Ab initio Modelling of Thermoelectricity

DFT-based and Semi-Classical Boltzmann Transport Approaches with a Focus on the Electronic Properties

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GDR NAME – Ecole MONACOST – 08-13/05/2022

Content of This Lecture

1. Thermoelectric Effects: Macroscopic View
2. Thermoelectric Coefficients: Microscopic View
3. Transport Equation To Calculate Thermoelectric Coefficients
4. Semi-Classical Approaches To Calculate The TE Coefficients
5. Examples

References

Some of the slides presented in this lecture are inspired from

Mark LUNDSTROM and Supriyo DATTA

lectures:

Near-Equilibrium Transport: Fundamentals and Applications

@https://www.youtube.com/watch?v=SddB0DWrc7g

Introduction à la thermoélectricité

@ https://www.youtube.com/watch?v=2w7NBuu5w9c

Fundamental of Nanoelectronics A&B

@
https://www.youtube.com/watch?v=p5nsWUKiG9k&list=PLtkeUZItwHK6lvGu8kFKBdhz3XaIZQDFj

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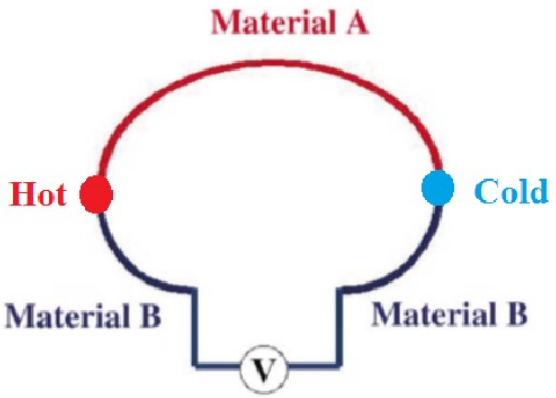
Macroscopic View on Thermoelectric Effects

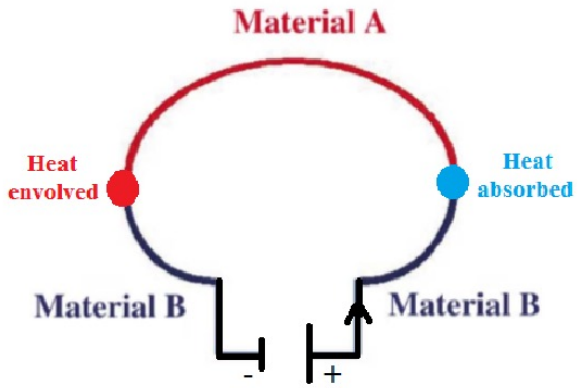
- 1794: Thermoelectric effect first evidenced by Volta
- 1822– 1851: Three effects evidenced

1822: Seebeck effect



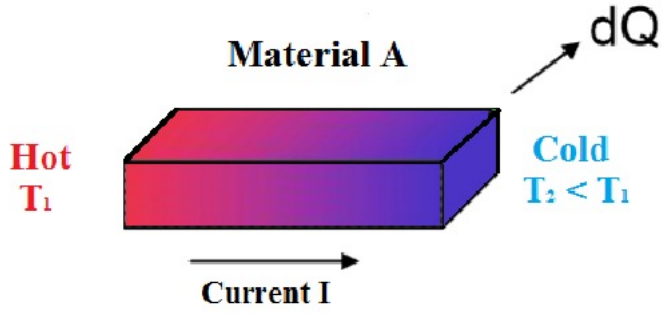
$$S = \frac{\Delta V}{\Delta T}$$

1834: Peltier effect



$$\Pi = \frac{Q}{I}$$

1851: Thomson effect



$$\tau = \frac{dQ}{I\Delta T}$$

Figure of Merit in Thermoelectricity

- Materials Properties to take into account
  - Electronic properties:
    - Seebeck coefficient: S (μV K^{-1})
    - Electrical conductivity σ (Ω^{-1} m^{-1})
    - Electrons thermal conductivity κ_e (W m^{-1} K^{-1})
  - Lattice property:
    - Lattice thermal conductivity (phonons): κ_L (W m^{-1} K^{-1})

- Properties gathered in one expression: the figure of merit

$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_L} \times T$$

(Z in K^{-1}, ZT adimensional)

Figure of Merit in Thermoelectricity

$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_L} \times T$$

Ideally: ZT should be as large as possible, hence

- Large Seebeck coefficient and electrical conductivity
- Low thermal conductivities

BUT: things are not that easy and TE properties are interrelated:

$$S \propto 1/\sigma$$

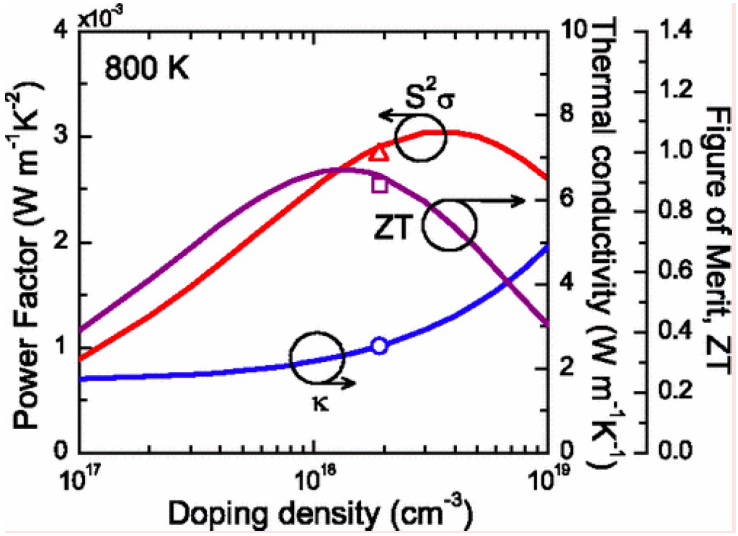
$$\sigma \propto \kappa_e$$

Electronic Properties: S, σ and κ_e

Very dependent on:

- The carriers concentration

Pisarenko-type of plot:



Best power factor $S^2\sigma$ and ZT for moderately doped SC

- The band structure $\Longrightarrow$ influence of strains, resonant levels
- Carriers scatterers: e.g., impurities, defects

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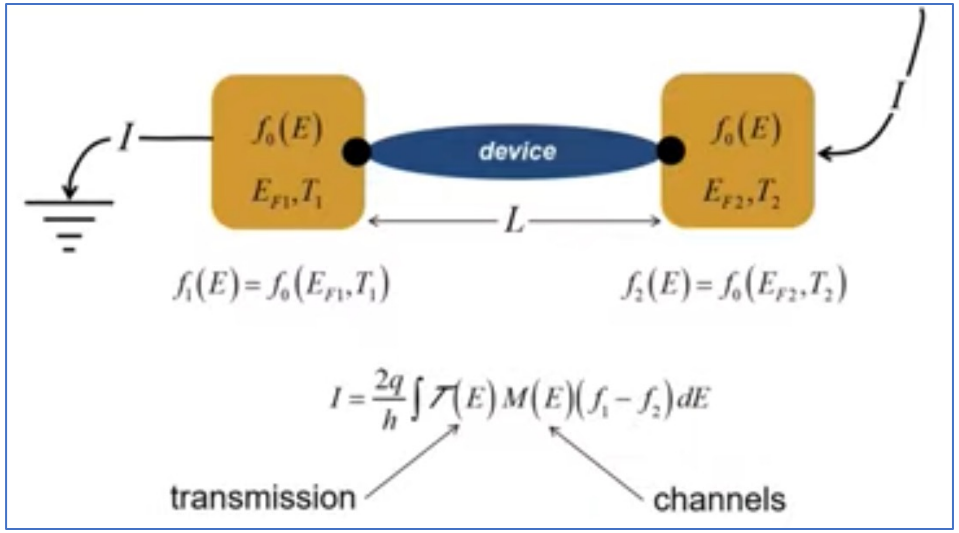
Microscopic View of The Electrical Conductivity

- We take the view of the *Landauer approach* (≠ the Boltzmann one)
- Start with the electrical conductivity



- A device of length L is connected to two contacts
- The one on the left is grounded
- The current flow from right to left

Difference $f_1 - f_2$ due to difference in chemical potentials
Current is proportional to:

- So: $f_1 - f_2 \approx -\left(\partial f_0 / \partial E\right)(q\Delta V)$
- Transmission coefficient (0 ≤ T ≤ 1 semi-classical approach)
- Number of channels (prop. to carriers velocity x DOS)
- Difference in Fermi functions caused by a difference in the Fermi levels (electrochemical potential)

Expressions derived in https://www.youtube.com/watch?v=d5WQS0kZwZU

Microscopic View of The Electrical Conductivity

- Expressions for J and σ:

$$J_x = \sigma_n \frac{d(F_n/q)}{dx} \rightarrow \qquad \sigma_n = \frac{2q^2}{h} \int \lambda(E) \frac{M(E)}{A} \left(-\frac{\partial f_0}{\partial E}\right) dE$$

- F_n is the *quasi-Fermi level* that varies across the device (or material) due to the applied voltage (F_n/q = electrochemical potential)
- $\lambda(E)$ is the *mean-free path* of electrons with energy E, A is the cross section
- f_0 is the *Fermi-Dirac distribution* at equilibrium: approximate $f_1 - f_2$

Microscopic View of The Electrical Conductivity

Recast the electrical conductivity expression as

$$\sigma = \int \sigma'(E) dE$$

with:

$\sigma' = \frac{2q^2}{h} \lambda(E) \frac{M(E)}{A} \left(-\frac{\partial f_0}{\partial E}\right) = q^2 \Xi(E) \left(-\frac{\partial f_0}{\partial E}\right)$ the *differential electrical conductivity*, and

$\Xi(E) = \frac{2}{h} \frac{M(E)}{A} \lambda(E)$ called the *transport function*

The transport function is hence prop. to the mean-free path of the electrons and to the number of conduction channels

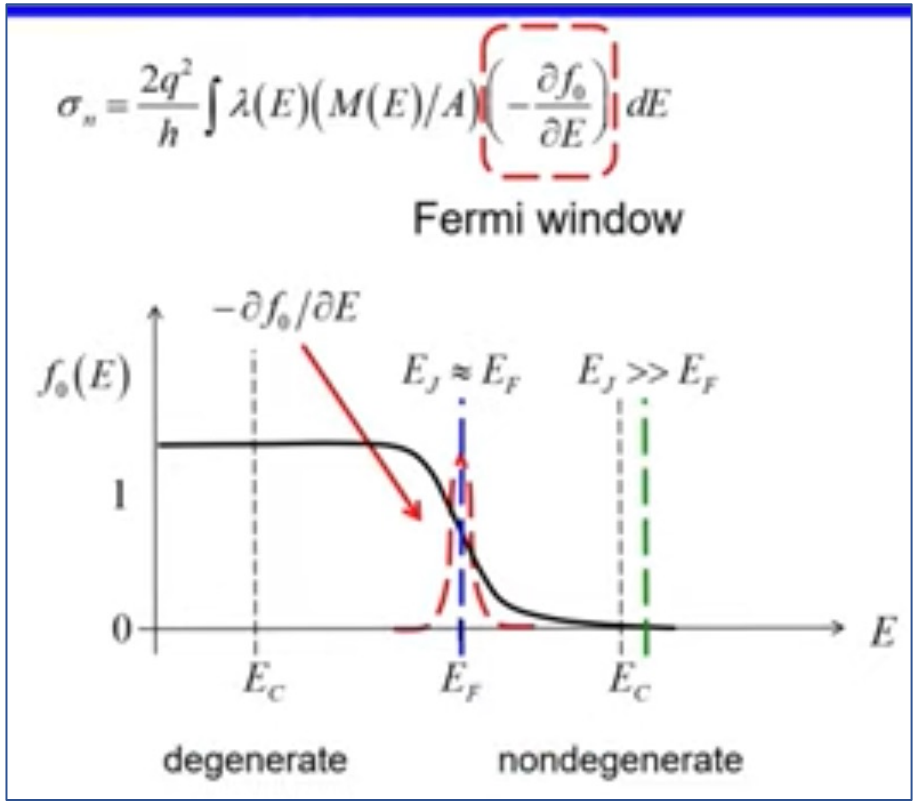
For the transport function see Mahan & Sofo, PNAS, 1996, 93, 7436-7439: ``The best thermoelectric''

Microscopic View of The Electrical Conductivity

At what energy does the current flow? In the conduction band, but where?

Dictated by the *Fermi Window*

- For a non-degenerate SC: $E_F << E_J$
  Only the tail of the FW is responsible for the conduction that occurs close to the bottom of the CB
- For a degenerate SC: $E_F \approx E_J$
  The current is flowing near the Fermi energy where the FW is. This occurs for metal of heavily doped SC



Microscopic View of The Seebeck Coefficient

- Recall: the Seebeck coefficient is *responsible for the current to flow when a temperature difference is applied*
- Seebeck coefficient also called the *thermopower*
- Temperature difference causes electrons to flow because of a *difference between the Fermi functions of the two contacts*

$$I = \frac{2q}{h}\int T(E)M(E)[f_1(E) - f_2(E)]\,dE$$

But now the difference $f_1 - f_2$ is caused by a *difference in temperatures*

So, now: $f_1 - f_2 \approx -\frac{\partial f_0}{\partial T}\Delta T \propto -\frac{\partial f_0}{\partial E}\Delta T$ (See: https://www.youtube.com/watch?v=5iTehoVGYeE)

Microscopic View of The Seebeck Coefficient

The electrical current becomes

$$I = -\left\{\int \left(\frac{E - E_F}{qT}\right)\sigma'(E)dE\right\}\Delta T = (SG)\Delta T$$

$$J_x = -S\sigma\frac{dT}{dx}$$

$$S\sigma = -\int \left(\frac{E - E_F}{qT}\right)\sigma'(E)dE \rightarrow S = -\frac{\int \left(\frac{E - E_F}{qT}\right)\sigma'(E)dE}{\int \sigma'(E)dE}$$

Microscopic View of The Seebeck Coefficient

- What is the sign of the Seebeck coefficient?

$J = \sigma \mathcal{E}$ (voltage gradient only)

$J_x = -S\sigma \frac{dT}{dx}$ (temperature gradient only)

$J_x = -\sigma \frac{dV}{dx} - S\sigma \frac{dT}{dx}$

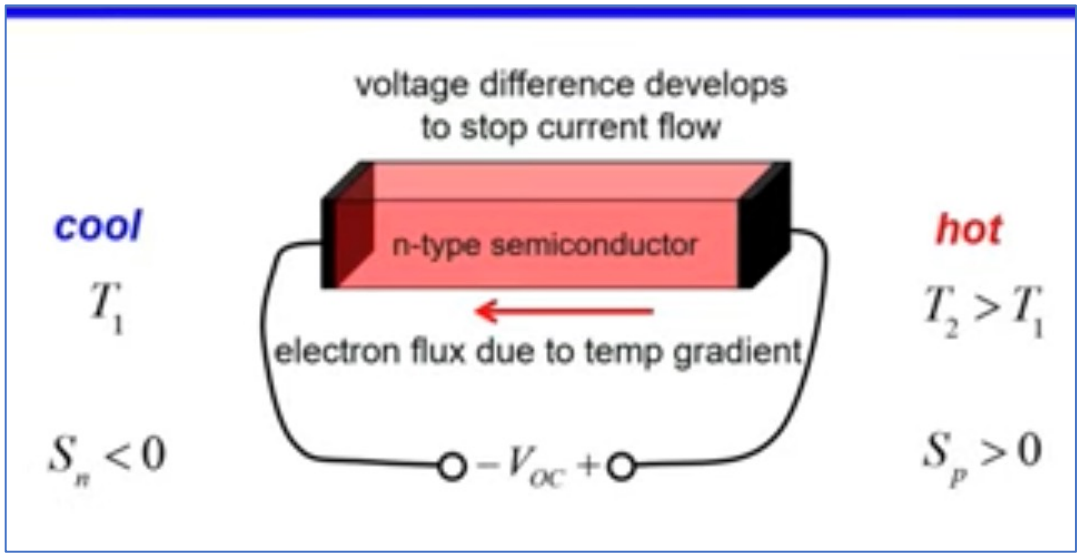
$J_x = 0$

measure open-circuit voltage

$V_{OC} = -S\Delta T$

$V_{OC} = V_2 - V_1$

$\Delta T = T_2 - T_1$

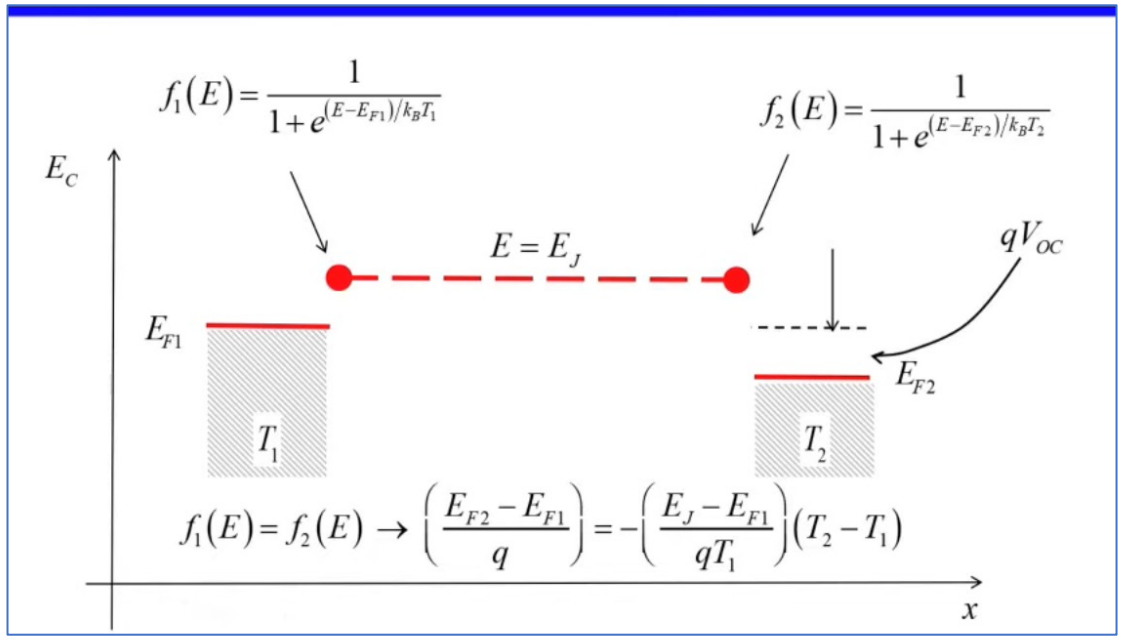


- We are dealing with a n-type SC
- Hot side on the right / cool side on the left
- Electrons diffuse from hot side to cool side

- A positive voltage appears to drag the electrons back to counteract the diffusion and give a zero current under open circuit voltage (V_{OC})
- Because V_{OC} is $-S\Delta T$ (Seebeck coefficient) we conclude That S is negative for n-type SC

Microscopic View of The Seebeck Coefficient

Simple meaning and expression of the Seebeck coefficient



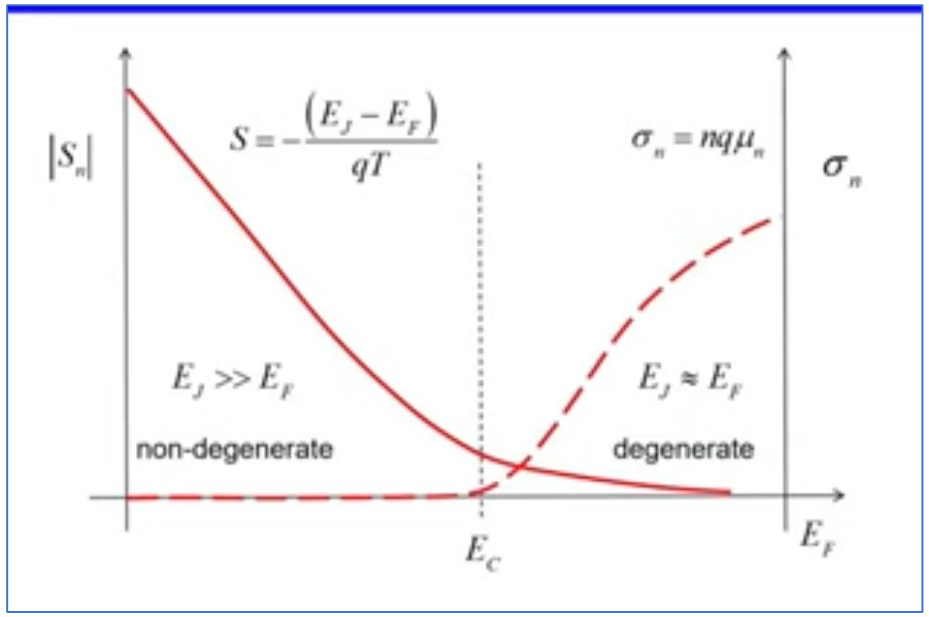
- E_J: Average energy at which current flows near the bottom of the conduction band in a non-degenerate n-type SC
- In OC conditions: $f_1 = f_2$
- $V_{OC} = -S\Delta T$

$$V_{OC} = \left(\frac{E_J - E_F}{-qT_1}\right)\Delta T \quad \text{and} \quad S = -\frac{\int\left(\frac{E-E_F}{qT}\right)\sigma'(E)dE}{\int\sigma'(E)dE}$$

Average expression: $\left\langle\frac{E-E_F}{qT}\right\rangle$

Hence:
The Seebeck coefficient is *related to the average energy at which the current flows with respect to the Fermi energy*

Seebeck coefficient Versus Electrical Conductivity



- If the Fermi level approaches the level at which conduction occurs, S decreases
- *If the "gap" is large, S is large too*
- When the Fermi level gets close to the level at which conduction occurs, σ increases
- *If the "gap" is small, σ is large*

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How to Calculate These Coefficients?

The TE coefficients = transport coefficients hence
Need for a transport equation

Boltzmann transport equation

If no need to account for strong e-e quantum correlation?

Mean-field approach (e.g. DFT) +
Semi-classical considerations +
Relaxation time approximation

The Boltzmann Transport Equation

$$\frac{df}{dt} = 0$$

f: the distribution of electrons (Fermi-Dirac) → electronic props.
or phonons (Bose-Einstein) → thermal-related props.

f is 6-dimensional function that evolves with time: $f(r, p, t)$

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \overrightarrow{F_e} \cdot \nabla_p f = 0$$

(no collision processes accounted for here)

The Boltzmann Transport Equation

If one accounts for collisions:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \overrightarrow{F_e} \cdot \nabla_p f = \left.\frac{df}{dt}\right|_{coll} = \hat{C} f = G_{in} - G_{out}$$

$$\hat{C} f = -\frac{f(p) - f_0(p)}{\tau_m} = -\frac{\delta f}{\tau_m}$$

with δf a small variation of the distribution function with respect to equilibrium ($f_0(p)$) and τ_m the scattering time of the carriers.

$\Longrightarrow$*Relaxation Time Approximation*.

1) RTA not valid in general! Justified when isotropic and/or elastic scatt.

2) Widely used in practice, though.

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Tools to Calculate Thermoelectric Properties

- Electronic structures $\Longrightarrow$ quantum ab initio approaches
- Electronic TE properties: Seebeck coefficient, electrical and electronic thermal conductivities and
- Lattice TE property: thermal conductivity

$\Longrightarrow$ at least apply semi-classical approaches to the *BTE*

Electronic Structure Calculation

- Any code can do the job: VASP, Quantum Espresso, Wien2k, SIESTA, CP2K,…

```
SYSTEM = PbSnTeSe
PREC = Normal
ISYM = 0
ISTART = 0; ICHARG = 2
ENCUT = 300
ISMEAR = 0; SIGMA = 0.02
INIMIX = 1; IMIX = 1; AMIX = 0.2; BMIX = 0.001
GGA = PZ
LREAL = Auto
######### SCF SETTING ########
IBRION = -1; ISIF = 2
NSW = 0
EDIFF = 1e-7
ALGO = Damped; IALGO = 53; TIME = 0.4
#############################
NCORE = 8; KPAR = 8
```

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&CONTROL
  title          = 'Pb2Bi2Te5',
  calculation    = 'scf',
  nstep          = 50,
  etot_conv_thr  = 1d-7,
  restart_mode   = 'from_scratch',
  verbosity      = 'high',
  prefix         = '225.opt',
  pseudo_dir     = '/ccc/work/cont003/gen6881/gen6881/packages/qe/PSP'
  wf_collect     = .true.,
/
&SYSTEM
  ibrav          = 0,
  celldm(1)      = 1.000000000000d0,
  nat            = 9,
  ntyp           = 3,
  ecutwfc        = 50.d0,
  ecutrho        = 500.d0,
  occupations    = 'fixed',
  nbnd           = 100,
  noncolin       = .true.,
  lspinorb       = .true.,
/
&ELECTRONS
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  mixing_beta    = 0.2d0,
  startingpot    = 'atomic',
  startingwfc    = 'atomic+random',
/

ATOMIC_SPECIES
Pb 107. Pb.rel-pbe-dn-rrkjus_psl.1.0.0.UPF
Bi 209. Bi.rel-pbe-dn-rrkjus_psl.1.0.0.UPF
Te 128. Te.rel-pbe-n-rrkjus_psl.1.0.0.UPF

K_POINTS automatic
4 4 2 1 1 1

CELL_PARAMETERS alat
 8.510135436547301d0   -1.215303952543845d-13  1.797830763980544d-20
-4.255067718345414d0    7.369993477081541d0   -1.218922858649270d-20
 7.308332310332742d-20 -2.398019053344136d-20  35.41739576994752d0
```

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PbSnTeSe
P                          64    1 P1
           RELA
 24.831001 24.831001 24.831001 90.000000 90.000000 90.000000
ATOM  -1: X=0.98683803 Y=0.02333037 Z=0.75873896
          MULT= 1          ISPLIT= 8
Se         NPT=  781  R0=0.00005000 RMT=    2.5000   Z:  34.00000
                      1.0000000 0.0000000 0.0000000
                      0.0000000 1.0000000 0.0000000
                      0.0000000 0.0000000 1.0000000
ATOM  -2: X=0.48483973 Y=0.00176046 Z=0.76309299
          MULT= 1          ISPLIT= 8
Se         NPT=  781  R0=0.00005000 RMT=    2.5000   Z:  34.00000
                      1.0000000 0.0000000 0.0000000
                      0.0000000 1.0000000 0.0000000
                      0.0000000 0.0000000 1.0000000
ATOM  -3: X=0.99362382 Y=0.52076864 Z=0.76440142
          MULT= 1          ISPLIT= 8
Se         NPT=  781  R0=0.00005000 RMT=    2.5000   Z:  34.00000
                      1.0000000 0.0000000 0.0000000
                      0.0000000 1.0000000 0.0000000
                      0.0000000 0.0000000 1.0000000
ATOM  -4: X=0.48399564 Y=0.50343080 Z=0.75407842
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                      0.0000000 1.0000000 0.0000000
                      0.0000000 0.0000000 1.0000000
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                      0.0000000 1.0000000 0.0000000
                      0.0000000 0.0000000 1.0000000
ATOM  -6: X=0.49533243 Y=0.00570859 Z=0.26231032
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Te         NPT=  781  R0=0.00001000 RMT=    2.5000   Z:  52.00000
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                      0.0000000 1.0000000 0.0000000
                      0.0000000 0.0000000 1.0000000
ATOM  -7: X=0.98727580 Y=0.50993181 Z=0.25765265
          MULT= 1          ISPLIT= 8
Te         NPT=  781  R0=0.00001000 RMT=    2.5000   Z:  52.00000
                      1.0000000 0.0000000 0.0000000
```

As far as their output data can be processed by other programs: e.g. BoltzTraP, phonopy, phono3py, etc.

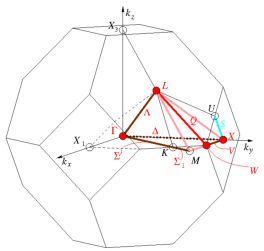
Electronic Structure Calculation

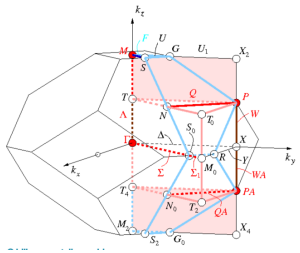
Reminder on how to solve the Kohn-Sham equations of DFT →

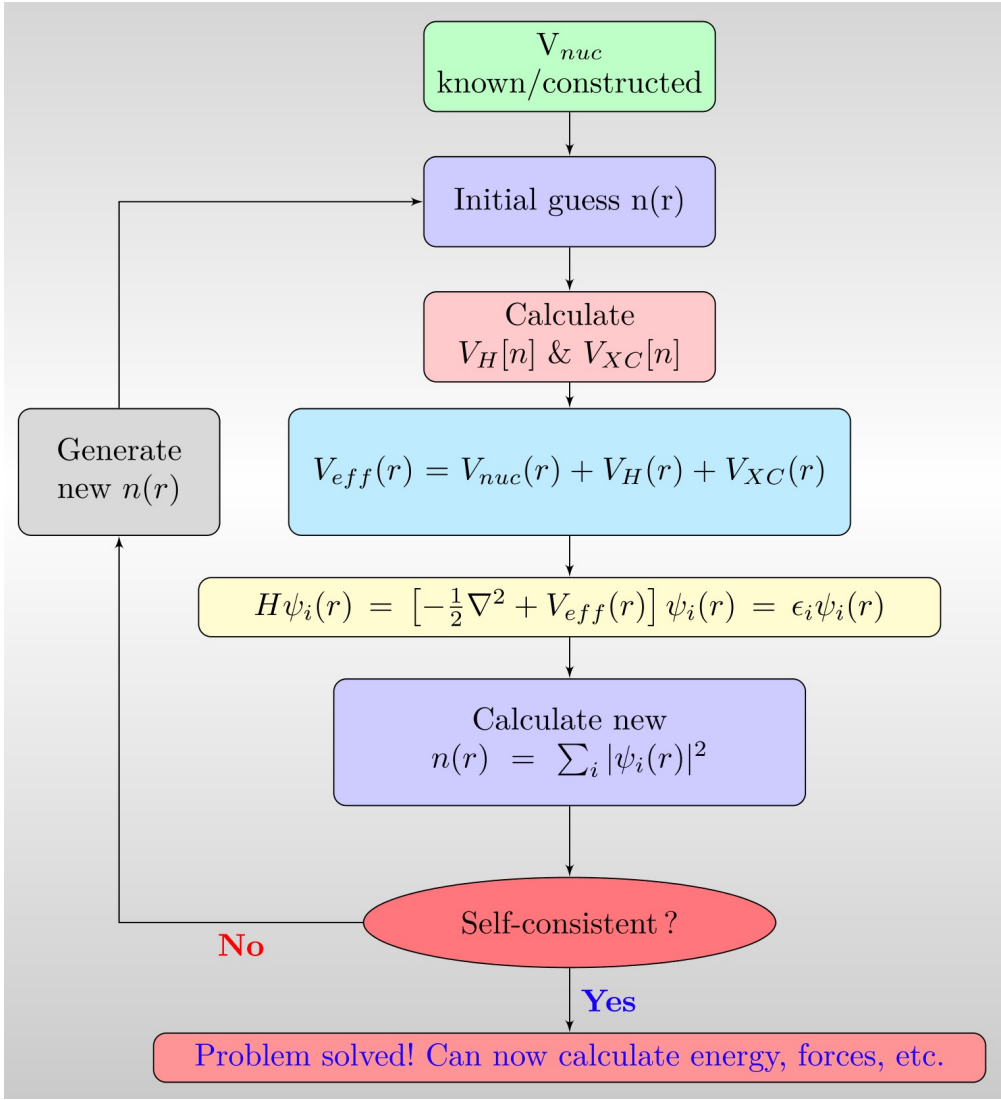
Allows one to obtain:

- Electrons energies
- orbitals

for a set of k-points spread over the Brillouin zone





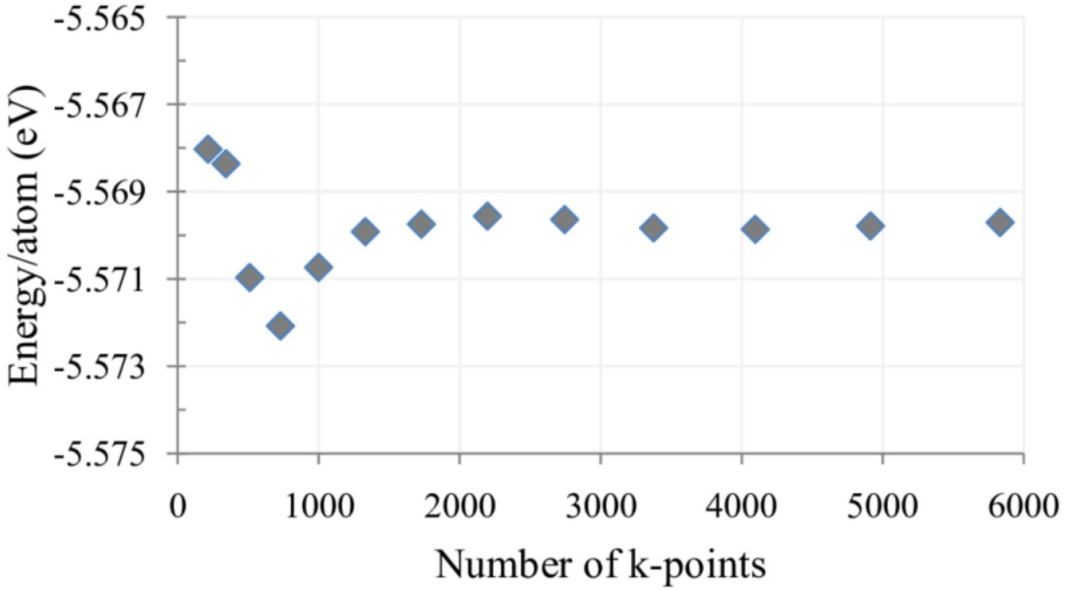


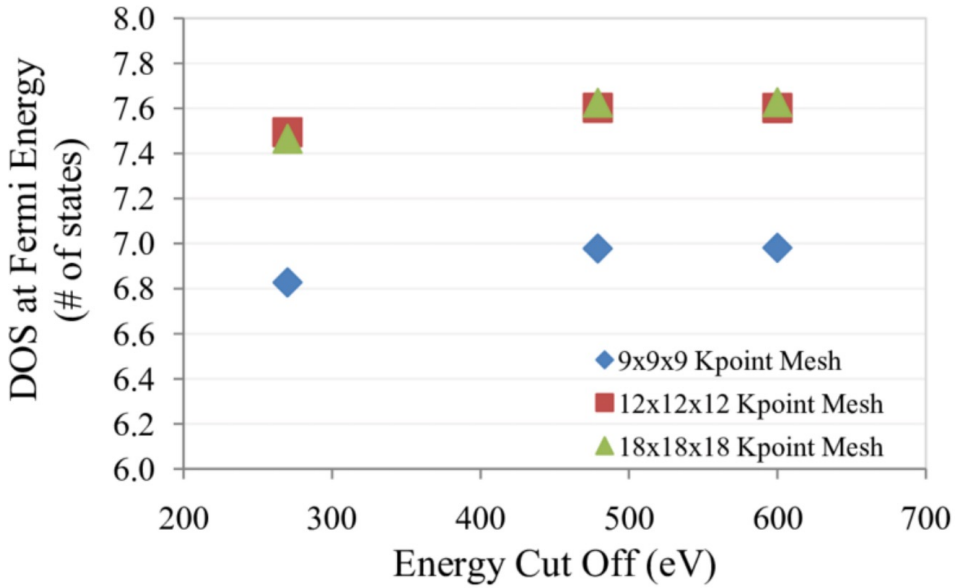
Convergence With k-Points And Cutoff Energy

- K-points grid: used to sample the Brillouin zone

  Small lattice → large reciprocal lattice ⟹ *lot of k-points needed*

- Cutoff energy: defines the plane wave basis set size





How To Solve The Boltzmann Equation

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \overrightarrow{F_e} \cdot \nabla_p f = -\frac{\delta f}{\tau_m}$$

Linearize the equation: analytically develop expressions for the transport coefficients expressions (RTA) and calculate them numerically

For electronic coefficients → *BoltzTraP*(2) Code (Boltzmann Transport Program)

(GNU, https://www.imc.tuwien.ac.at/index.php?id=21094)

Theory Behind BoltzTraP

Linearization of the Boltzmann equation

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \overrightarrow{F_e} \cdot \nabla_p f = -\frac{\delta f}{\tau_m}$$

$$f = f^{(0)}(E) + f^{(1)}(E) = \frac{1}{1 + \mathrm{e}^{\frac{E-\mu}{kT}}} + f^{(1)}(E)$$

Recall that $E = \epsilon(k)$

$$\frac{\partial f^{(1)}}{\partial t} + v\left(\frac{E-\mu}{T}\nabla_r T + \nabla_r \mu - q\mathcal{E}\right)\left(-\frac{\partial f^{(0)}}{\partial \mu}\right) + \frac{q}{\hbar c}(v \times B)\nabla_k f^{(1)} = -\frac{f^{(1)}}{\tau_m}$$

Note: μ is the (electro-)chemical potential

τ_m depends on k

Theory Behind BoltzTraP

- Assume $\epsilon_k = \frac{\hbar^2 k^2}{2m^*}$ and $v_k = \frac{\hbar k}{m^*}$

$$f^{(1)} = \tau(\epsilon) v \left[(q\mathcal{E} - \nabla\mu) - \frac{\epsilon - \mu}{T} \nabla T \right] \left(-\frac{\partial f^{(0)}}{\partial \epsilon_k} \right)$$

Kinetic coefficient:

$$K_p = \frac{1}{3} \int v^2 (\epsilon - \mu)^p n(\epsilon) \tau(\epsilon) \left(\frac{\partial f^{(0)}}{\partial \epsilon} \right) \mathrm{d}\epsilon \,, \qquad p = 0,1,2$$

Electrical current:

$$J = K_0 (q\mathcal{E} - \nabla\mu) - K_1 \frac{\nabla T}{T}$$

Electronic thermal current:

$$J_Q = K_1 (q\mathcal{E} - \nabla\mu) - K_2 \frac{\nabla T}{T}$$

Theory Behind BoltzTraP

- Kinetic coefficient:

$$K_p = \frac{1}{3}\int v^2(\epsilon-\mu)^p n(\epsilon)\tau(\epsilon)\left(\frac{\partial f^{(0)}}{\partial \epsilon}\right)\mathrm{d}\epsilon\,, \qquad p = 0,1,2$$

- Electrical conductivity:

$$\sigma = q^2 K_0$$

- Seebeck coefficient:

$$S = \frac{1}{qT}\frac{K_1}{K_0}$$

- Electronic thermal conductivity:

$$\kappa_e = \frac{K_0 K_2 - K_1^2}{K_0 T}$$

Note: σ, S and κ_e are tensors, so BoltzTraP outputs tensors

Practical Equations Calculated in BoltzTraP

- Velocity vector:

$$v_\alpha(i,k) = \frac{1}{\hbar}\frac{\partial \epsilon_{ik}}{\partial k_\alpha}$$

- Conductivity tensor expressions:

$$\sigma_{\alpha\beta}(i,k) = q^2 \tau_{ik} v_\alpha(i,k) v_\beta(i,k)$$

$$\sigma_{\alpha\beta}(\epsilon) = \frac{1}{N_k}\sum \sigma_{\alpha\beta}(i,k)\frac{\partial(\epsilon - \epsilon_{ik})}{\partial \epsilon}$$

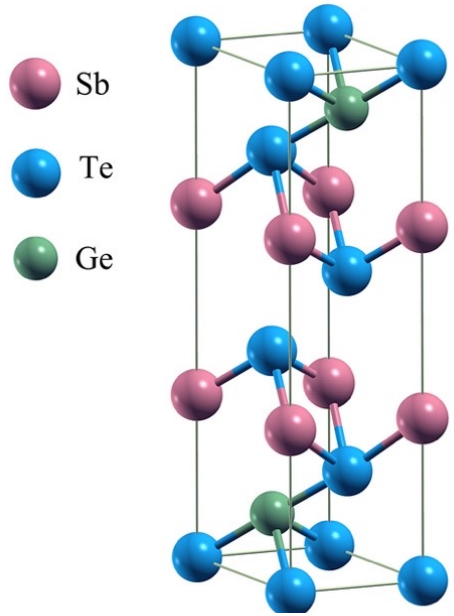
$$\sigma_{\alpha\beta}(T,\mu) = \frac{1}{\Omega}\int \sigma_{\alpha\beta}(\epsilon)\left(-\frac{\partial f(T,\epsilon)}{\partial \epsilon}\right)d\epsilon$$

A Note On The Convergence With k-Point Grids

How many k-points should I use for a transport calculation?

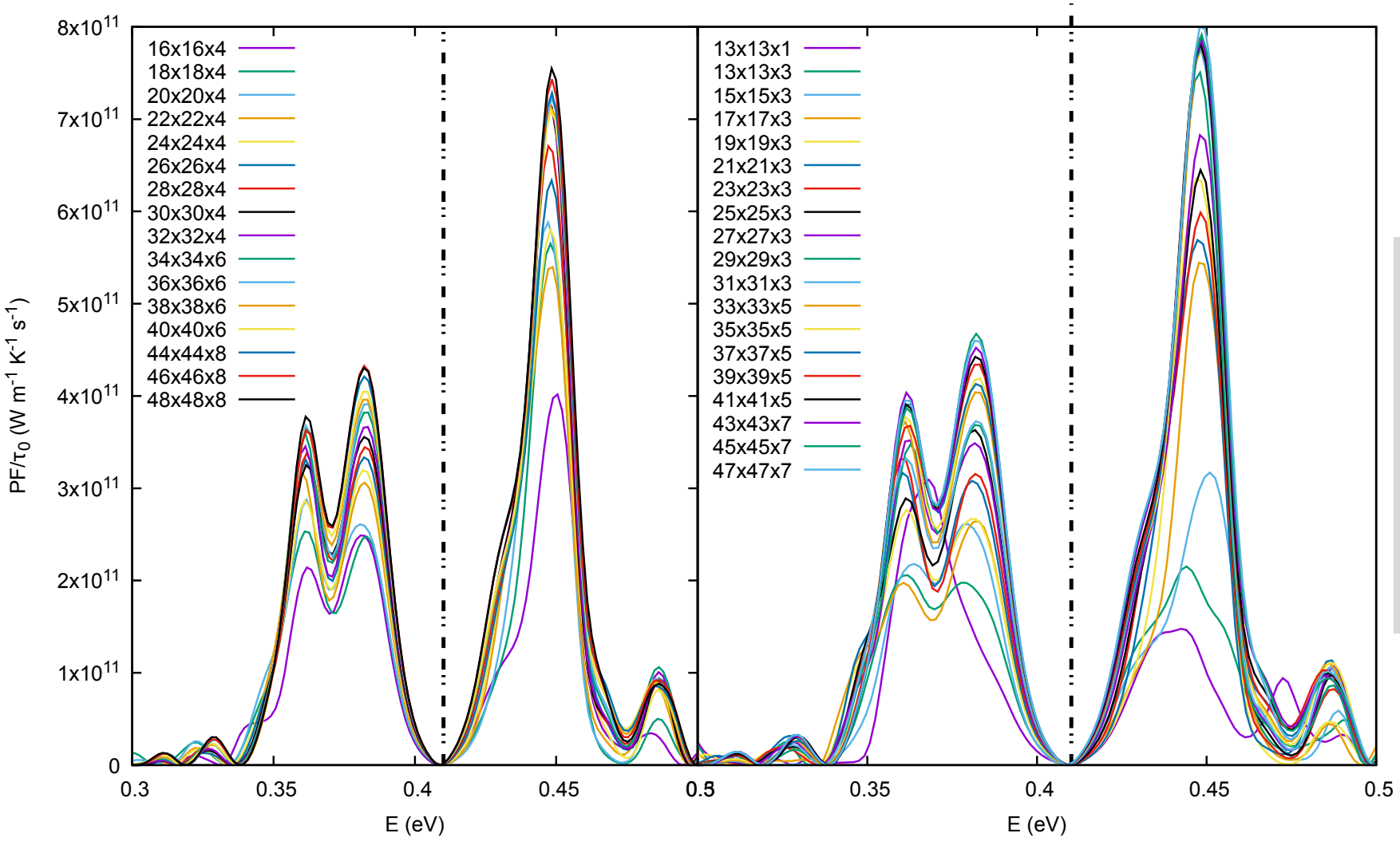
- According to BoltzTraP2 authors: ``*a lot*''
- As a rule of thumb: convergence tests should start at *$16x10^6$ k-points in the IBZ*

Test on $Pb_2Sb_2Te_5$:



Hexagonal structure
4.23 x 4.23 x 16.92 Å

A Note On The Convergence With k-Point Grids



Comments

- Rather slow convergence with k-point grid
- Same convergence rate with both odd and even grid
- Faster calculations with odd grid than with even one

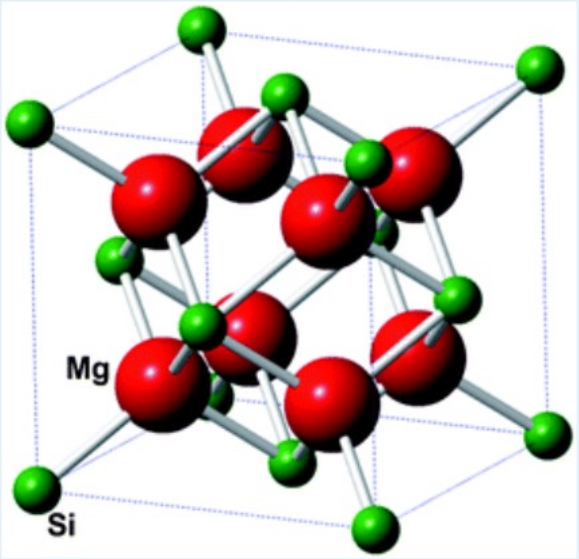
Investigation performed by J. Tian, PhD student

Content of This Lecture

1. Thermoelectric Effect: Macroscopic View
2. Thermoelectric Coefficients: Microscopic View
3. Transport Equation To Calculate Thermoelectric Coefficients
4. Semi-Classical Approaches To Calculate The TE Coefficients
5. Examples

A Simple Silicide Compound: Mg_2Si

- **Cubic anti-fluorite structure; a=0.635 nm.**
- **Si atoms occupy the 4a (0, 0, 0) sites**
- **Mg atoms occupy the 8c (0.25, 0.25, 0.25) sites.**
- The $Fm\bar{3}m$ space group fixes the fractional coordinates of all atoms.



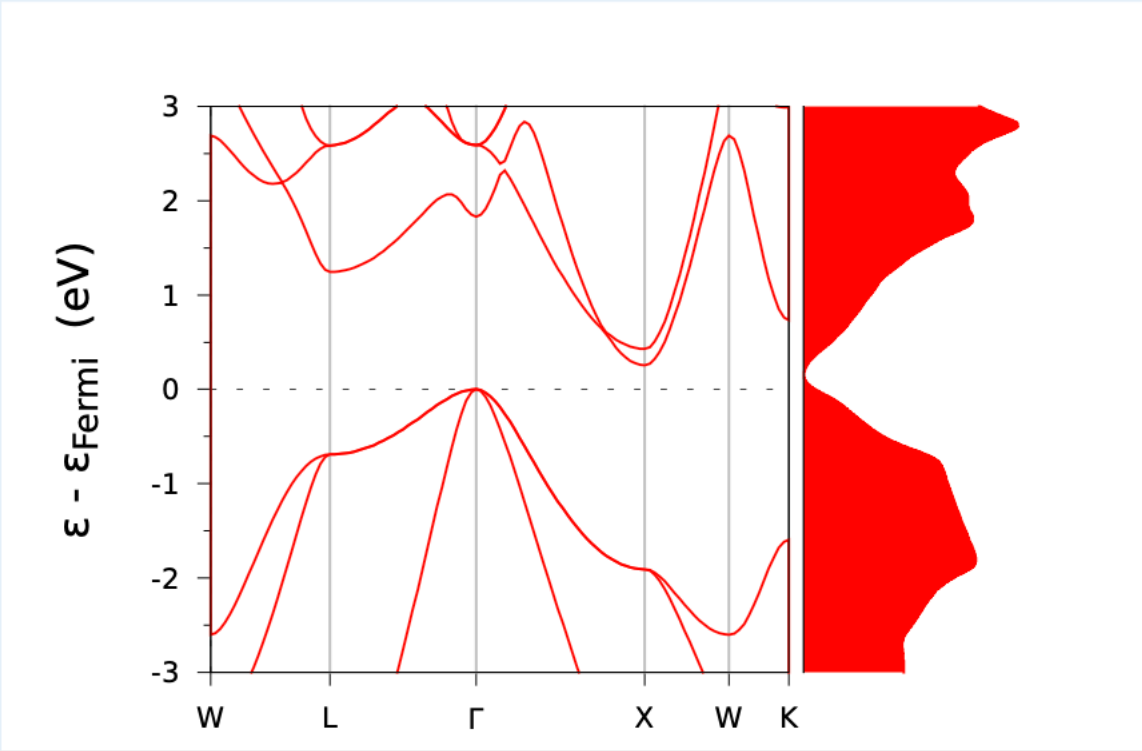
References:

Studies by H. Balout et al.

- J. Mol. Model., 2017 (23) 130
- Eur. Phys. J. B, 2015 (88) 209
- J. Electron. Mater., 2014 (43) 3801
- Intermetallics, 2014 (50) 8
- J. Electron. Mater., 2013 (42) 3458

Band Structure of Mg_2Si

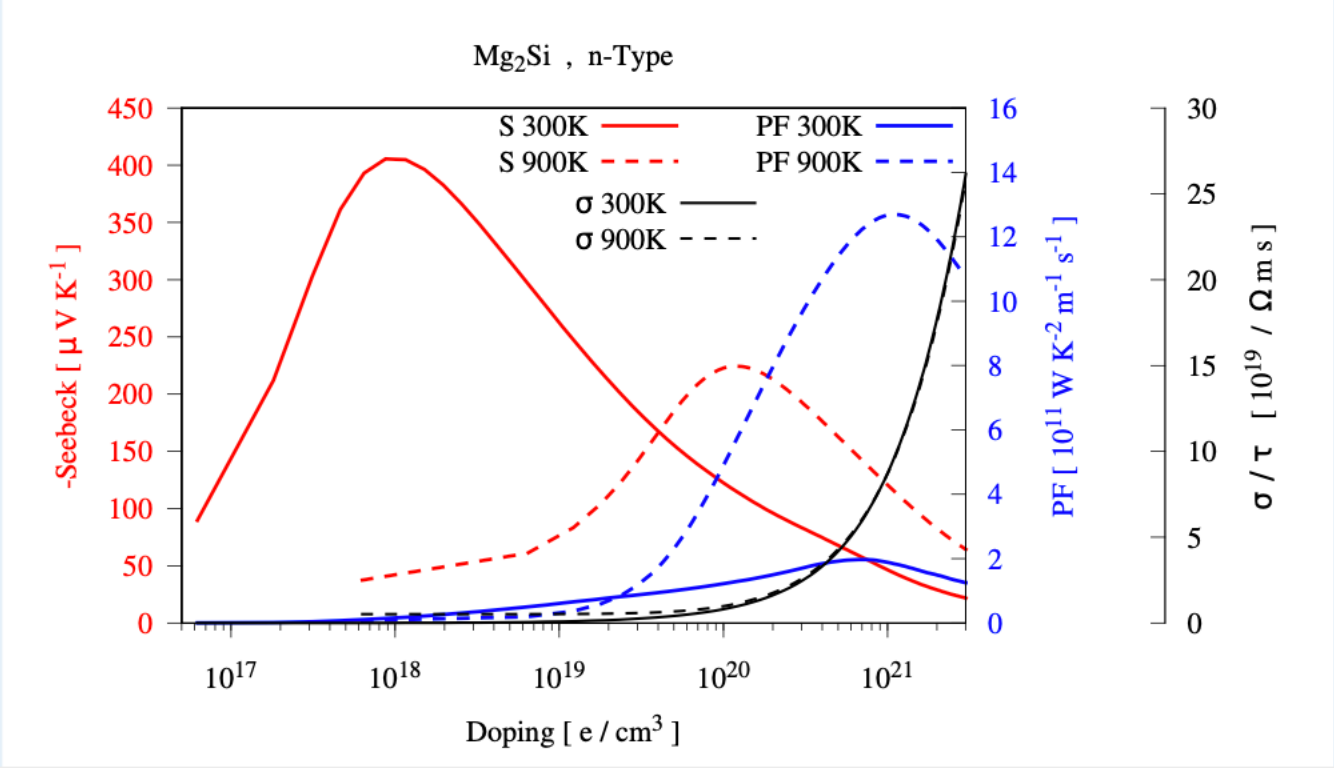
- **Mg_2Si** Is a **Semiconductor** with Narrow Band Gap.
- Indirect Band Gap $E_{\Gamma-X} = 256$ **meV**.
- **Conduction Band** Bears Two Sets of Low-Lying, 3-Fold Degenerated Orbitals **Separated by 173 meV**



- Calculated with the GGA-PBE functional
- Exp. ~ 0.7-0.8 eV

Transport Coefficients of Bulk n-type Mg_2Si

- At 300 K and $\sim 10^{18} e/cm^3 \rightarrow S_{max} = 400\ \mu V/K$
- At 900 K and $\sim 1.2 \times 10^{20} e/cm^3 \rightarrow S_{max} = 225\ \mu V/K$
- σ/τ Increases dramatically $\Rightarrow$ Doped Semiconductor.
- PF_{max} is Observed at around 10^{21} e/cm^3.



Comments

- S is high for lightly doped Mg_2Si
- σ is high for heavily doped Mg_2Si

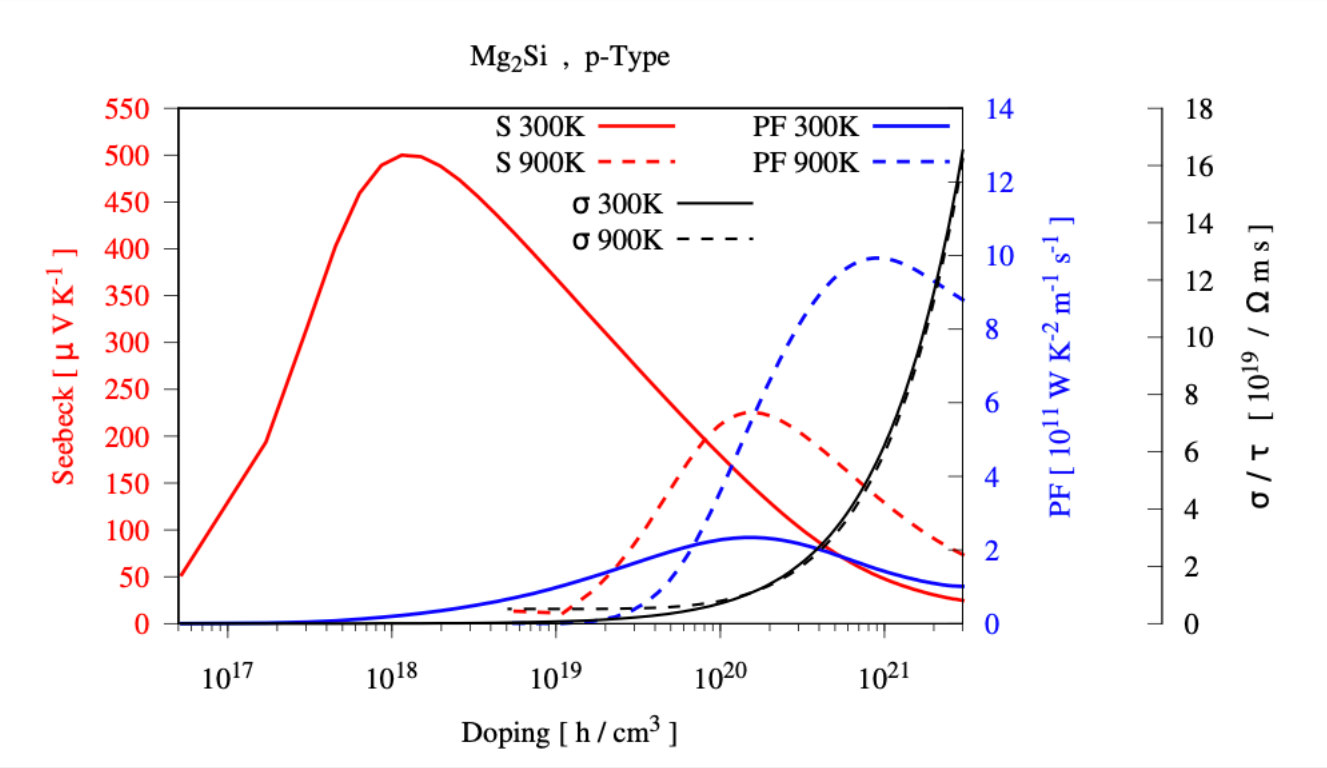
- S and PF decrease as T increases
- σ not much sensitive to T

Note

σ and PF in units of per second because τ_m is unknown

Transport Coefficients of Bulk p-type Mg_2Si

- At 300 K and $\sim 10^{18} h/cm^3 \rightarrow S_{max} = 500\ \mu V/K$
- At 900 K and $\sim 1.2 \times 10^{20} h/cm^3 \rightarrow S_{max} = 225\ \mu V/K$
- σ/τ Increases dramatically $\Rightarrow$ Doped Semiconductor.
- PF_{max} is Observed in the Range $10^{20} - 10^{21}$ h/cm^3.



Comments

Same observations as for n-type doping but

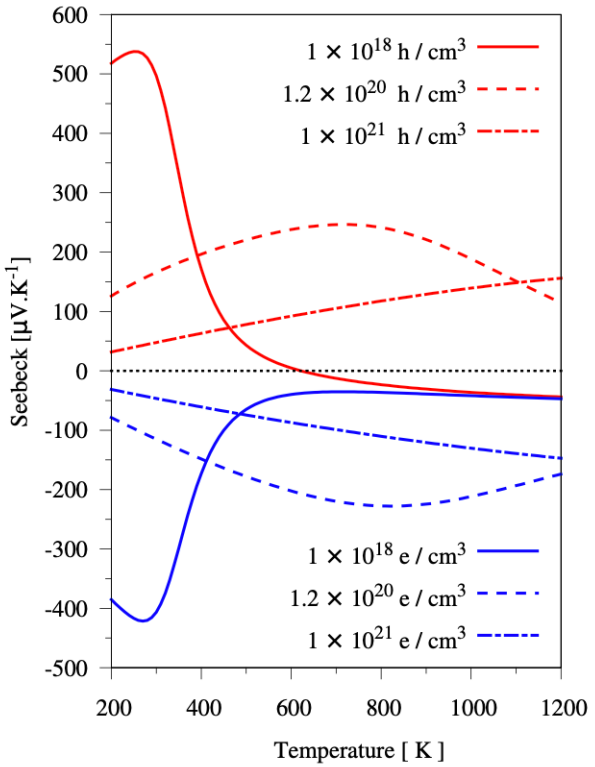
- Seebeck coefficient slightly larger for the same T and doping: 500 μV/K at 300 K and 10^{18} h/cm^3 instead of 400 μV/K
- σ slightly smaller for the same T and doping

Transport Coefficients w.r.t. Temperature

- S_{max} { n-type , S = -450 μV/K ; p-type , S = 540 μV/K }
- T↗ ⇒ S ↘ and ⟶ −50 μV/K (bipolar regime)
- Heavily Doping ⇒ S = a×T

⇓

Mott Relation



Mott relation of thermopower

$$S = \left(\frac{\pi^2}{3}\frac{k^2 T}{q}\right)\frac{1}{\sigma_E}\frac{d\sigma_E}{dE}\bigg|_{E=E_F}$$

where σ_E is the *transport function*

$$\sigma_E = \frac{q^2}{3}\tau(E)v^2(E)N(E)$$

Can We Improve The Thermopower?

From the Mott formula:

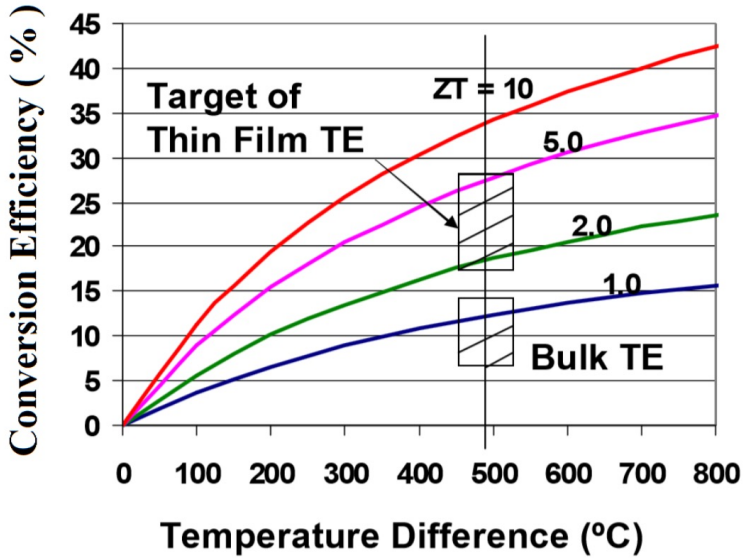
$$S = \left(\frac{\pi^2}{3}\frac{k^2 T}{q}\right)\frac{1}{\sigma_E}\frac{d\sigma_E}{dE}\Big|_{E=E_F} \quad \text{and} \quad \sigma_E = \frac{q^2}{3}\tau(E)v^2(E)N(E)$$

$$\frac{d\sigma_E}{dE} \approx \frac{dN(E)}{dE}$$

$\Longrightarrow$ if we can *make the DOS increase subtantially near the Fermi level*, then S may increase notably

Can We Improve The Thermopower?

1) Design of *low-dimensional* materials



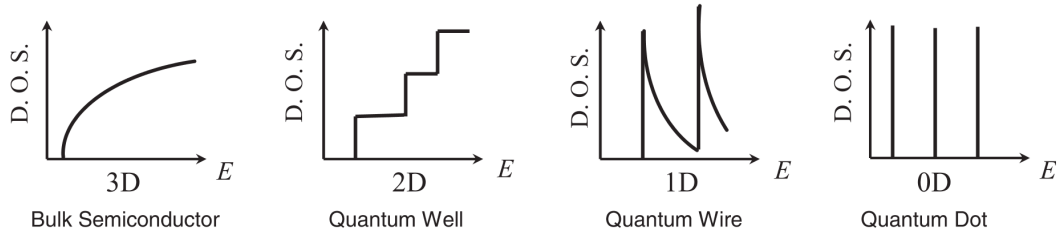


Figure 1. Electronic density of states for a) a bulk 3D crystalline semiconductor, b) a 2D quantum well, c) a 1D nanowire or nanotube, and d) a 0D quantum dot. Materials systems with low dimensionality also exhibit physical phenomena, other than a high density of electronic states (DOS), that may be useful for enhancing thermoelectric performance (see text).

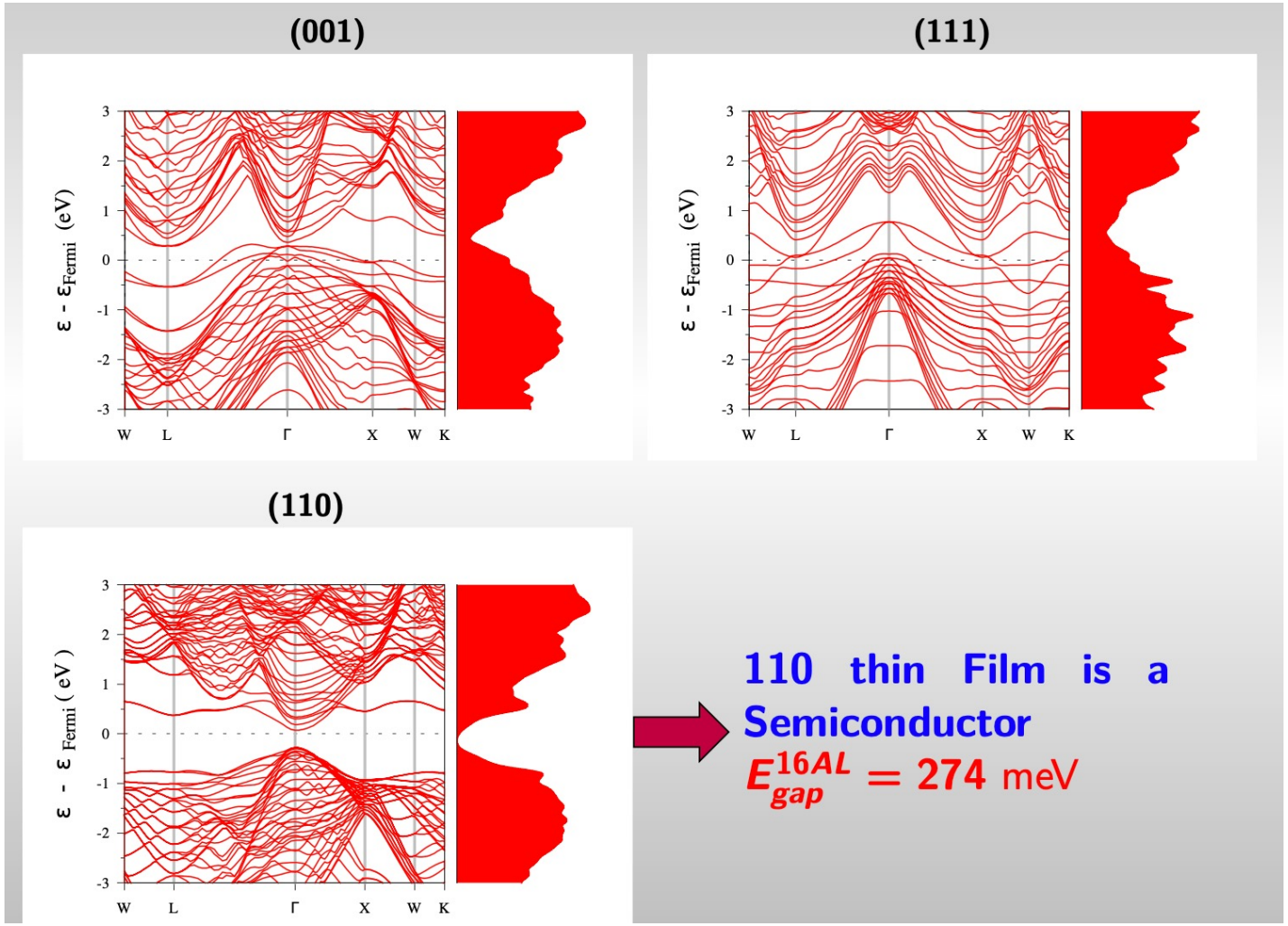
From: Dresselhaus et al., Adv. Mater. 2007, 19, 1-12

2) *Merge bands* near the Fermi level by applying *strains*

3) Introduce foreign atoms to *create resonant levels*

Examples with Mg_2Si and HMS

Band Engineering in Mg_2Si: Band Structures



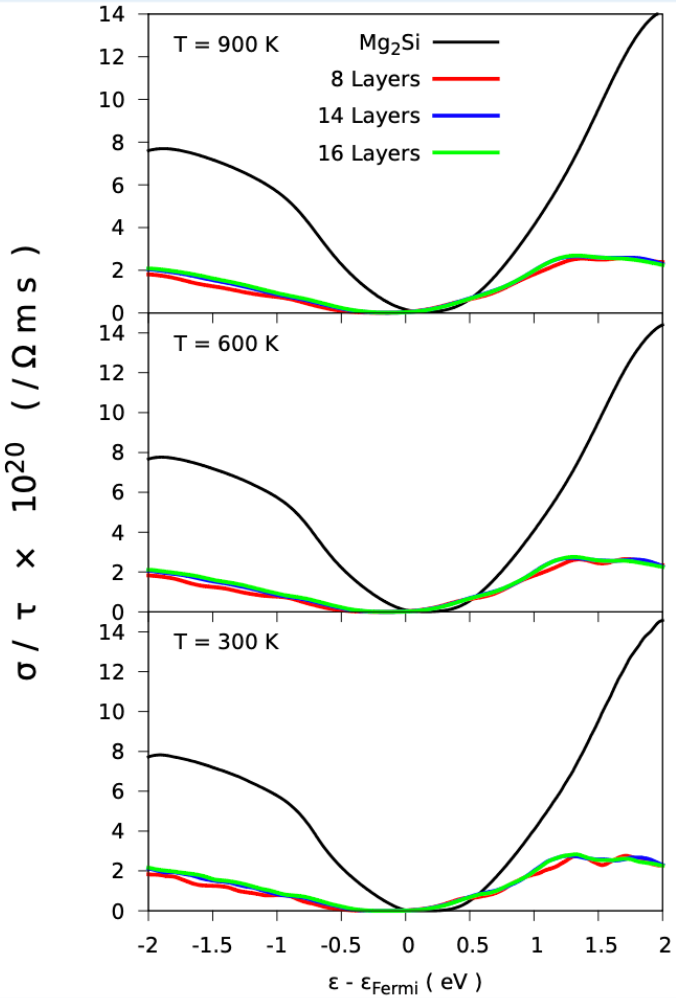
Comments

- Only the (110)-oriented thin film is SC
- Flat bands localized in the conduction bands of the (110) film
- Energy gap slightly larger than that of the bulk
- Energy gap evolves with the number of layers

Band Engineering in Mg_2Si: Electrical Conductivity

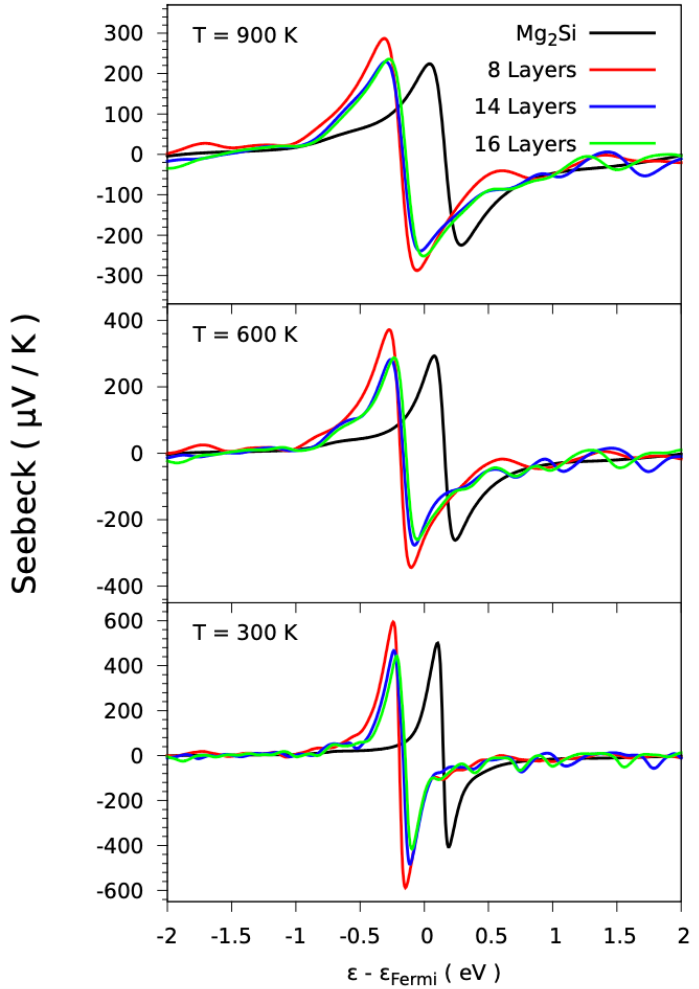
- **σ Curves of the Slabs Are Almost Superimposed**
- **Temperature Marginally Affects σ**
- **$0 \leqslant \Delta E \leqslant 0.5$ eV $\Rightarrow$ Thin Film Exhibits the Highest σ**

(110) Mg_2Si Thin Film Have Better Conduction then Bulk



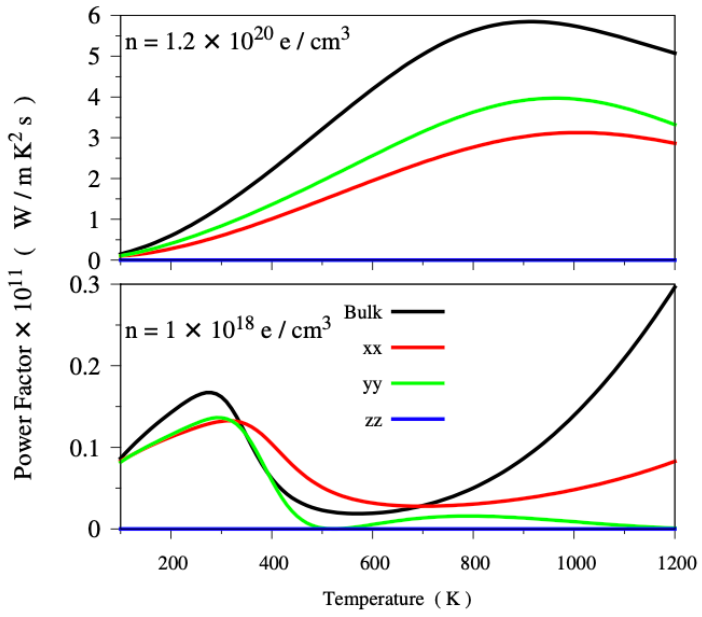
Band Engineering in Mg_2Si: Seebeck Coefficient

- **Shift (Between Films and Bulk) Results from the Fermi Level Positions**
- **The Thinner the Films, the Larger the S**
- **S Increases Strongly when the Fermi Level Falls into Gap**
- **Temperature Affects Sensibly S**

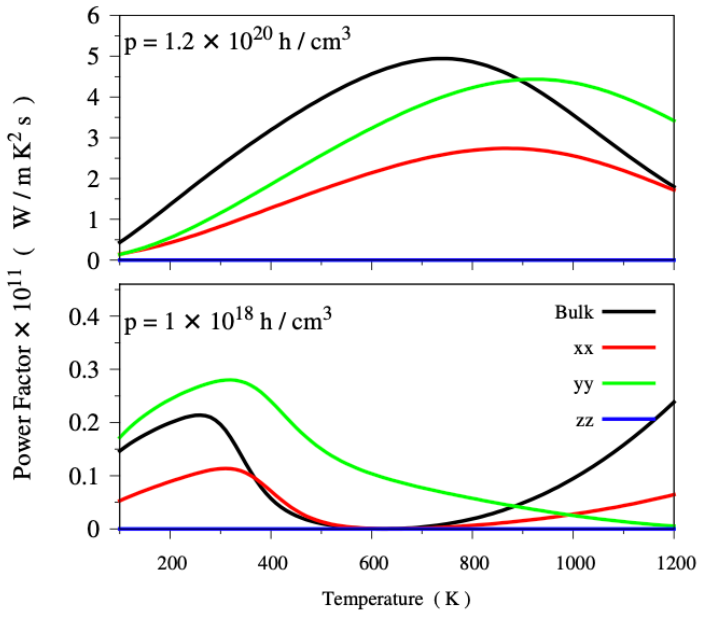


Band Engineering in Mg_2Si: Power Factor

- **Anisotropy in Structure ⇒ Anisotropy in TE Properties.**
- **PF_{xx} Highest for Low n-Doped Thin Film for $350 \leq T \leq 650$ K**
- **PF_{yy} Highest for Low p-Doped Thin Film for $T \leq 850$K**



n—Type



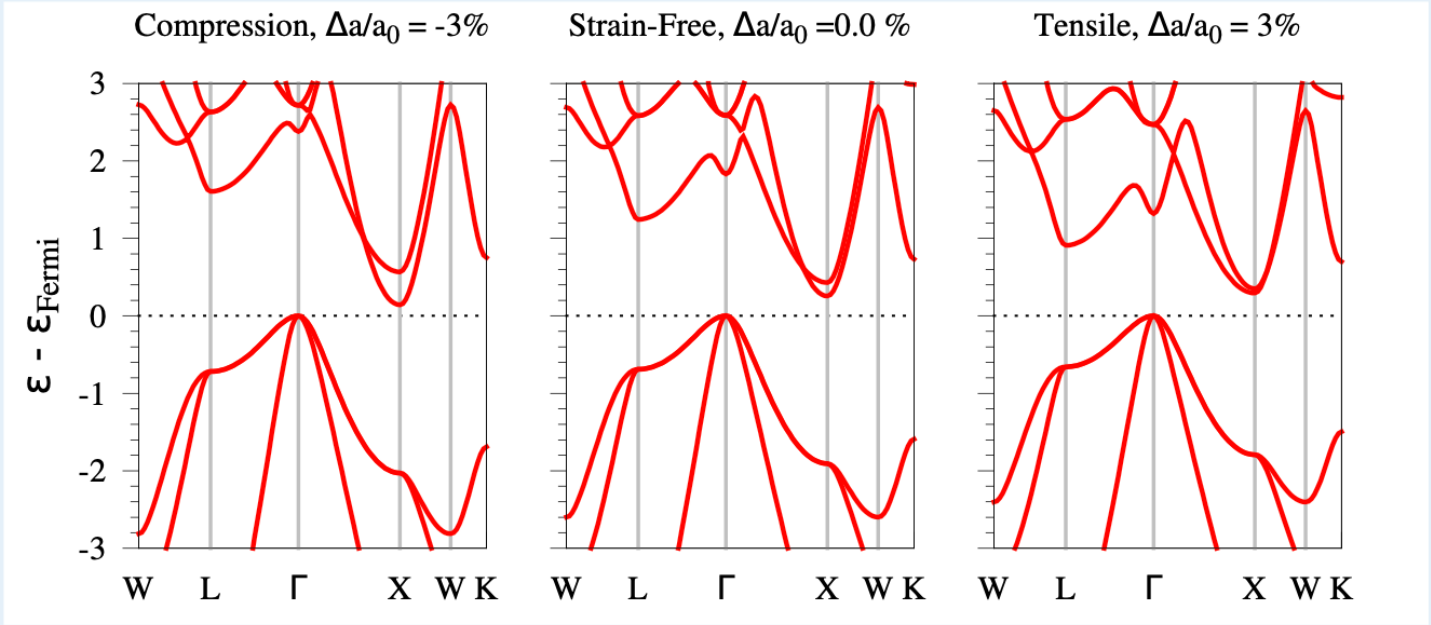
p—Type

Conclusions

- Both S and σ can be improved
- Idea of decoupling S and σ through band engineering
- S is highest for the thinnest film
- Best performance at low doping and moderate T

Band Engineering in Mg_2Si: bands Convergence

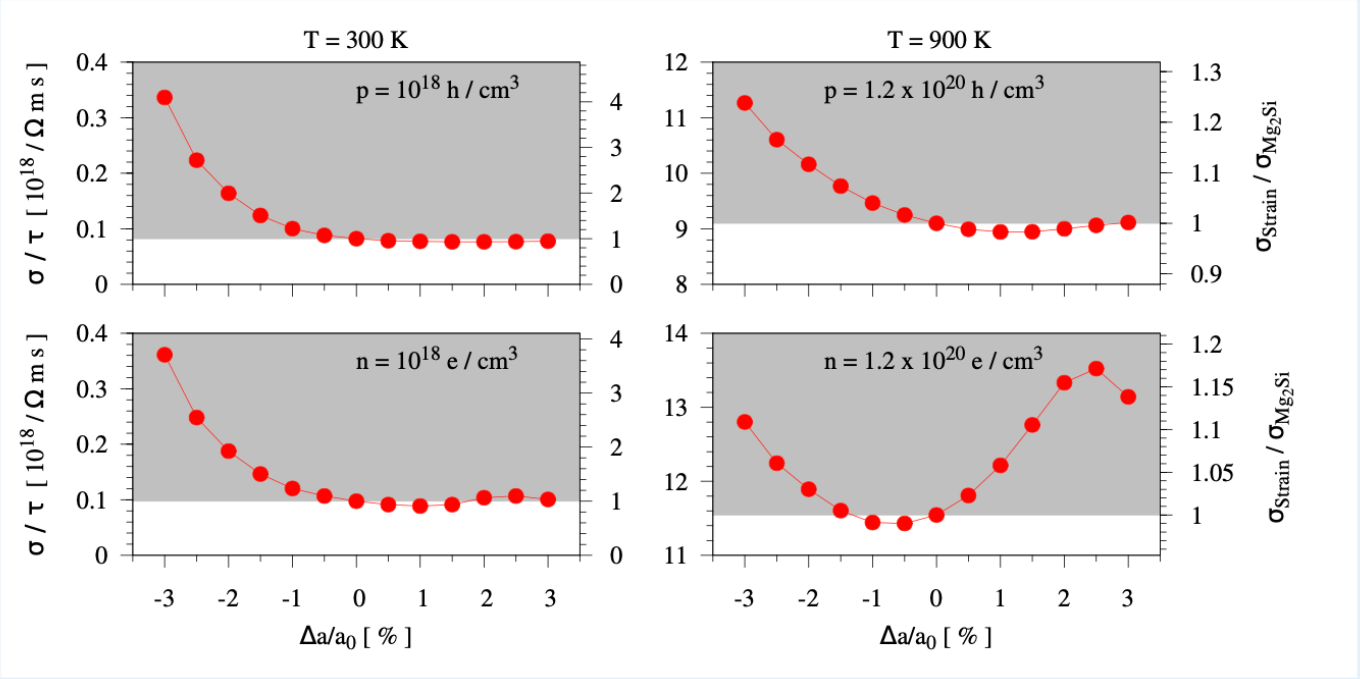
✠ **Isotropic Strain ⇒ Changing *a* ($\Delta a/a_o$ going from -3% to +3%)**



- **NO Removing of Bands Degeneracy.**
- **Compressive Strain Tends to Close up the Band Gap.**
- **Tensile Strain Tends to Enlarge the Band Gap.**

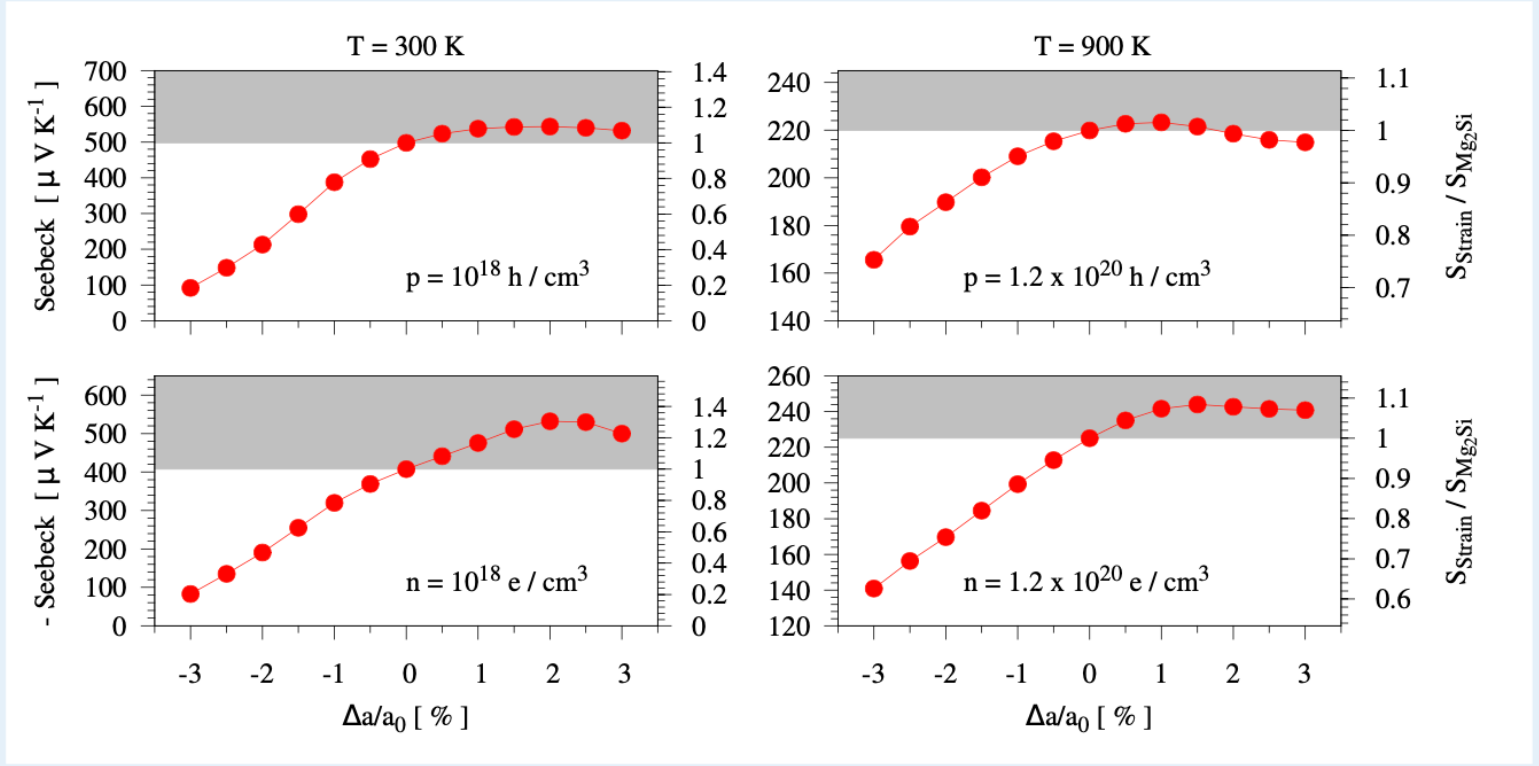
Band Engineering in Mg_2Si: Electrical Conductivity

- **The Higher the Compression, the Higher the σ**
- **Tensile Strain Affects Marginally σ, for p-type and Low n-Type Doping Level**
- **At High Electron Doping Level, Tensile Strain Enhances σ (at 2.5 %)**
- **All of these Features Depend on the Magnitude of the Band Gap Energy**



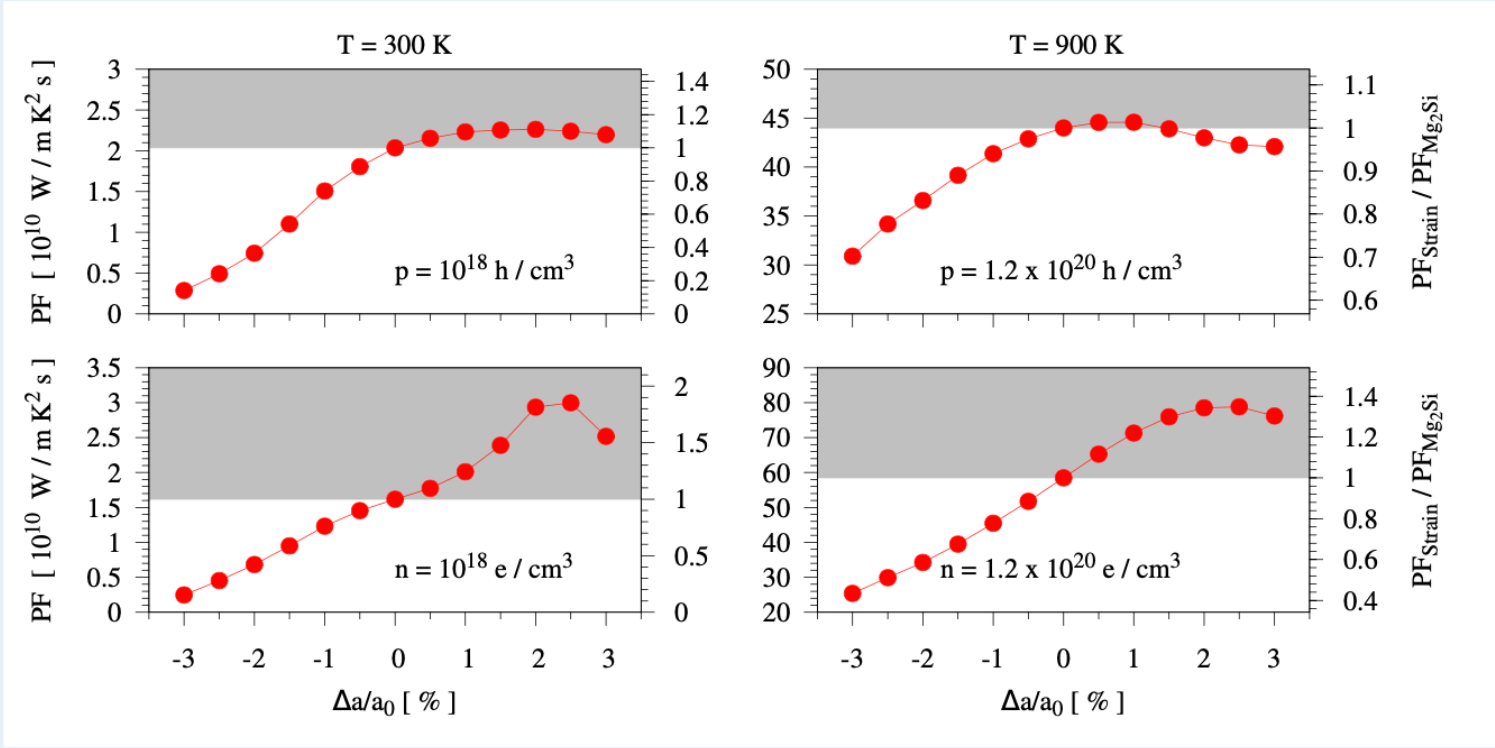
Band Engineering in Mg_2Si: Seebeck Coefficient

- **S Decreases Monotonically Under Compressive Strain**
- **Tensile Strain Enhances S, Specially at Low Doping Level 10^{18} cm^{-3}**



Band Engineering in Mg_2Si: Power factor

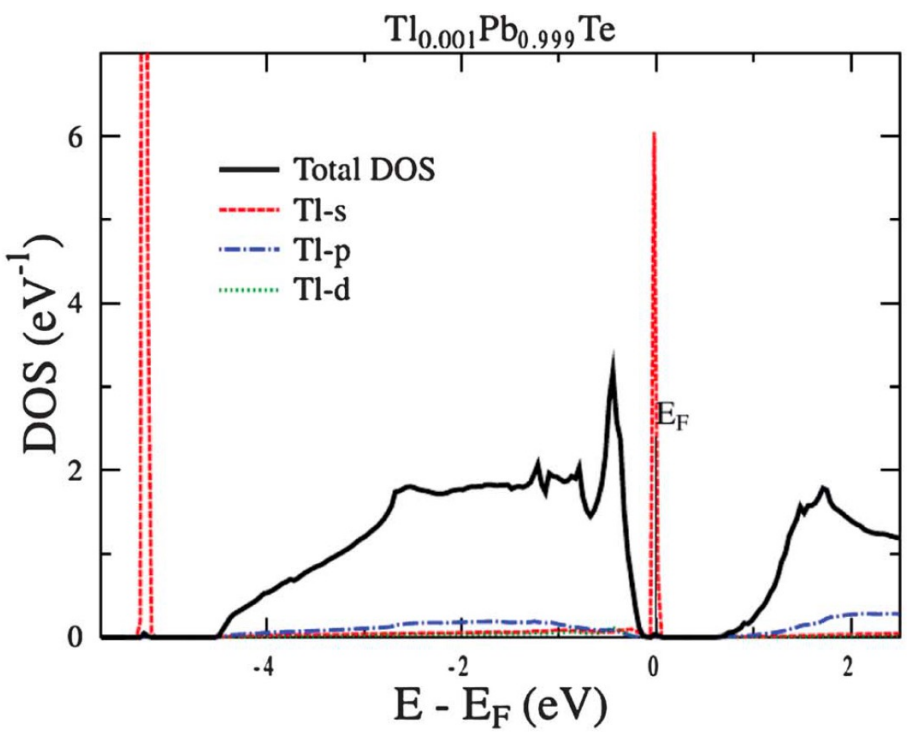
- **Since $S \propto 1/\sigma \Rightarrow PF =$ Compromise Between S and σ**
- **Under Tensile Strain**
  - **Low e-doping : $\sigma \simeq cte$ and Higher S $\Rightarrow$ Higher PF.**
  - **High e-doping : Higher σ and Higher S $\Rightarrow$ Higher PF.**

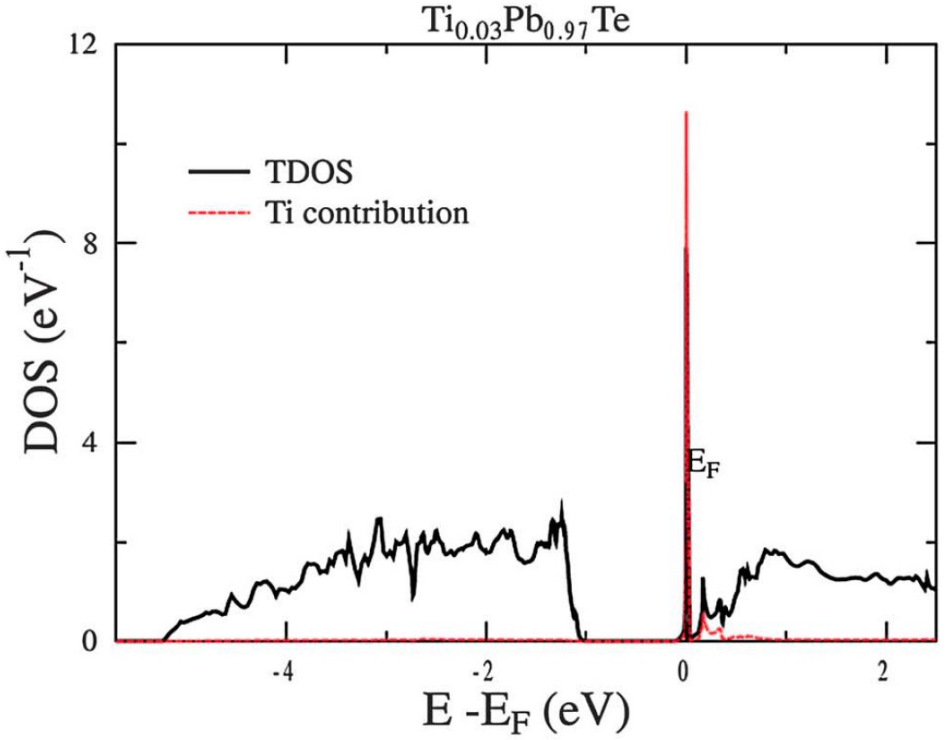


Band Engineering: Resonant Levels

What is a *resonant level*?

Energy states located at or near E_F in the DOS due to impurities





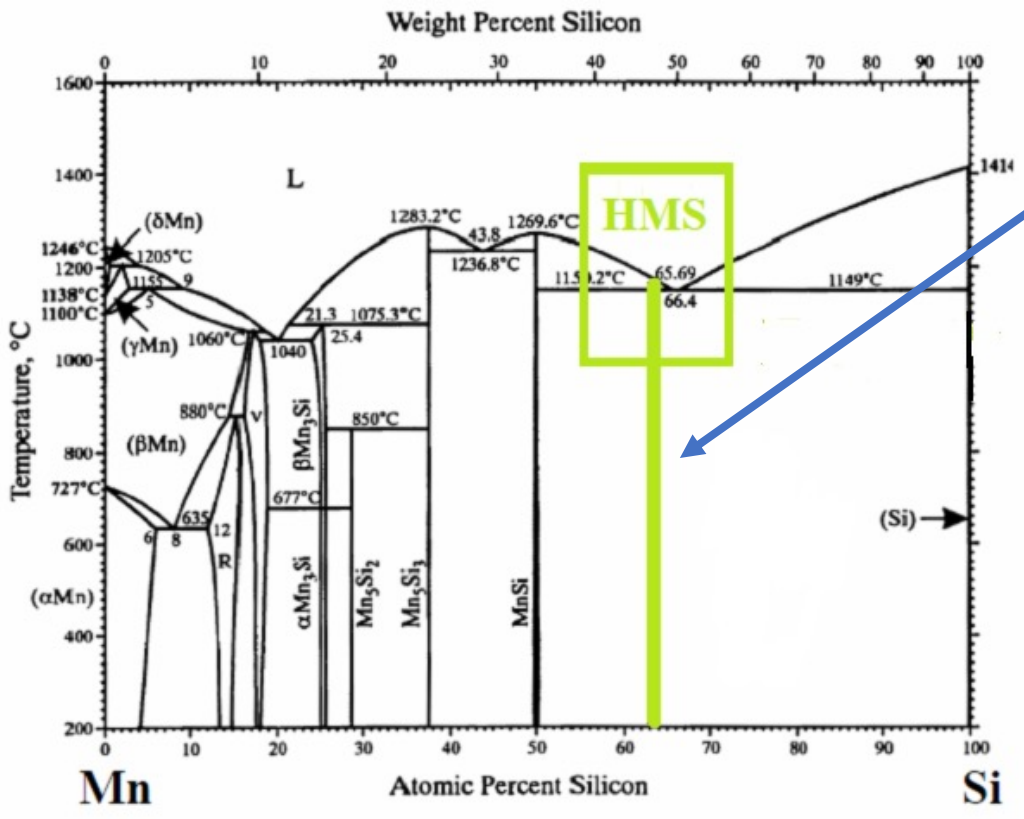
From:

J. P. Heremans et al.,

Energy Environ. Sci., 2012, 5, 5510

Higher-Manganese Silicides

Higher Manganese Silicides



Homogeneity range

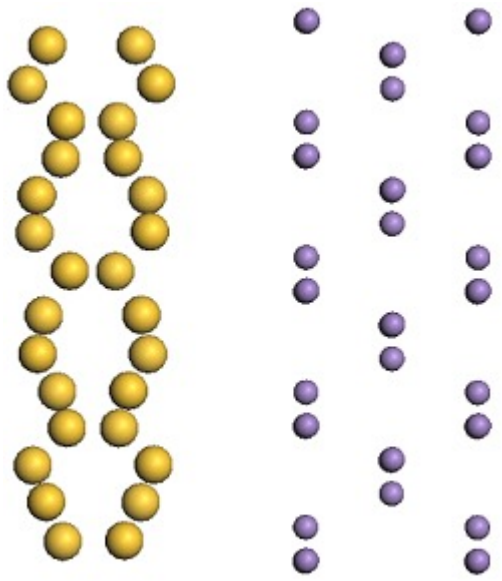
63.2 at.%Si – 63.6 at.%Si

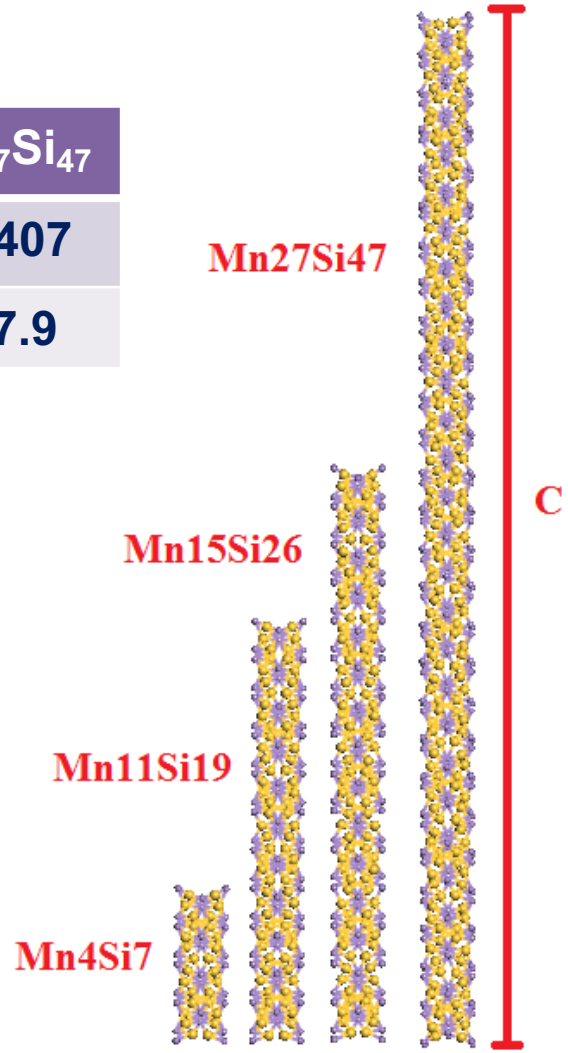
$MnSi_{1.72}$ – $MnSi_{1.75}$

Higher-Manganese Silicides

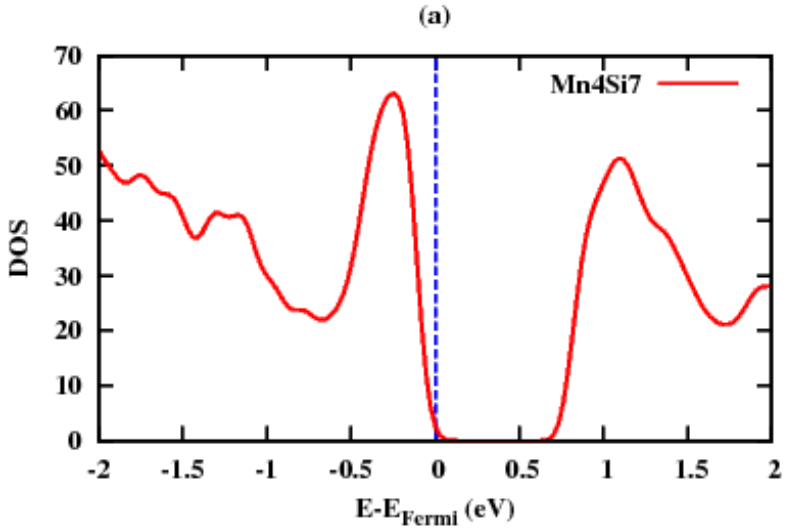
Nowotny Chimney-ladder phases (a ≈ 5.2 Å)

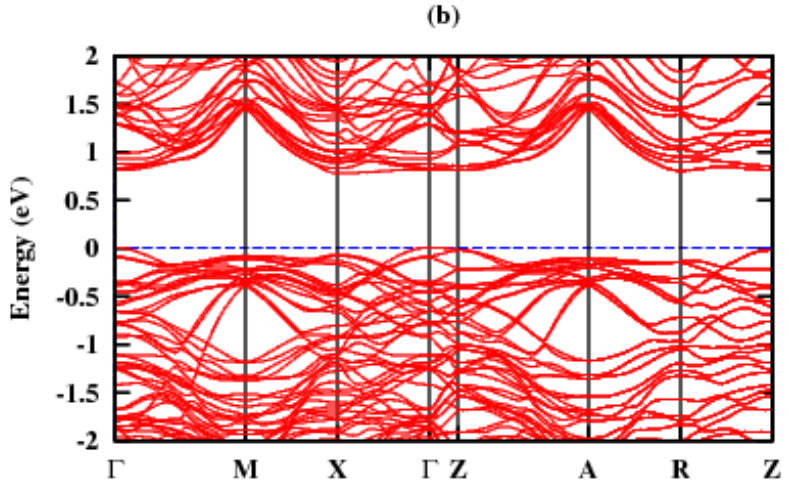
	Mn_4Si_7	$Mn_{11}Si_{19}$	$Mn_{15}Si_{26}$	$Mn_{27}Si_{47}$
X ($MnSi_x$)	1.75	1.727	1.733	1.7407
C (Å)	17.45	48.13	65.55	117.9





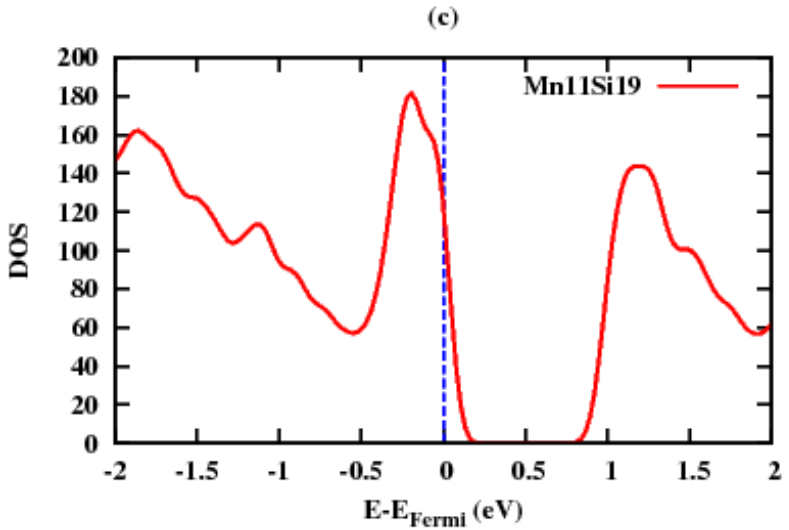
Resonant levels in HMS

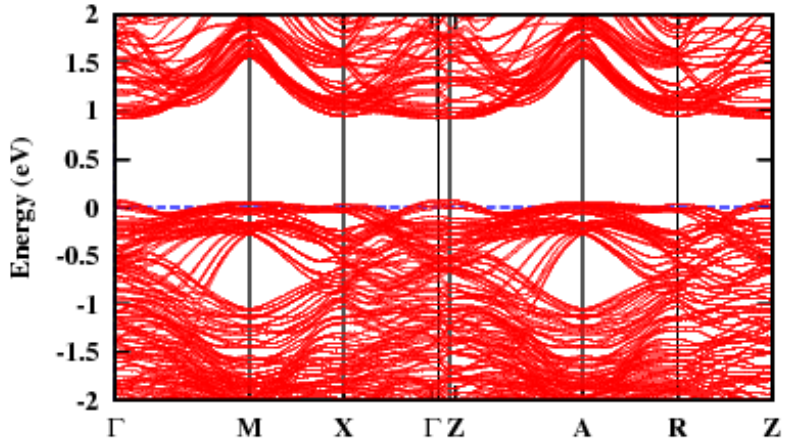




Mn_4Si_7

Semiconductor





$Mn_{11}Si_{19}$

Degenerate p-type SC

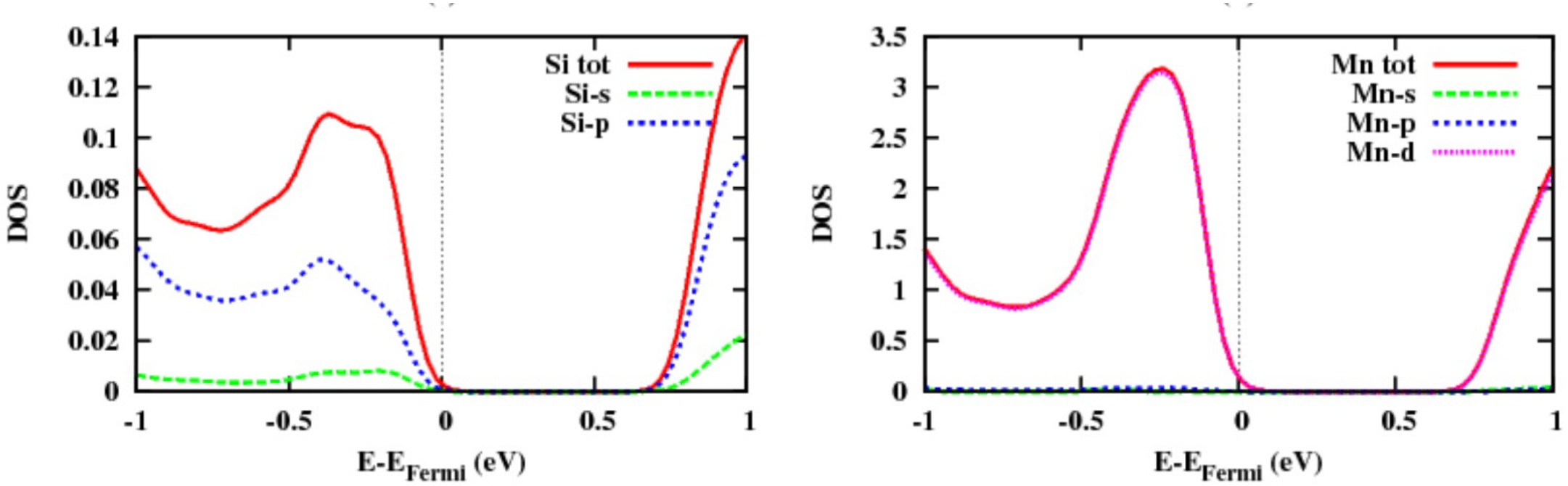
References:

Studies from A. Allam et al.

- J. Electron. Mater., 2014 (43) 761
- J. Alloy Compnd., 2014 (584) 279

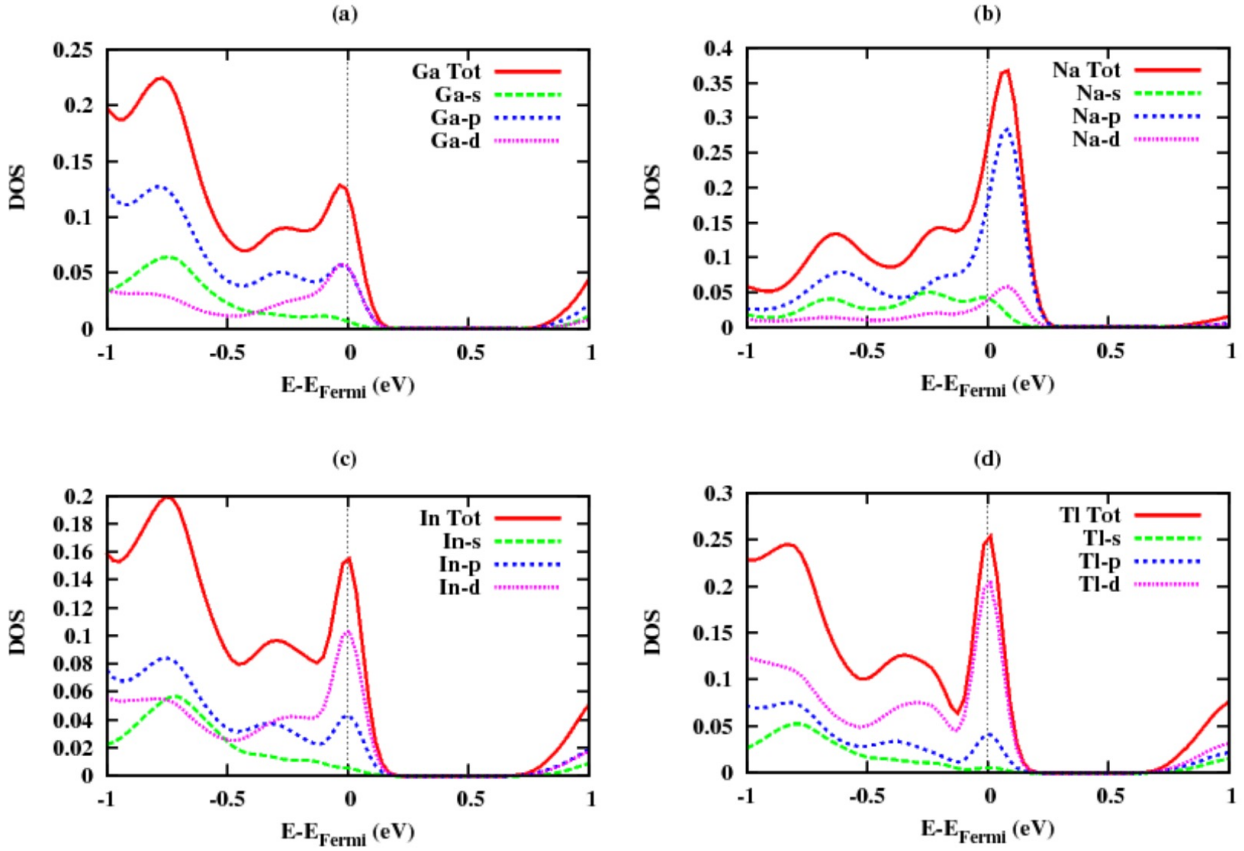
Resonant levels in HMS

Density of states of Mn_4Si_7 HMS



Resonant levels in HMS

Substitutions of 1.1at.% Ga, Na, In and Tl

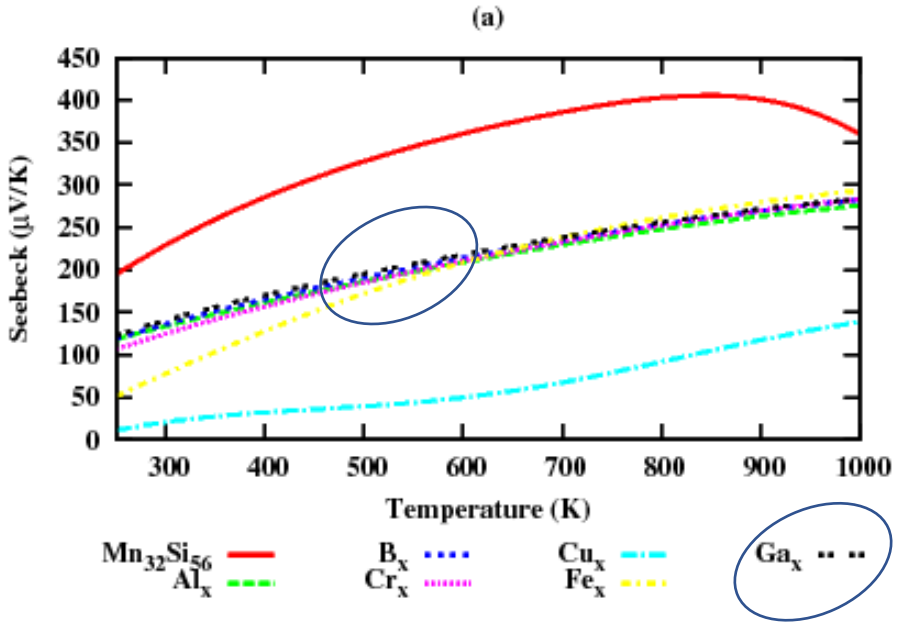


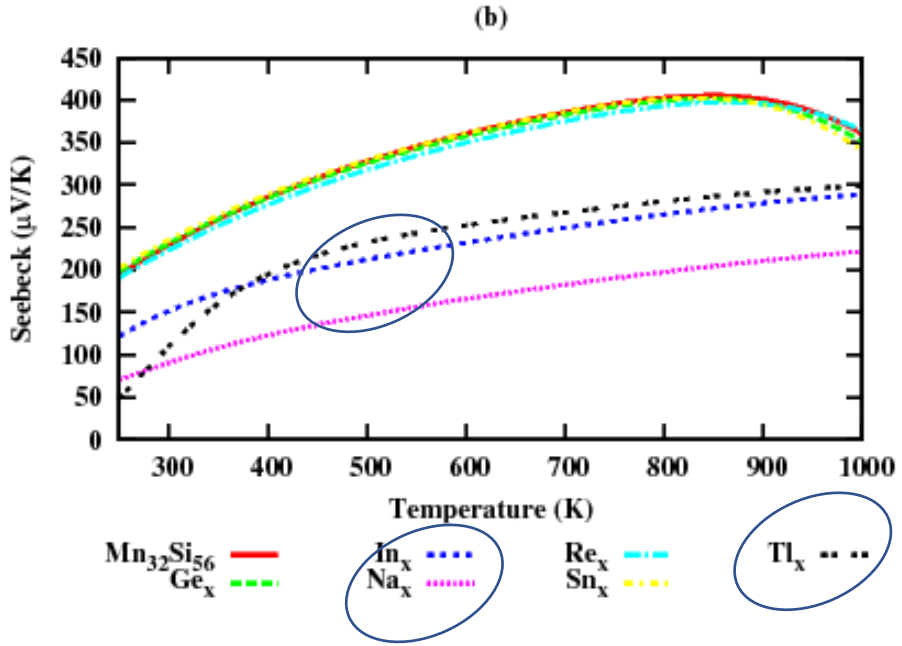
Comments

- Mn_4Si_7 is p-doped
- Large peak appears near E_F
- Peak caused by d-orbitals for In and Tl, mixed p/d-orbitals for Ga and p-orbitals for Na
- In the case of Na, E_F is deep in the valence band

Resonant levels in HMS

- Seebeck coefficient of substituted Mn_4Si_7





Comments

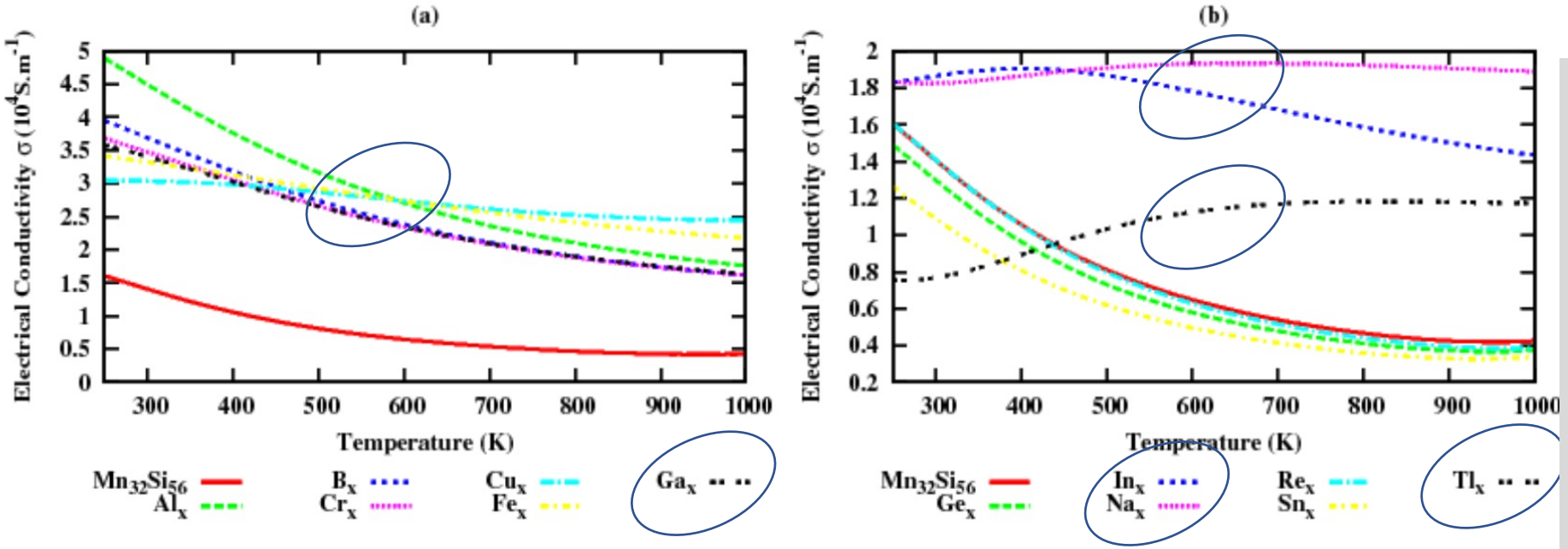
- None of the candidates yield better Seebeck coefficient
- Ge/Sn: isoelectronic with Si
- Re: isoelectronic with Mn
- Cu: yields a metallic state

Why?
- Peak width should be as small as possible
- The background DOS should be as small as possible
- In SC, for complex reasons, the states involved should be s or p

See J. P. Heremans et al., Energy Environ. Sci., 2012, 5, 5510

Resonant levels in HMS

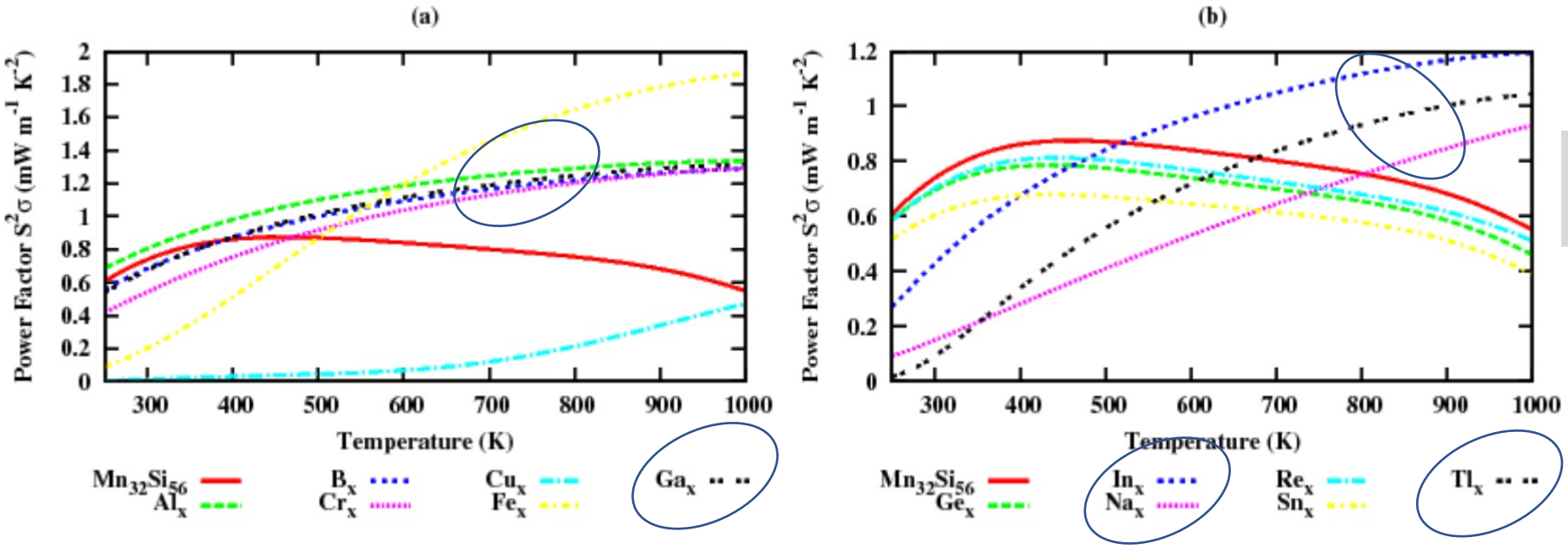
Electrical conductivity of substituted Mn_4Si_7



Comments

- Conduction by holes where the Fermi level is, so high electrical conductivity of Ga-, Na-, In- and Tl-substituted Mn_4Si_7
- Metallic compounds have inherently high electrical conductivity (Cu-, Fe-substituted Mn_4Si_7)

Resonant levels in HMS



Comment

Power factor improved due to high electrical conductivity

Conclusion

- Electronic thermoelectric properties of HMS could be improved by substitutions of impurities
- Not that clear that these impurities induce resonant levels in the compound
- Resonant levels are easy to identify in theoretical toy-models, but not that easy in ``real '' compounds

Conclusions

- The Landauer approach is well suited to understand the physics of the phenomena (Seebeck coefficient, Peltier effect, electrical conductivity and electronic thermal conductivity)
- The Boltzmann approach is well suited to solve problems numerically, in particular when one wants to include magnetic field
- {DFT + BTE} approach is interesting as it yields adequate preliminary results but there are weaknesses such as the lack of the treatment of collisions and of the relaxation time. To go beyond, Monte Carlo is more appropriate
- Transport is quite demanding in terms of the quality of the DFT calculations, especially regarding the thin sampling of the Brillouin zone.