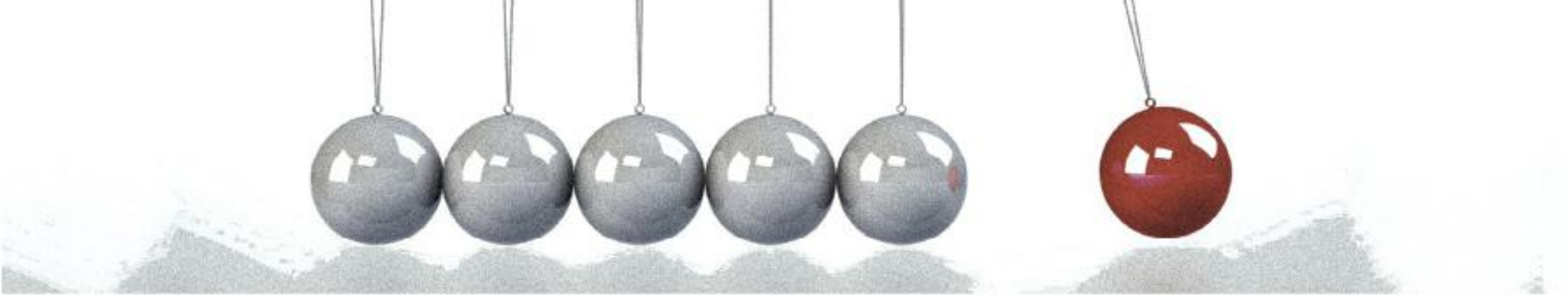


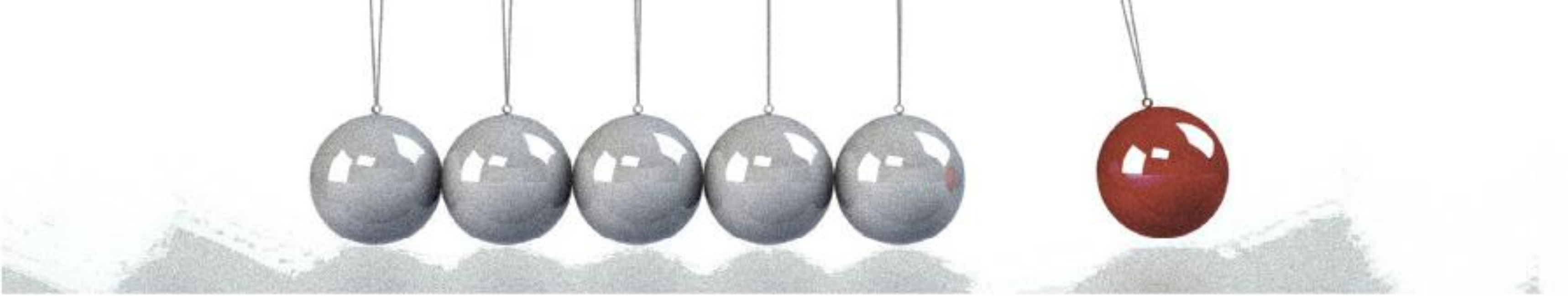
UiO : Department of Physics
University of Oslo

Thermoelectric material ZnSb

--- its defects and impurity band conduction

For 17th Conference of Gettering and Defect Engineering in Semiconductor Technology (GADEST 2017) Oct 01-06, 2017
Lopota Resort, Georgia

Xin Song, Postdoc
Department of Physics
University of Oslo



UiO : Department of Physics
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① Thermoelectric material ② ZnSb

--- its defects and ③ impurity band conduction

Xin Song, Postdoc
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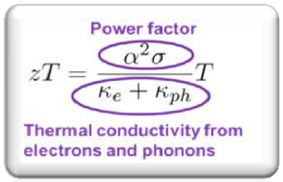
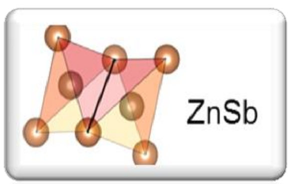
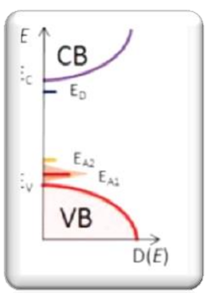


- **What matters to thermoelectrics**

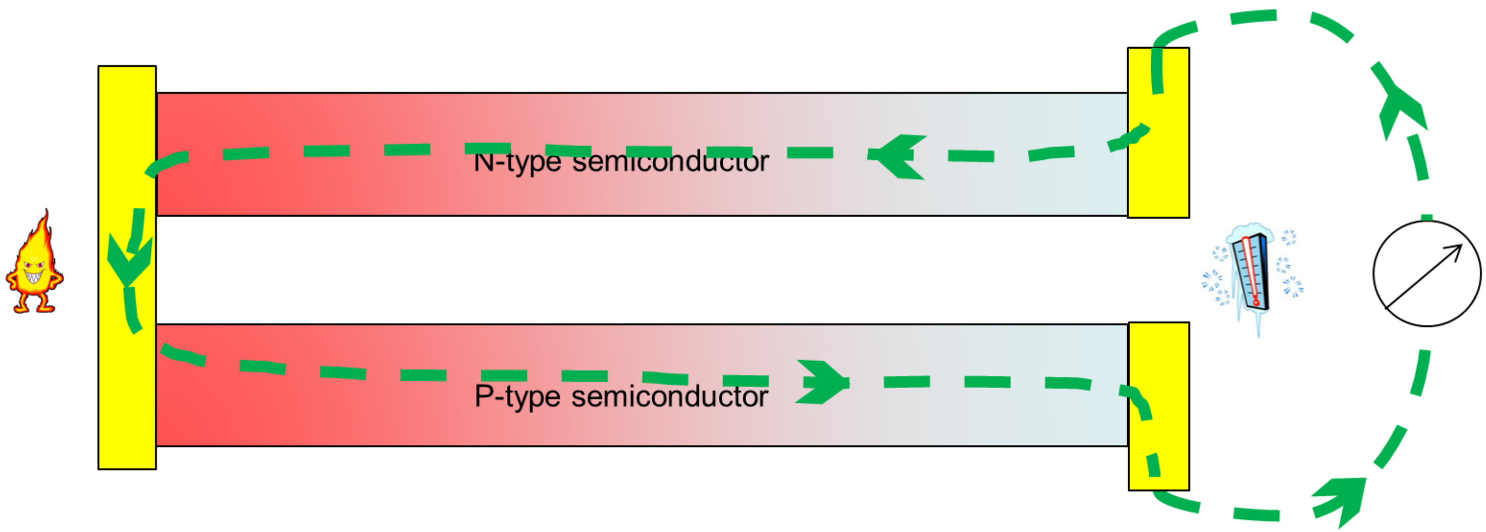


- **ZnSb and its defects**



- **Impurity band conduction and its impact on Thermoelectric performance**

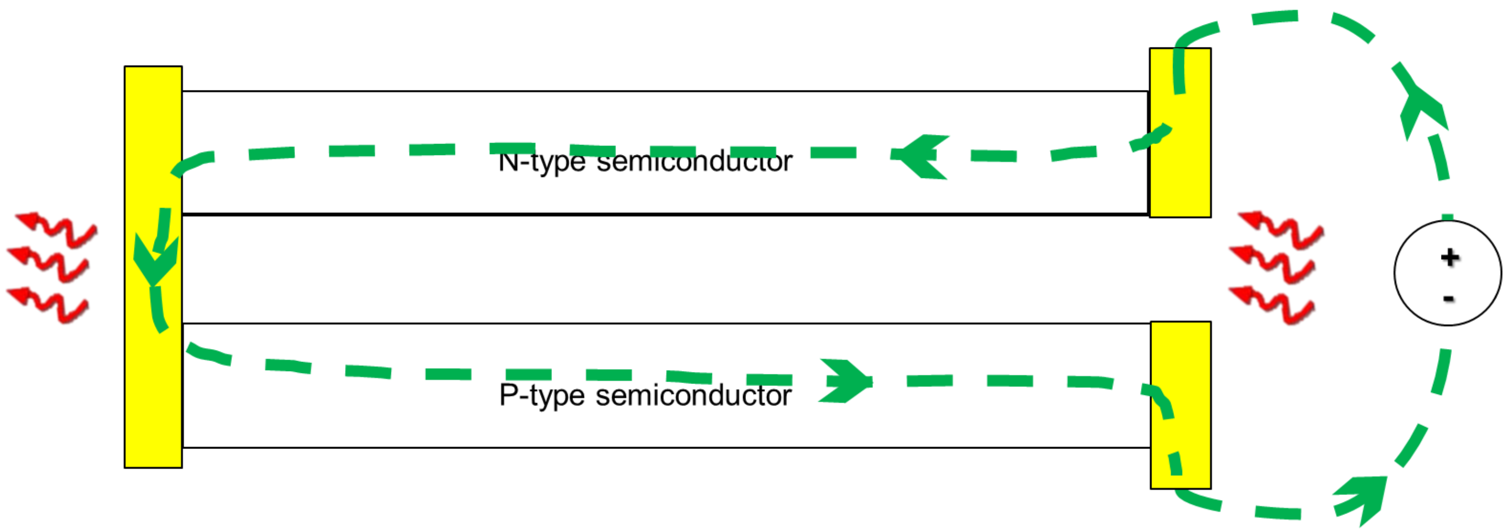
Phenomenological transport of thermoelectrics



Seebeck effect

Seebeck coefficient $\alpha = \frac{\Delta V}{\Delta T}$

Phenomenological transport of thermoelectrics



Seebeck effect

Seebeck coefficient $\alpha = \frac{\Delta V}{\Delta T}$

Peltier effect

Peltier coefficient $\Pi = \frac{J_Q}{J}$

Performance of thermoelectric module and material

The coefficient of performance (COP) for a thermoelectric module

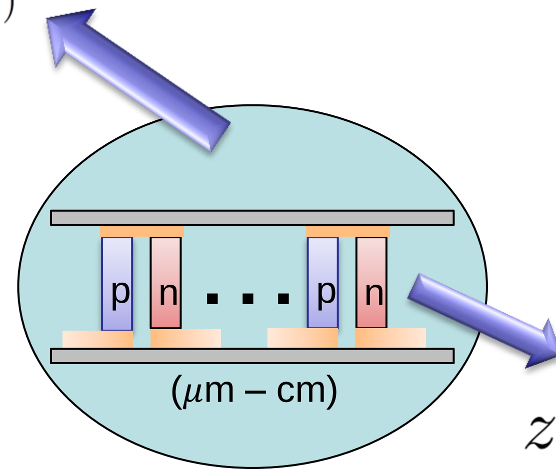
$$\eta_{COP} = \left(\frac{T_H - T_C}{T_H}\right)\left(\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}\right)$$

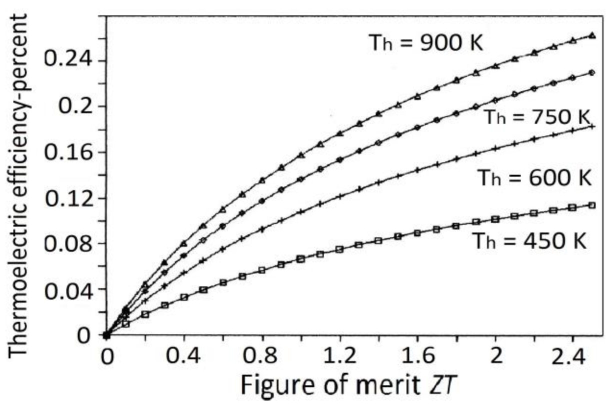
Carnot limit

T_C -- Temperature at the cold reservoir

T_H -- Temperature at the hot reservoir

ZT -- Dimensionless thermoelectric figure of merit of module, including $(zT)_n$ and $(zT)_p$





M. H. Cobble, *CRC Hand book of Thermoelectrics,* Chap.39 (1995)

Power factor

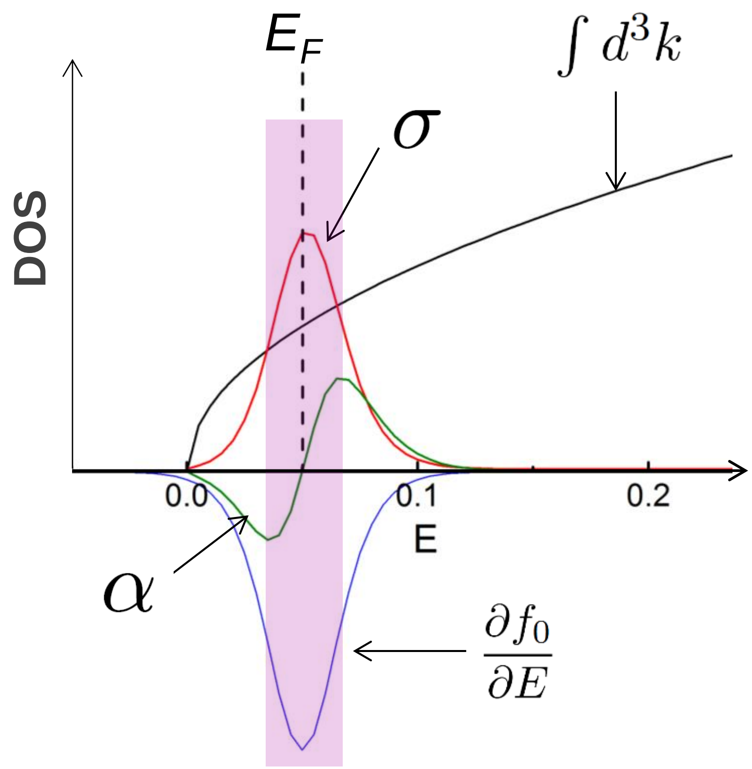
$$zT = \frac{\alpha^2\sigma}{\kappa_e + \kappa_{ph}}T$$

Thermal conductivity from electrons and phonons

- High Seebeck coefficient α
- High electrical conductivity σ
- Low thermal conductivity κ

What matters to thermoelectrics

- Optimizing power factor



Seebeck coefficient

$$\alpha = \frac{1}{qT} \frac{\int \tau v^2 (E - E_F)(-\frac{\partial f_0}{\partial E}) d^3k}{\int \tau v^2 (-\frac{\partial f_0}{\partial E}) d^3k}$$

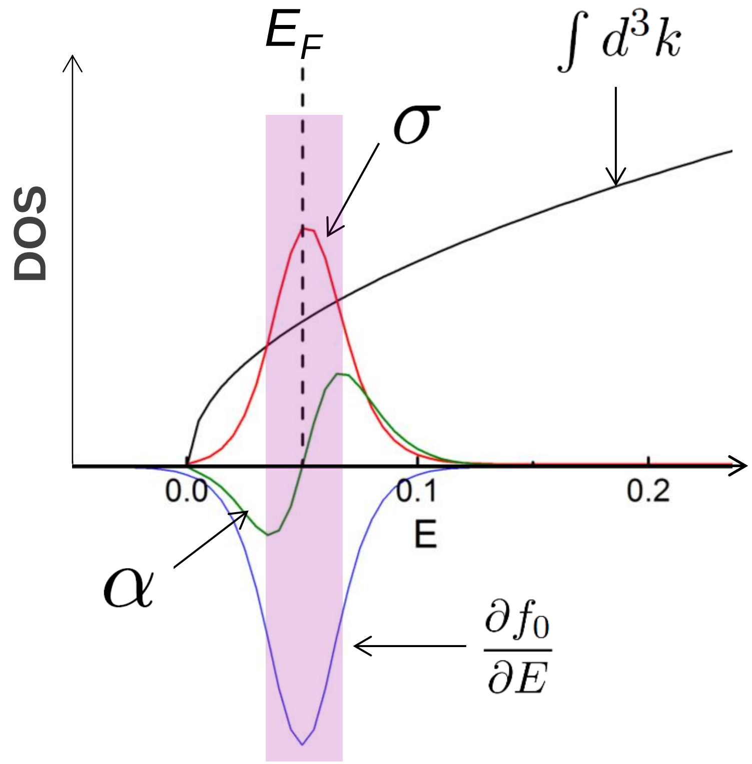
Electrical conductivity

$$\sigma = \frac{q^2}{4\pi^3} \int \tau v^2 (-\frac{\partial f_0}{\partial E}) d^3k$$

$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

What matters to thermoelectrics

- Optimizing power factor



Seebeck coefficient

$$\alpha = \frac{8\pi^2 k_B^2}{3qh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}$$

Electrical conductivity

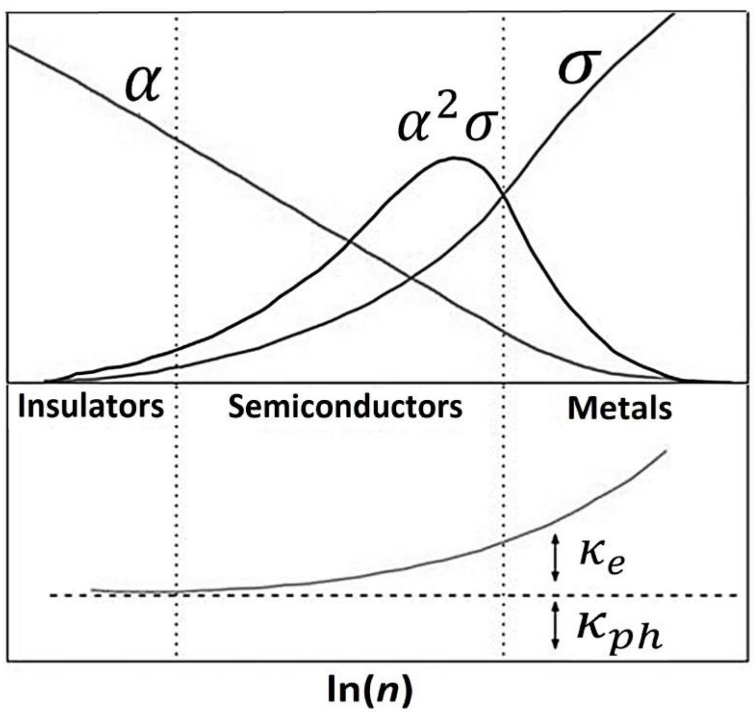
$$\sigma = qn\left(\frac{q\tau}{m^*}\right)$$

$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

- Optimize the interaction between transport coefficients
- Doping, defects scattering, energy filtering

What matters to thermoelectrics

- Optimizing power factor



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Electrical conductivity

$$\sigma = qn\left(\frac{q\tau}{m^*}\right)$$

$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

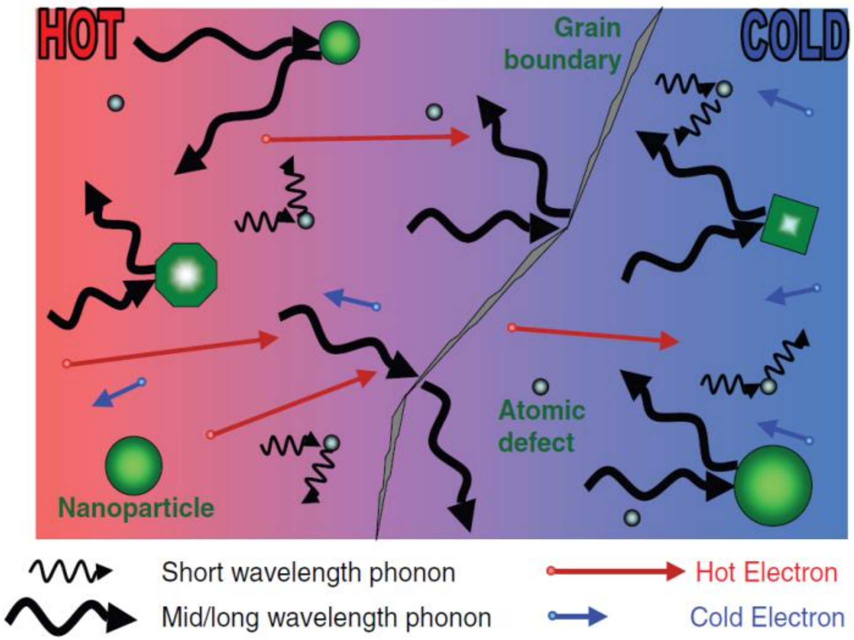
Wiedemann-Franz law

$$k_e = nq\mu\mathcal{L}T$$

- Optimize the interaction between transport coefficients
- Doping, defects scattering, energy filtering

What matters to thermoelectrics

- Reducing thermal conductivity



C. J. Vineis , *et al. Adv. Mater*. 2010, 22, 3970–3980

$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

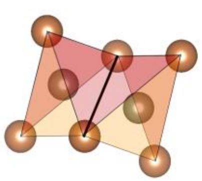
Wiedemann-Franz law

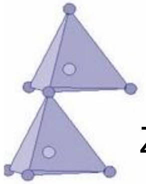
$$k_e = nq\mu\mathcal{L}T$$

- Phonon engineering.
- Nanostructuring, impurities.

Choosing a material

Expectation	ZnSb
• Non-toxic • Abundant • High price-performance	• Safe compound • Major industrial metals (Zn:13.7 MT; Sb 130 KT (2016)) • Estimated cost <10$/kg
• Relevant operation temperature	• 400K ~ 600K • Optimal temperature can be further tuned
• Narrow bandgap 6 ~ 10 $k_B T$ (0.2~1 eV)	• Band gap ~ 0.5 eV
• “Complex” structures	• Deformed Zinc-blende


ZnSb


ZnS

Choosing a material

Expectation

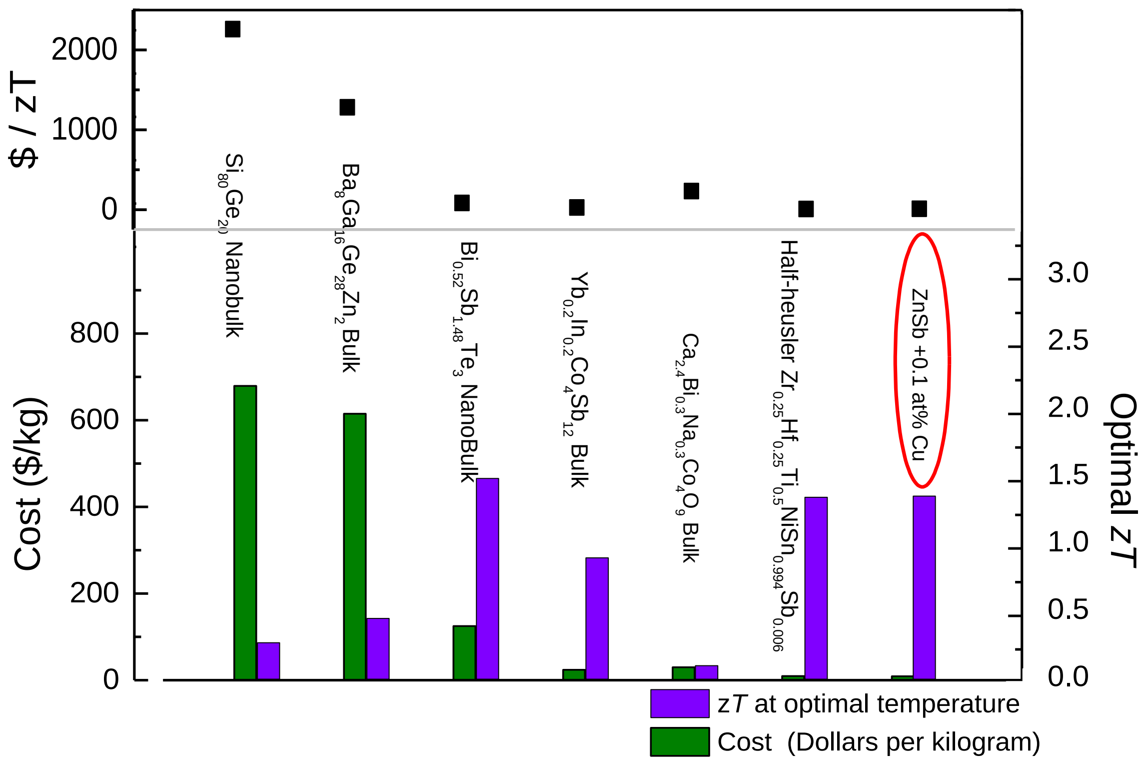
- Non-toxic
- Abundant
- High price-performance

- Relevant operation temperature

- Narrow bandgap $6 \sim 10\ k_B T$ (0.2~1 eV)

- "Complex" structures

ZnSb



A. LeBlanc, *et al. Renewable and Sustainable Energy Reviews* 32(2014) 313.-327
* **USGS,** *Energy minerals,* Mar, 2015, http://minerals.usgs.gov/minerals/pubs/commodity

Choosing a material

Expectation

- Non-toxic
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- Relevant operation temperature

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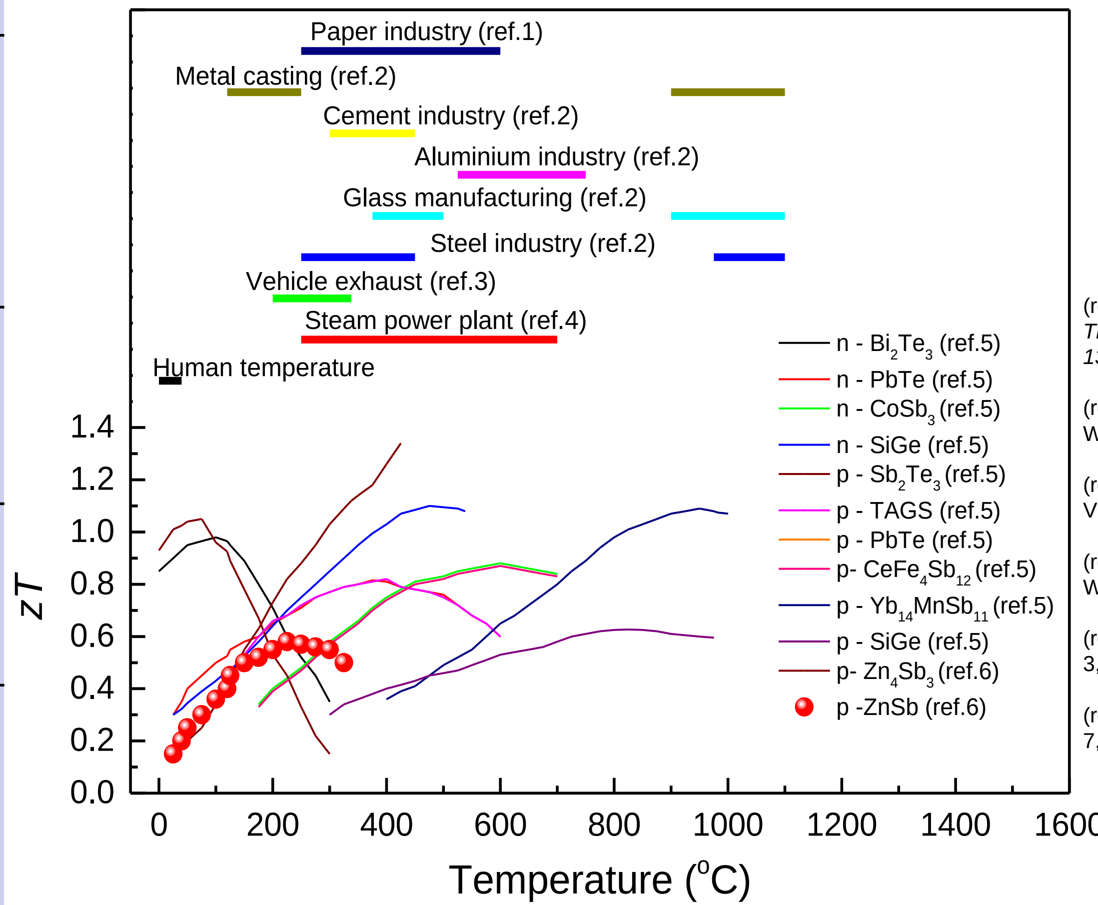
- "Complex" structures

ZnSb



(ref.1) *Thermal Science 13, 165-174 (2009)*

(ref.2) EERE Waste heat recovery, 2015

(ref.3) *J. Electron. Mater.*, Vol. 44, No. 6, 2015

(ref.4) EPA, Waste Heat to Power, 2012

(ref.5) *Nature Materials* 3, 458 - 463 (2004)

(ref.6) *Nature Materials* 7, 105 - 114 (2008)

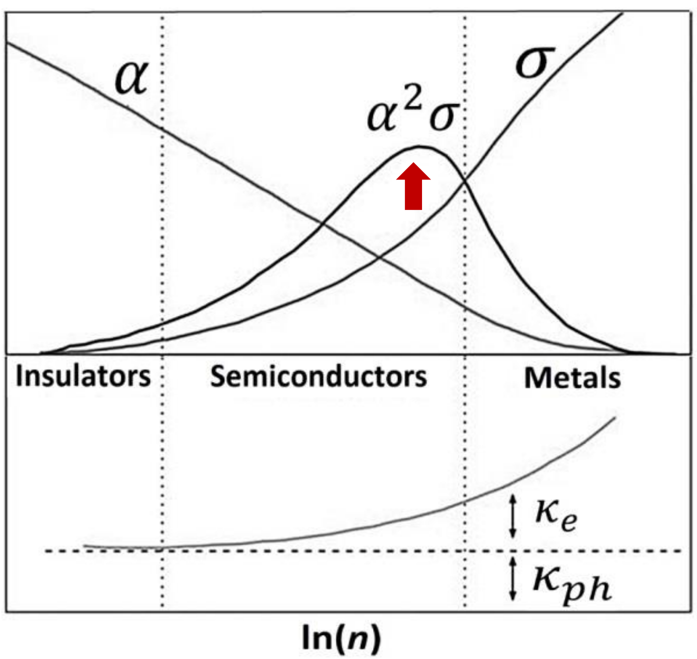
Doping defects

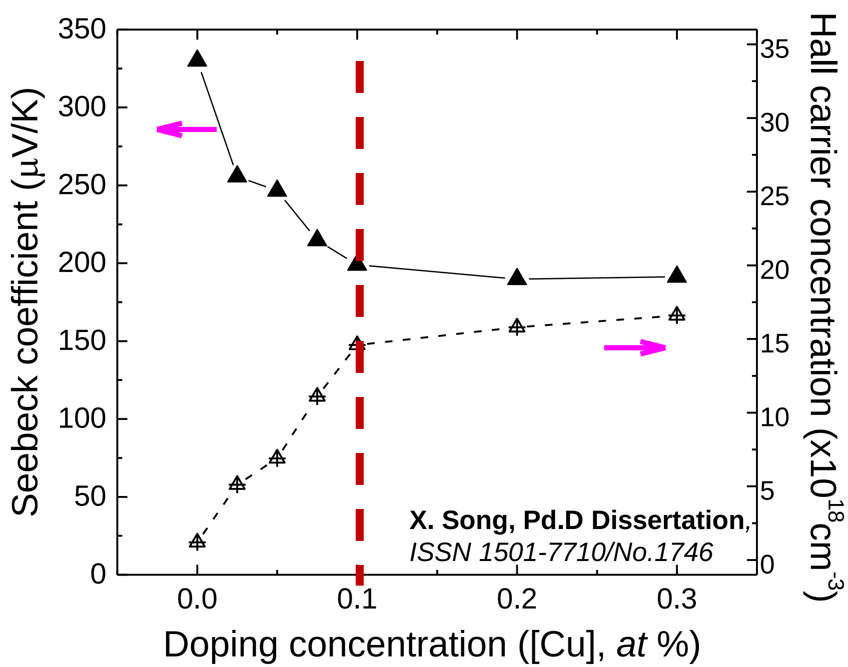
Given by $E_g = 0.53\ eV$ and $m^* = 0.42$ for ZnSb,

The theoretical intrinsic charge carrier concentrations at:

- Room temperature $2.41 \times 10^{14} \text{cm}^{-3}$;
- 300 ℃ : $8.42 \times 10^{16} \text{cm}^{-3}$

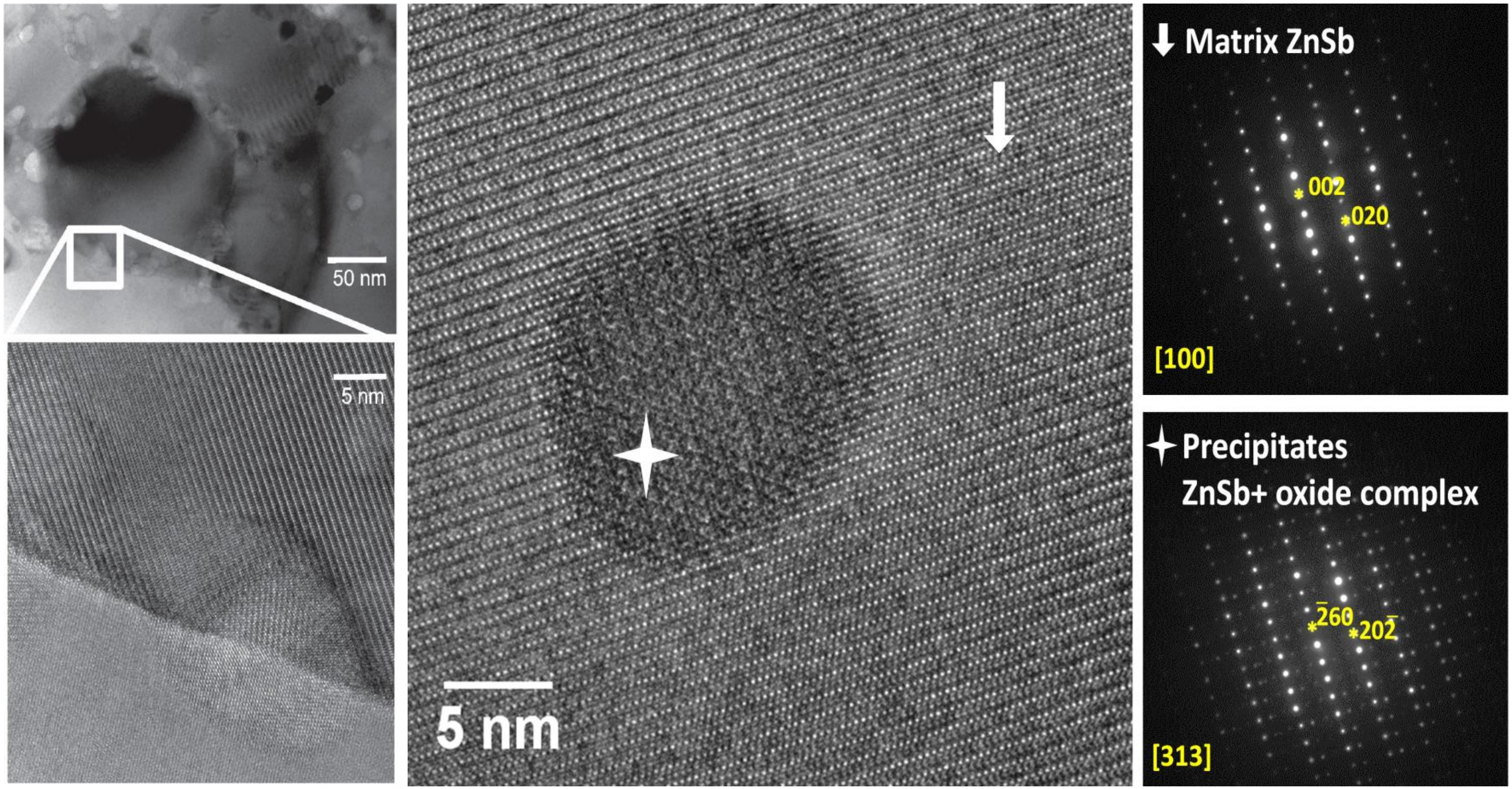
Acceptors:	**Donor:** **(Tricky and unsuccessful)**
I_{Zn} : Cu, Ag IV_{Sb} : Sn	III_{Zn} : In, Al, Ga VI_{Sb} : Te





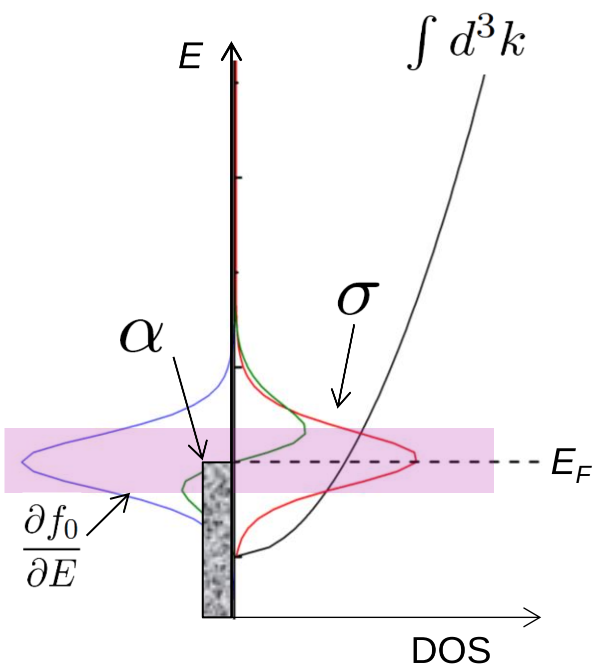
Power factor peaks at $2 \times 10^{19} \text{cm}^{-3}$ for ZnSb

Nano-oxide “defects”

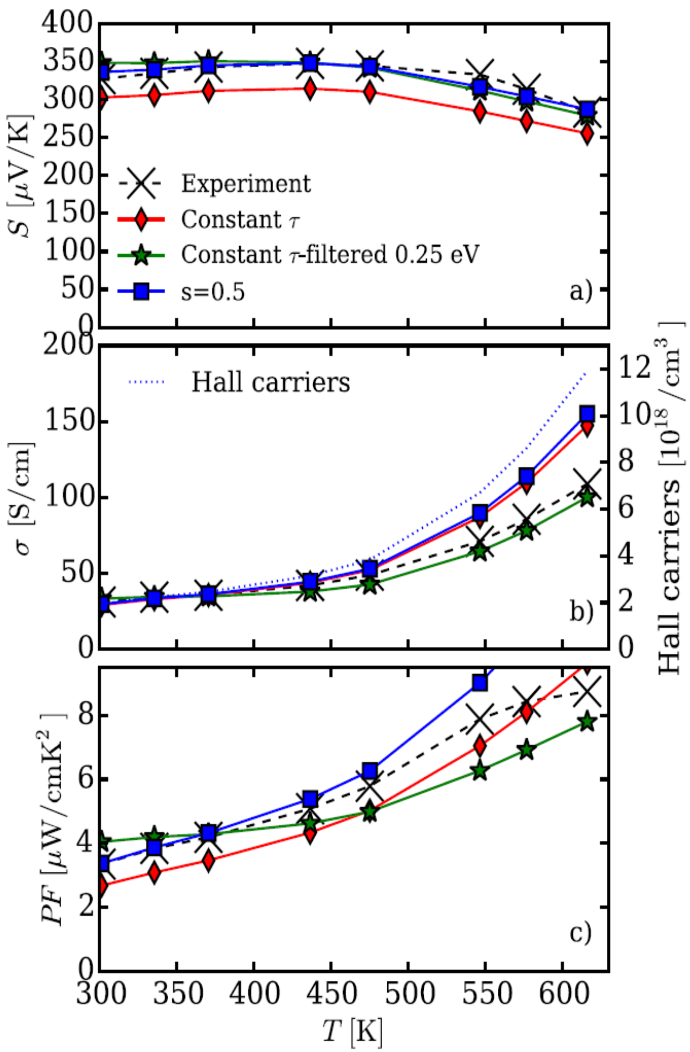


Transmission electron microscopy image of nano oxide particles in ZnSb
K. Berland, *et al, J. App. Phys. 119, 125103 (2016)*

Nano-oxide "defects"



Concept of energy filtering



K. Berland, *et al, J. App. Phys. 119, 125103 (2016)*

Intrinsic defects

The theoretical intrinsic charge carrier concentrations at room temperature

$2.41 \times 10^{14}\text{cm}^{-3}(E_g = 0.53\ eV \text{ and } m^* = 0.42)$;

However, most of reported on single crystal undoped ZnSb at RT : $1 - 2 \times 10^{16}\text{cm}^{-3}$;

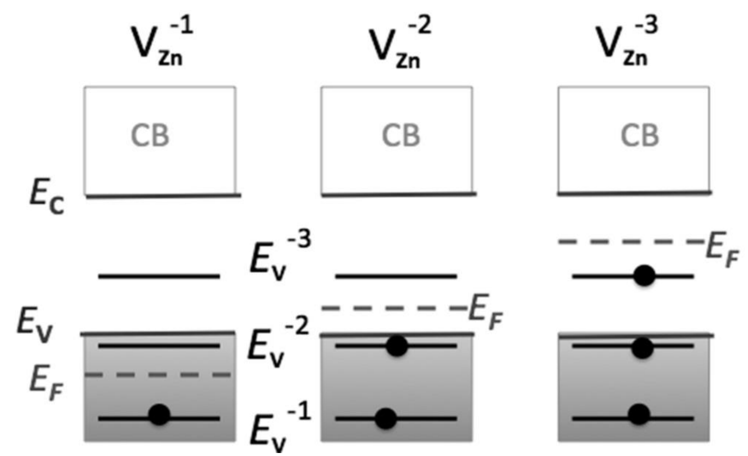
polycrystalline undoped ZnSb at RT : $\sim 10^{18}\text{cm}^{-3}$.

V_{Zn} V_{Sb} Zn_{Sb} Sb_{Zn} Zn_i Sb_i

Defect Formation Energies in eV for $\mu_e = \Delta\mu = 0$

q_d	V_{Zn}	V_{Sb}	Sb_{Zn}	Zn_{Sb}
−3	0.51	2.47	1.83	1.33
−2	0.30	2.05	1.50	1.26
−1	0.32	1.83	1.33	1.28
0	0.52	1.79	1.34	1.41
+1	0.88	1.70	1.39	1.67

L. Bjerg, *et al. Chem. Mater. 2012, 24, 2111−2116*

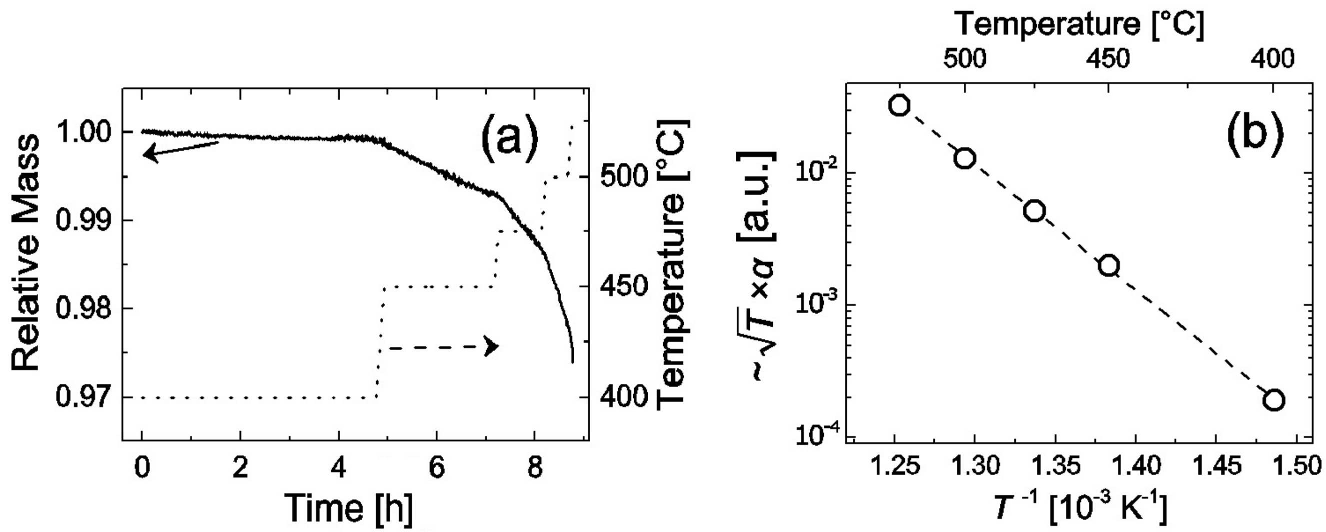


Occupancy of localized states accociated with different charged V_{Zn} in ZnSb.

X. Song & T. G. Finstad, *Review of Research on the Thermoelectric Material ZnSb*, in *Thermoelectrics for Power Generation - A Look at Trends in the Technology*, Intech, (2016), Chap. **6**

Intrinsic defects

$$V_{Zn}: \quad \mathrm{ZnSb(s)} \rightarrow \mathrm{Zn}_{1-x}\mathrm{Sb(s)} + x \cdot \mathrm{Zn(g)}$$

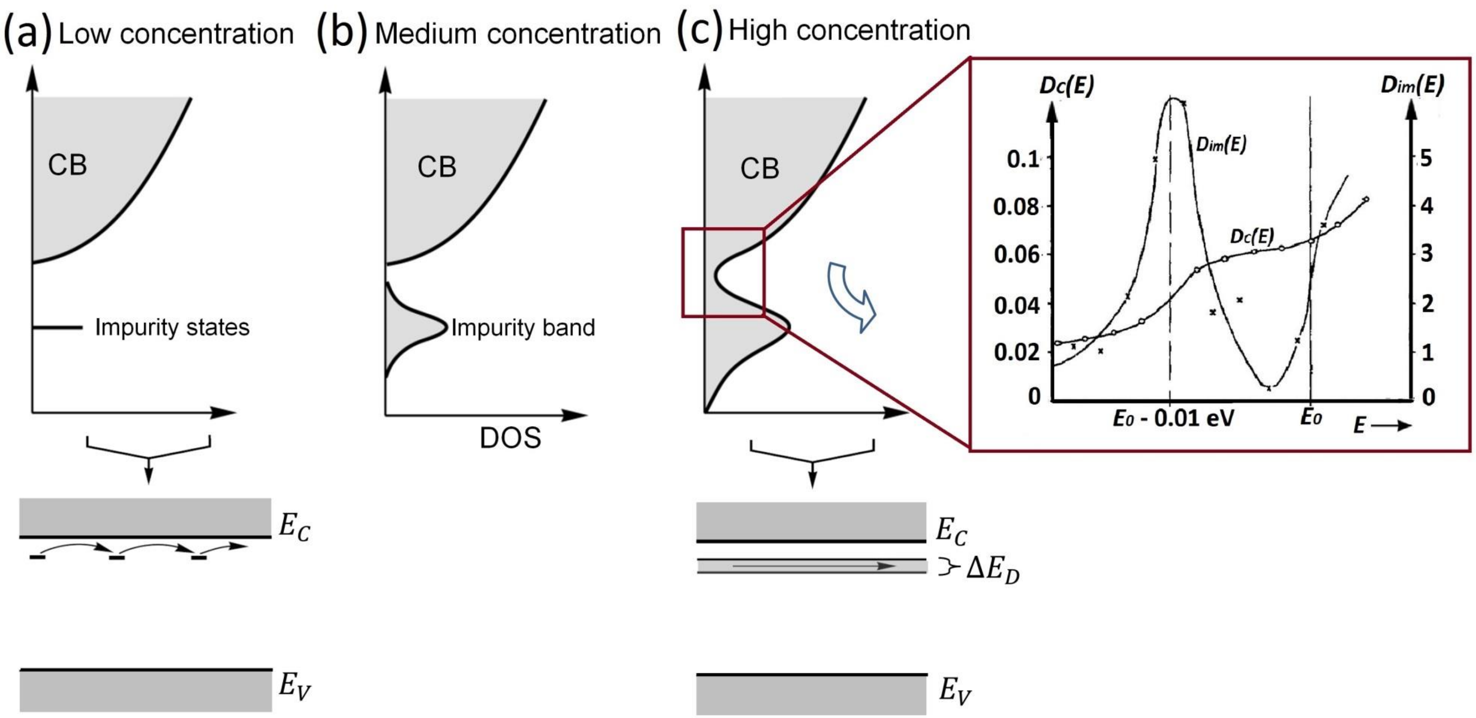


Influence of annealing at 400 ℃ for 30 minutes on the electronic properties of ZnSb at room temperature. The carrier concentration increases significantly for both samples, leading to an increased conductivity.

Sample	Annealing	p [10^{18} cm^{-3}]	σ [S cm]	μ [cm^{2}V^{-1}s^{-1}]
# 1	Before	7.95	202	159
	After	14.1	262	116
# 2	Before	3.57	134	235
	After	10.2	360	220

X. Song, *et al, J. Alloys Compd.*, *710 (2017) 762*

Impurity band conduction

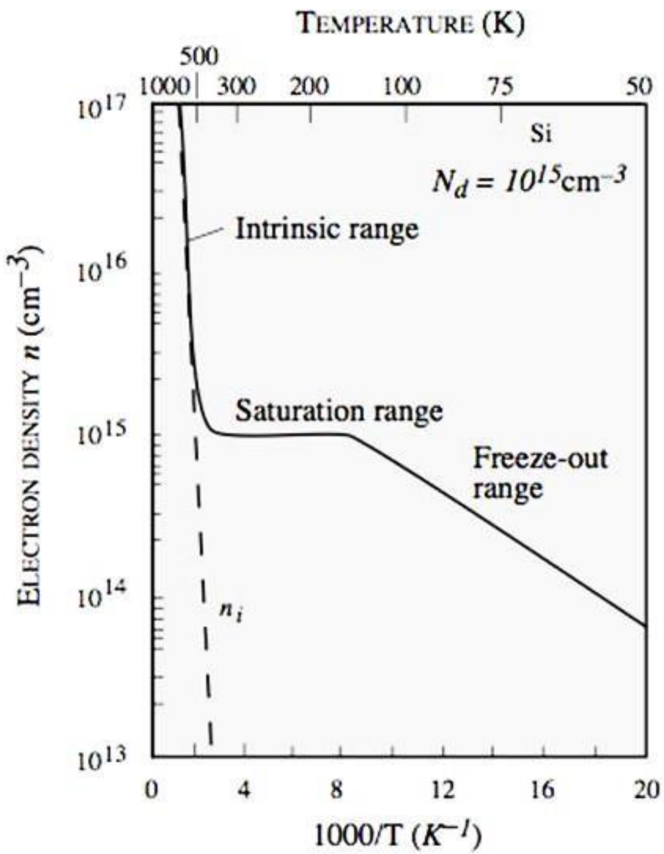


Mott transition criterion: N_i ~ $6X10^{17}$ cm $^{-3}$ for ZnSb

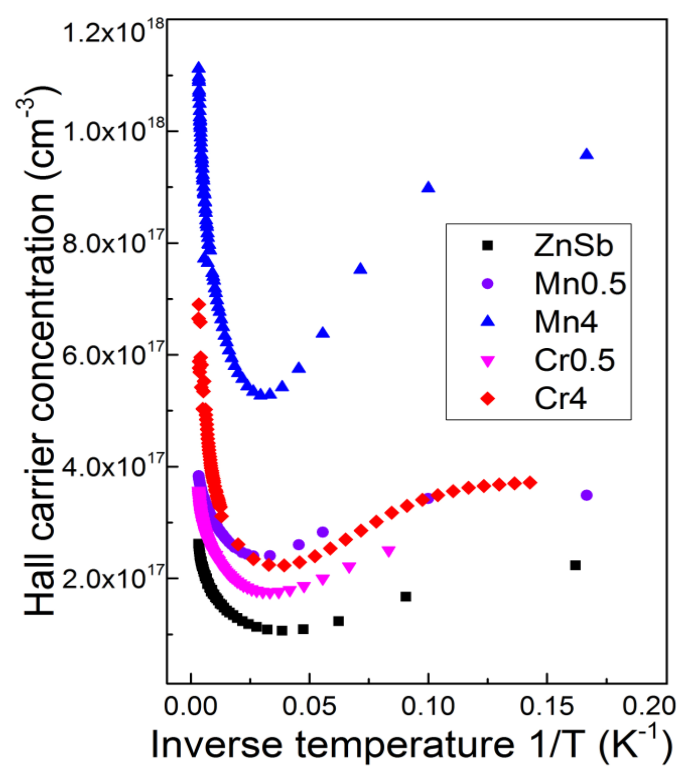
X. Song & T. G. Finstad, *Review of Research on the Thermoelectric Material ZnSb*, in *Thermoelectrics for Power Generation - A Look at Trends in the Technology,* Intech, (2016), Chap. **6**

Impurity band conduction

Classical semiconductor behavior in Si



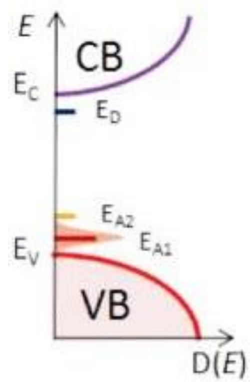
In ZnSb

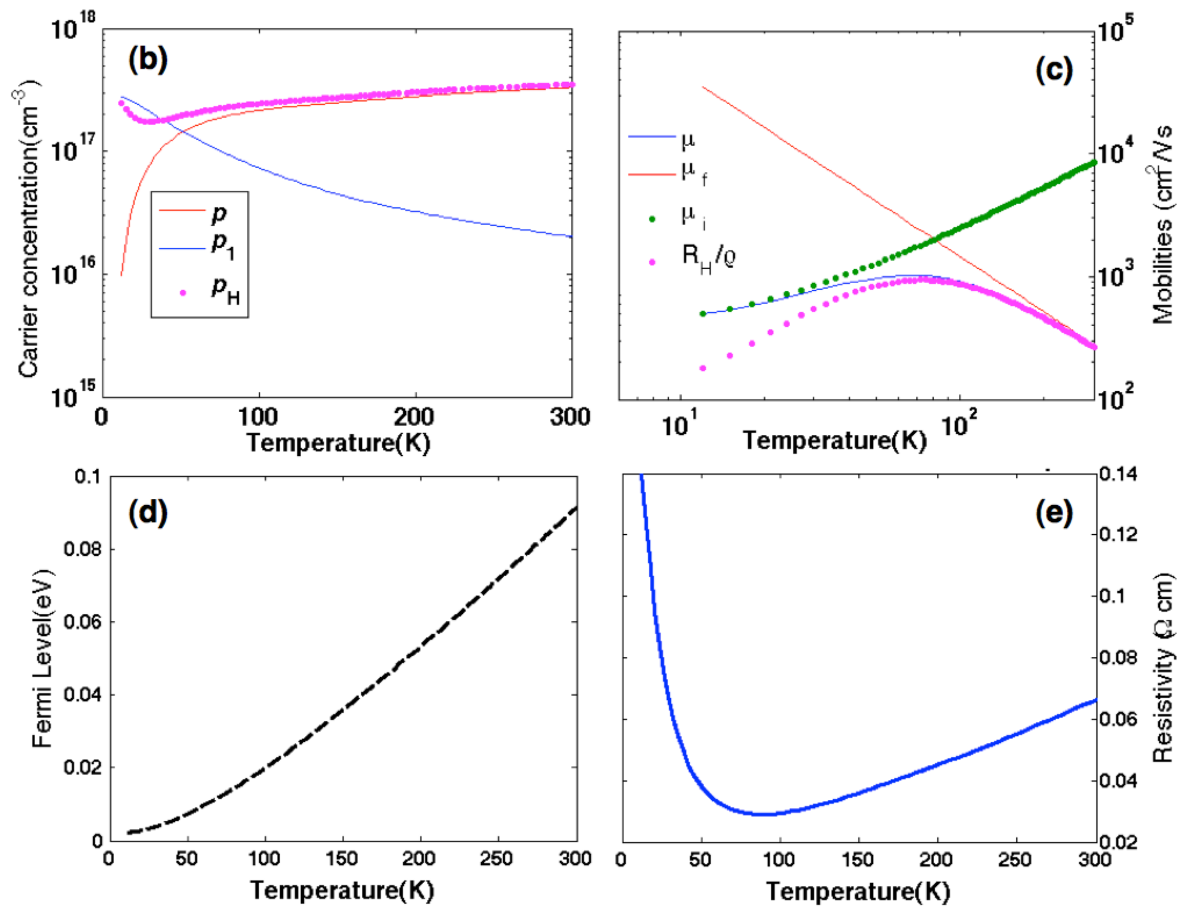


X. Song, *et al,* Phys. Scr. T148 (2012) 014001

Impurity band conduction

- Two types of carriers with different effective mass and mobilities
- Common in thermoelectrics, Also see in ZnSe, PdTe and BiTe, Ge, etc.

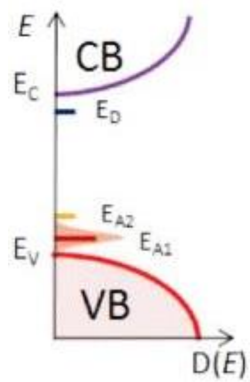




X. Song, *et al,* Phys. Scr. T148 (2012) 014001

Impurity band conduction

Modelling of two carriers (VB carriers and IB carriers) conduction



Variables: $E_{A1}, E_{A2}, N_{A1}, N_{A2}, N_D$

$$R_H = \frac{p_v\mu_v^2 + p_{im}\mu_{im}^2}{q(p_v\mu_v + p_{im}\mu_{im})^2}$$

$$\rho = \frac{1}{q(p_v\mu_v + p_{im}\mu_{im})}$$

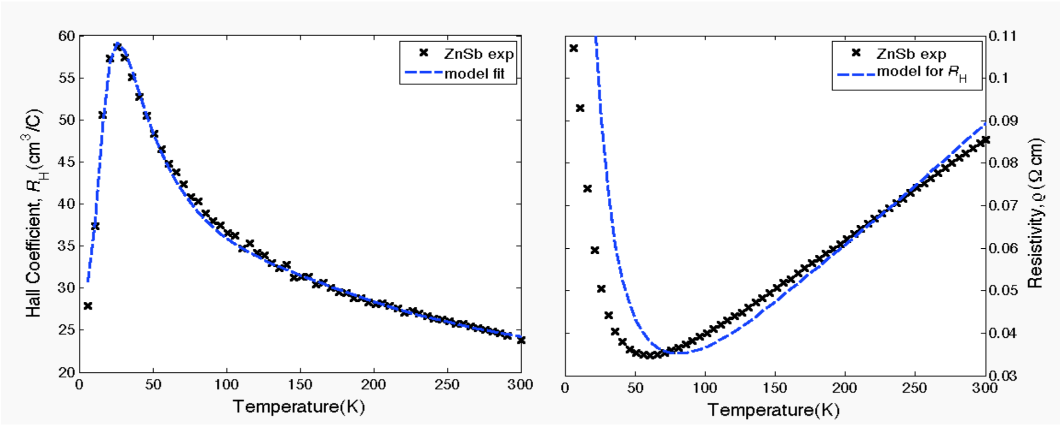
$p_v,\ \mu_v$

Carrier concentration, mobility in VB

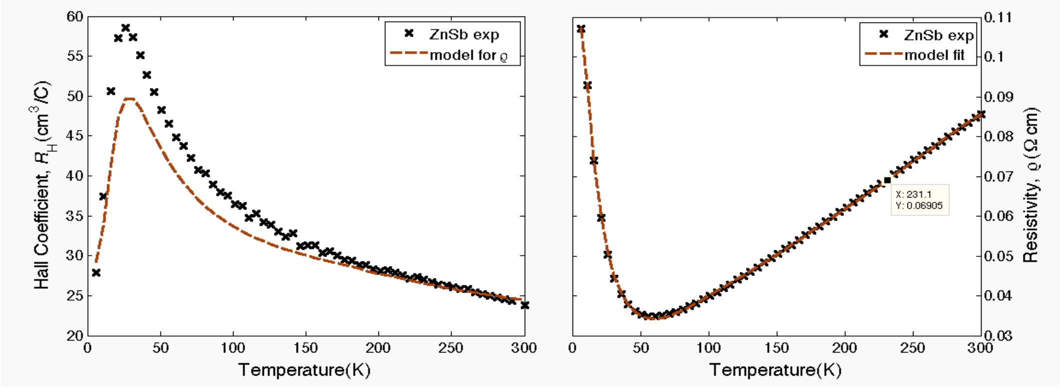
$p_{im},\ \mu_{im}$

Carrier concentration,mobility in IB

Fitting Hall coefficient, simulating resistivity



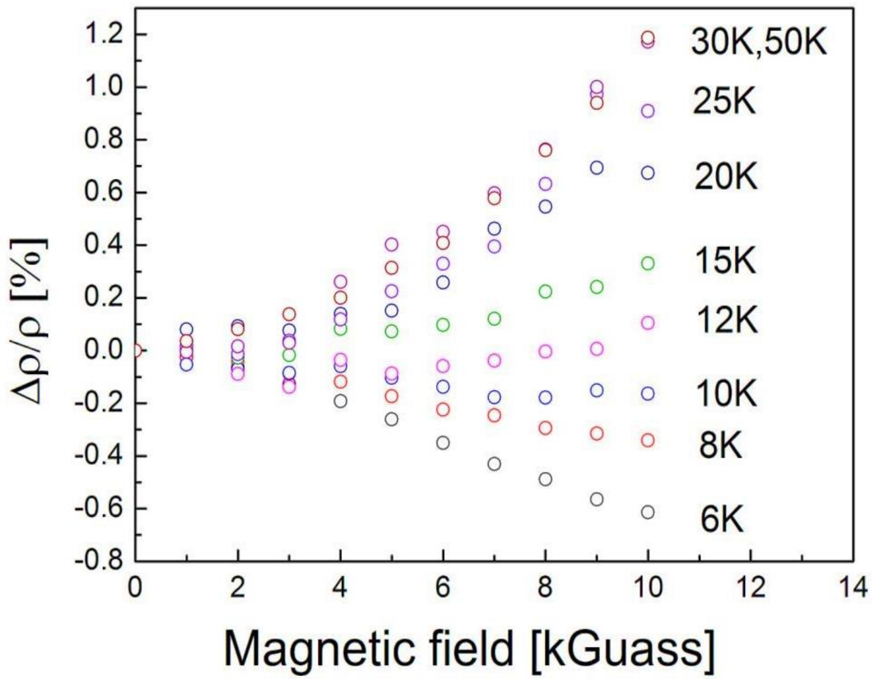
Fitting resistivity, simulating Hall coefficient

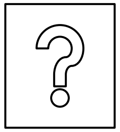


X. Song, *et al,* Phys. Scr. T148 (2012) 014001

Impurity band conduction

- Magnetoresistance experimental prove of two carriers conduction:
  (VB carriers and IB carriers)
- Bending down indicates contribution from IB





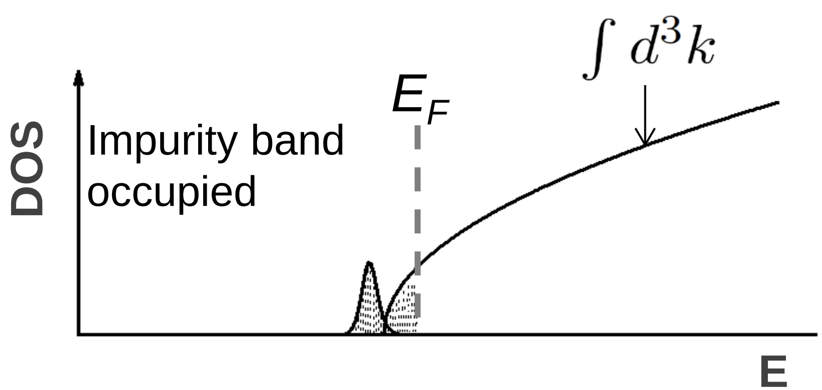
- How does it impact to thermoelectric performance?
- Can we manipulate impurity band?

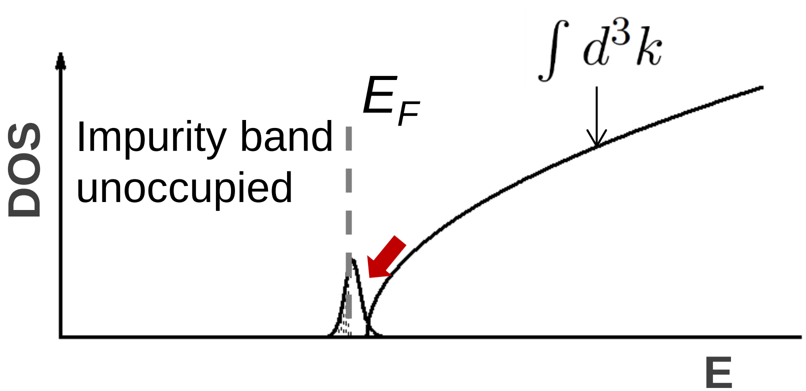
X. Song, *et al,* Phys. Scr. T148 (2012) 014001

Impurity band conduction

How does it impact to thermoelectric performance?

- Change shape of DOS





Seebeck coefficient

$$\alpha = \frac{1}{qT}\frac{\int \tau v^2 (E - E_F)(-\frac{\partial f_0}{\partial E}) d^3k}{\int \tau v^2 (-\frac{\partial f_0}{\partial E}) d^3k}$$

Electrical conductivity

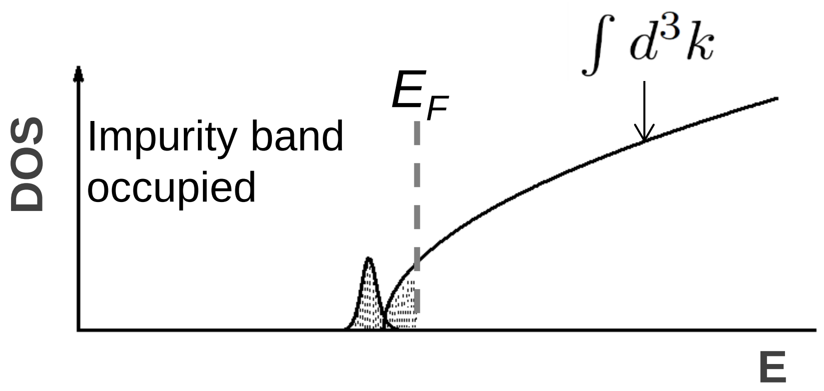
$$\sigma = \frac{q^2}{4\pi^3}\int \tau v^2 (-\frac{\partial f_0}{\partial E}) d^3k$$

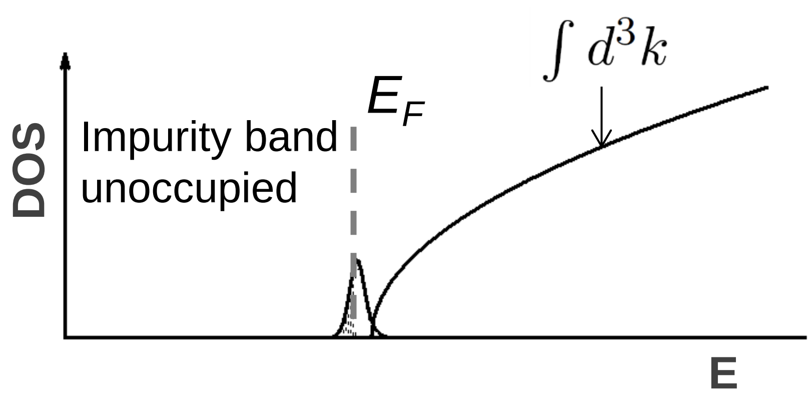
$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

Impurity band conduction

How does it impact to thermoelectric performance?

- Change shape of DOS
- Change position of Fermi level -- Seebeck coefficient





Seebeck coefficient

$$\alpha = \frac{1}{qT}\frac{\int \tau v^2 (E - E_F)(-\frac{\partial f_0}{\partial E}) d^3k}{\int \tau v^2 (-\frac{\partial f_0}{\partial E}) d^3k}$$

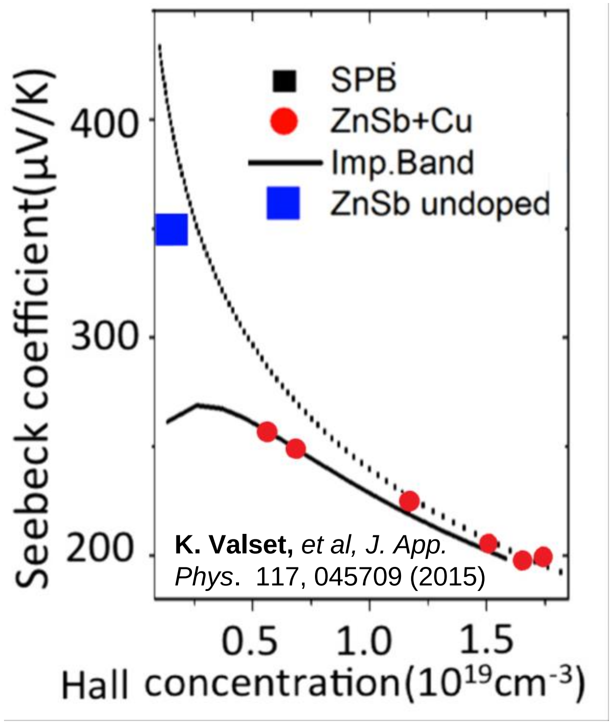
Position of Fermi level depends on

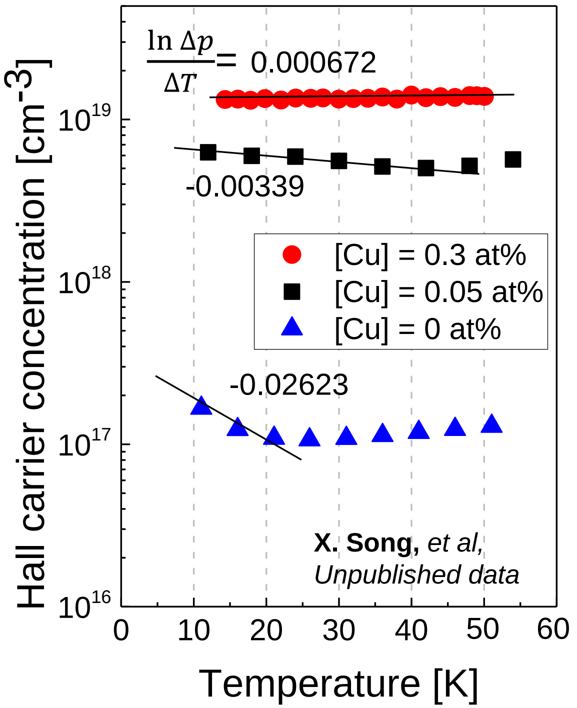
- Mass action law
- Charge neutrality

Fermi level goes between IB and VB at equilibrium

Impurity band conduction

Can we manipulate impurity band?



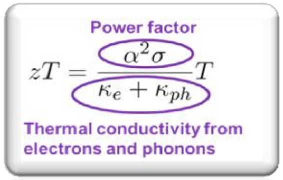


$$\alpha = \frac{\alpha_{VB} \cdot p_{VB} + \alpha_{IB} \cdot p_{IB}}{p_{VB} + p_{IB}}$$

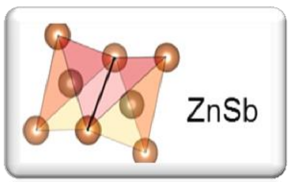
Impurity band at 0.065eV above VB with concentration $2.5 \times 10^{18} \mathrm{cm}^{-3}$

- Impurity band conduction in low concentration samples
- High concentration supress impurity band conduction

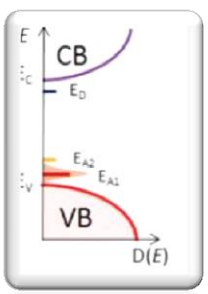
Summary



- **What matters to thermoelectrics**
  - Maximum *zT* at a particular carrier concentration
  - Optimising power factor
  - Reduing thermal transport



- **ZnSb and its defects**
  - Decent thermoelectric material around 300℃
  - Doping defects – increase carrier concentration
  - Nano-oxide – energy filtering
  - Zn vacancies defects – intrinsic charge carriers



- **Impurity band conduction and its impact on thermoelectric performance**
  - Elevated carrier concentration at cryo-temperature
  - Two type of carriers with different effective mass and mobility
  - Change DOS shape and Fermi level -- power factor