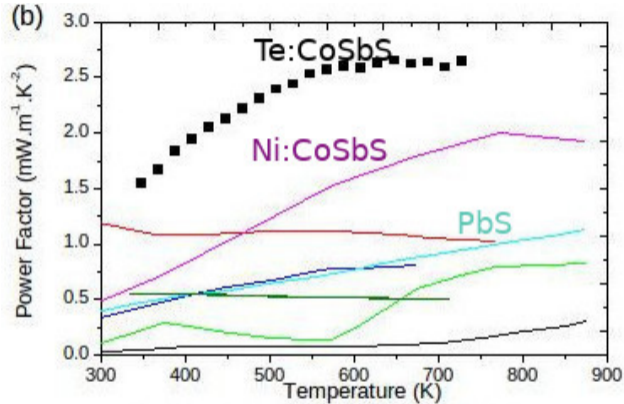
good dopants (theo + exp)

lanthanum		cerium		praseodymium		neodymium		promethium		samarium		europium		gadolinium		terbium		dysprosium		holmium		erbium		thulium		ytterbium		lutetium	
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97															
actinium		thorium		protactinium		uranium		neptunium		plutonium		americium		curium		berkelium		californium		einsteinium		fermium		mendelevium		nobelium		lawrencium	
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]															

CoSbS defects

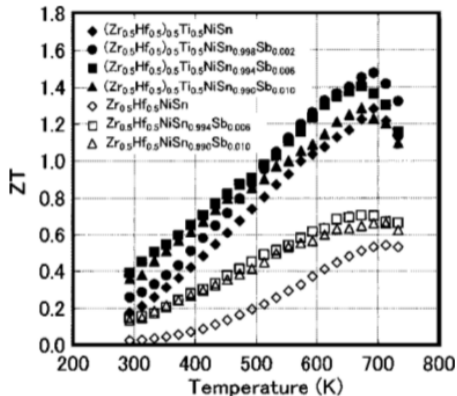
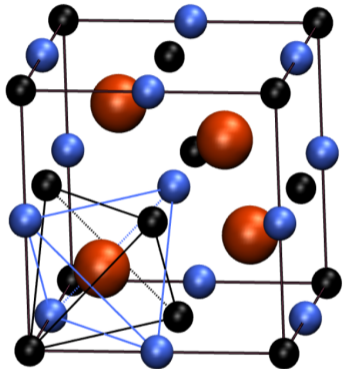


- PdSb_2 limiting competing phase in entire stability region when Pd doping
 - Work in Co AND Sb poor (sulfur rich) environment
- Ni-S phases set strict limits for Ni doping
- Te doping attractive in several limits



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

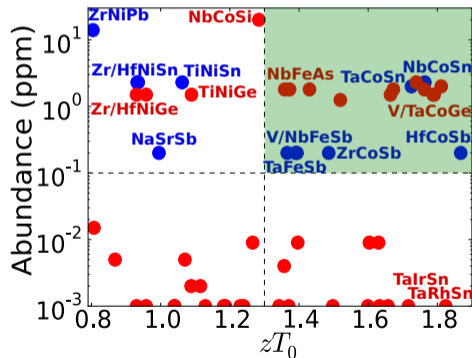
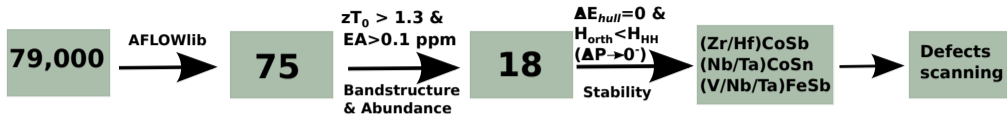
Half-Heusler thermoelectrics



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

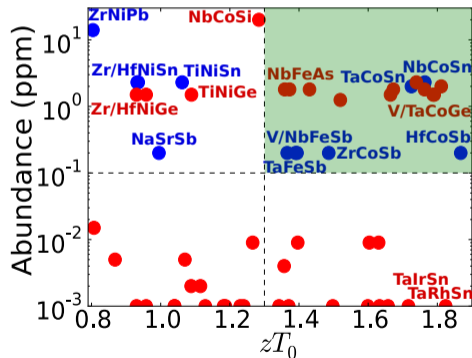
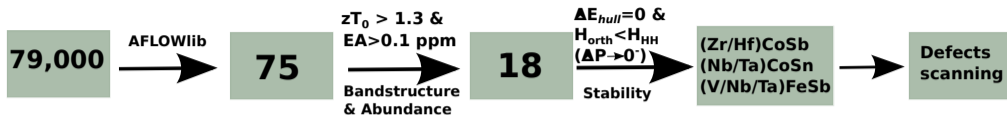
- 18 electron rule
- High intrinsic thermal conductivity
- Large chemical tunability

Screening: Band structure, abundance and stability.



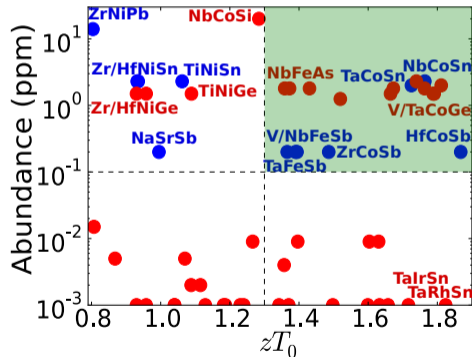
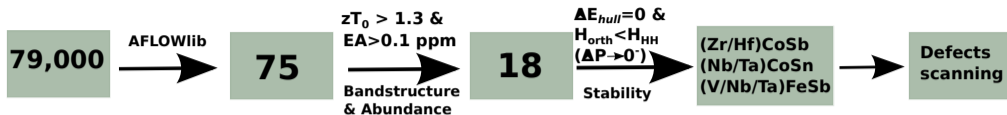
Compound	ΔE_{hull} (meV/atom)	orth phase
TaFeAs	33.03	yes
TaFeSb	0.00	no
NbFeAs	125.81	yes
NbFeSb	0.00	no
VFeSb	0.00	no
ZrCoAs	0.00	yes
ZrCoSb	0.00	no
WFeGe	64.34	no
NbCoGe	0.00	yes
HfCoAs	0.00	yes
TaCoSn	0.00	no
VCoSn	90.77	no
TiCoAs	0.00	yes
NbCoSn	0.00	no
TaCoGe	0.00	yes
VCoGe	0.00	yes
TaCoSi	91.47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

Screening: Band structure, abundance and stability.



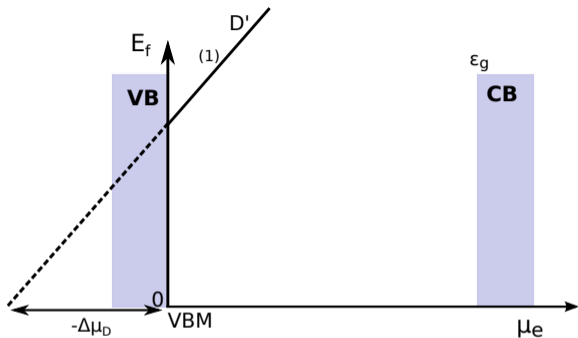
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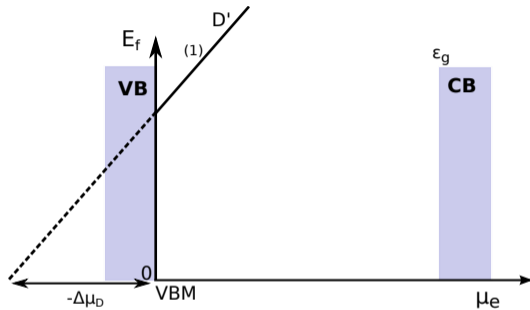
Intrinsic defects



	$\Delta\mu_{D'}$ (eV)	$D'^{(q)}$
NbCoSn	-0.27	$\text{Co}_{\text{Int}}^{(3)}$
VFeSb	-0.18	$\text{Fe}_{\text{Int}}^{(2)}$
ZrCoSb	-0.51	$\text{Sb}_{\text{Zr}}^{(1)}$
TaCoSn	-0.26	$\text{Co}_{\text{Int}}^{(2)}$
NbFeSb	-0.60	$\text{Fe}_{\text{Int}}^{(2)}$
HfCoSb	-0.37	$\text{Co}_{\text{Int}}^{(2)}$

No intrinsic doping limits

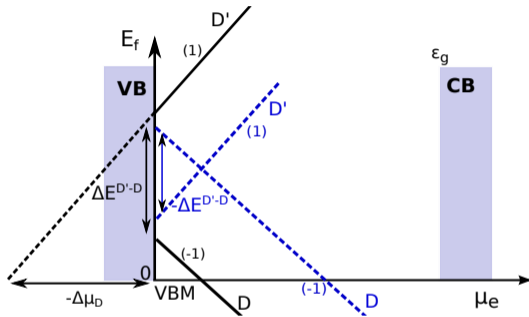
Extrinsic doping



	$E_f^D(\mu_{VB})$ (eV)	$D(q)$	$\Delta E^{D'-D}$ (eV)	$D'(q)$
NbFeSb	-0.01	Hf ⁽⁻¹⁾	1.20	Fe ⁽²⁾ _{int}
	0.09	Nb ⁽⁻¹⁾	1.10	Fe ⁽²⁾ _{int}
	0.21	Ti ⁽⁻¹⁾	0.72	Vac ⁽²⁾ _{Fe}
	0.41	Mn ⁽⁻¹⁾	0.78	Fe ⁽²⁾ _{int}
	0.55	Zr ⁽⁻¹⁾	0.70	Fe ⁽²⁾ _{int}
ZrCoSb	0.17	Sn ⁽⁻¹⁾	0.60	Sb ⁽¹⁾ _{Zr}
	0.61	Sc ⁽⁻¹⁾	0.35	Vac ⁽¹⁾ _{Co}
	0.61	Fe ⁽⁻¹⁾	-0.48	Vac ⁽¹⁾ _{Co}
	0.61	Co ⁽⁻¹⁾	-0.48	Vac ⁽¹⁾ _{Co}
NbCoSn	0.32	Hf ⁽⁻¹⁾	0.50	Co ⁽³⁾ _{int}
	0.62	Nb ⁽⁻¹⁾	-0.15	Fe ⁽²⁾ _{int}
	0.68	Fe ⁽⁻¹⁾	-0.15	Fe ⁽²⁾ _{int}
	0.72	Co ⁽⁻¹⁾	0.14	Co ⁽³⁾ _{int}
TaCoSn	0.44	Ti ⁽⁻¹⁾	0.10	Co ⁽³⁾ _{int}
	0.44	Zr ⁽⁻¹⁾	0.10	Co ⁽³⁾ _{int}
	0.87	Hf ⁽⁻¹⁾	0.33	Co ⁽²⁾ _{int}
	0.87	Ta ⁽⁻¹⁾	-0.10	Fe ⁽²⁾ _{int}
	0.87	Fe ⁽⁻¹⁾	-0.10	Fe ⁽²⁾ _{int}
	0.87	Co ⁽⁻¹⁾	-0.10	Fe ⁽²⁾ _{int}

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

Extrinsic doping



	$E_f^D(\mu_{VB})$ (eV)	$D(q)$	$\Delta E^{D'-D}$ (eV)	$D'(q)$
NbFeSb	-0.01	Hf ⁽⁻¹⁾	1.20	Fe ⁽²⁾ _{int}
	0.09	Nb ⁽⁻¹⁾	1.10	Fe ⁽²⁾ _{int}
	0.21	Ti ⁽⁻¹⁾	0.72	Vac ⁽²⁾ _{Fe}
	0.41	Mn ⁽⁻¹⁾	0.78	Fe ⁽²⁾ _{int}
	0.55	Zr ⁽⁻¹⁾	0.70	Fe ⁽²⁾ _{int}
ZrCoSb	0.17	Sn ⁽⁻¹⁾	0.60	Sb ⁽¹⁾ _{Zr}
	0.61	Sc ⁽⁻¹⁾	0.35	Vac ⁽¹⁾ _{Co}
	0.61	Fe ⁽⁻¹⁾	-0.48	Vac ⁽¹⁾ _{Co}
	0.61	Co ⁽⁻¹⁾	-0.48	Vac ⁽¹⁾ _{Co}
NbCoSn	0.32	Sc ⁽⁻¹⁾	0.50	Co ⁽³⁾ _{int}
	0.62	Nb ⁽⁻¹⁾	-0.15	Fe ⁽²⁾ _{int}
	0.68	Fe ⁽⁻¹⁾	-0.15	Fe ⁽²⁾ _{int}
	0.72	Ti ⁽⁻¹⁾	0.14	Co ⁽³⁾ _{int}
TaCoSn	0.44	Zr ⁽⁻¹⁾	0.10	Co ⁽³⁾ _{int}
	0.44	Nb ⁽⁻¹⁾	0.10	Co ⁽³⁾ _{int}
	0.87	Hf ⁽⁻¹⁾	0.33	Co ⁽²⁾ _{int}
0.87	Ta ⁽⁻¹⁾	-0.10	Fe ⁽²⁾ _{int}	
0.87	Fe ⁽⁻¹⁾	-0.10	Fe ⁽²⁾ _{int}	

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