First principles study of heavily doped full Heusler Fe_2YZ for high thermoelectric power factor

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Introduction

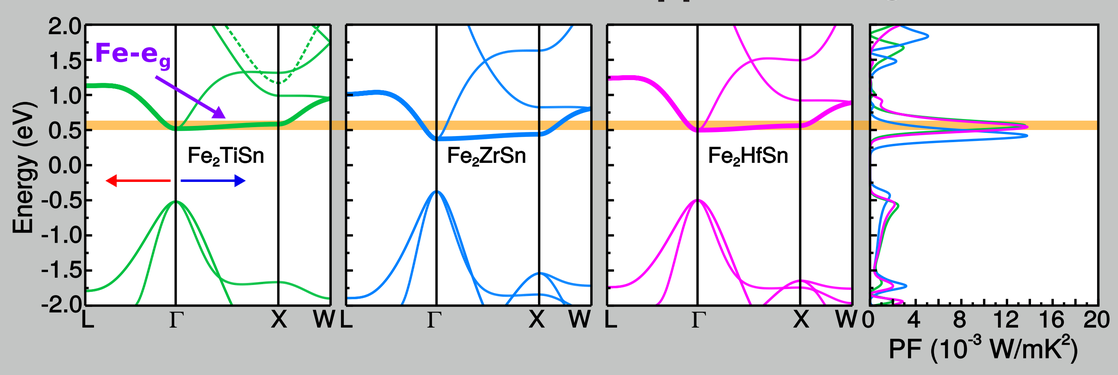
- The performance of thermoelectric materials is characterized by the Figure of Merit ZT, related to the Carnot efficiency:

$$ZT = \frac{S^2\sigma}{\kappa_l + \kappa_e}T \qquad \eta = \eta_{Carnot}\frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}$$

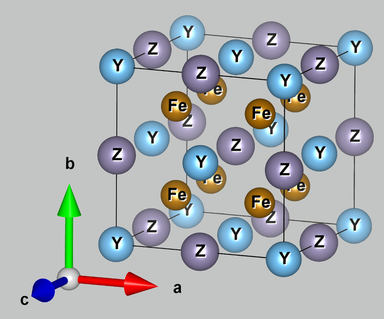
- The Power Factor $S^2\sigma$ is the key quantity to optimize for practical applications, such as heat waste recovery.
- S requires **low** effective mass carriers, σ requires **high** effective mass carriers.

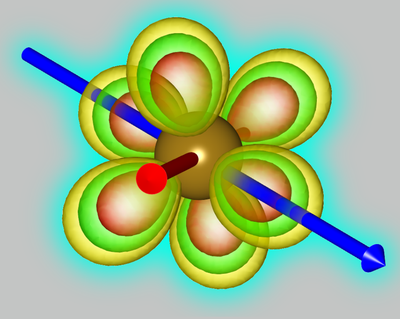
$$m^*_{\alpha\beta} = \left[\frac{1}{\hbar^2}\frac{\partial^2\epsilon(i,\mathbf{k})}{\partial k_\alpha \partial k_\beta}\right]^{-1}$$

- Both characters can be met in a single band from orbitals with highly directional characters → **HIGH** Power Factor !
- Where can we find such a band ? In **Fe_2YZ** semiconductors, bottom of the conduction band ! Extensive work from Ref. [1] → Promising **bulk** TE !



- Fe_2YZ compounds presents $Fe - e_g$ orbitals, main contribution to the bottom of the conduction band with the aformentionned features.

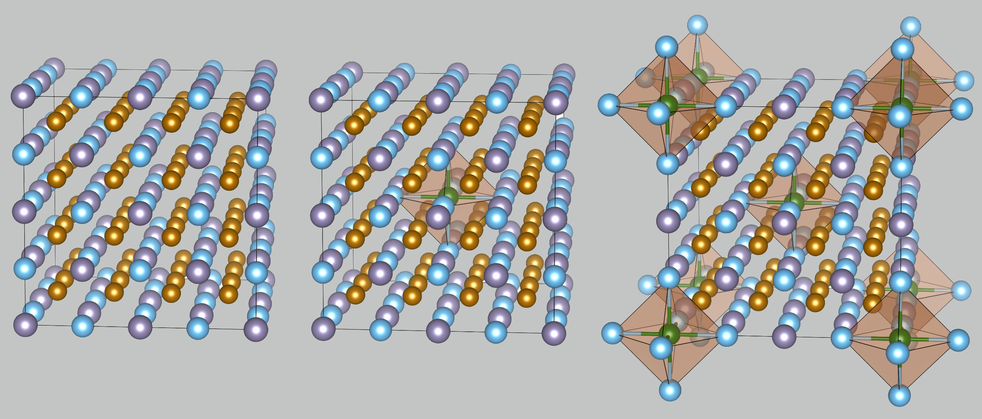




- In the rigid band approx., n-type doping from 0.2×10^{21} cm^{-3} to 1.0×10^{21} cm^{-3} shift the Fermi level to the flat part of the $Fe - e_g$ band, ensuring maximum $S^2\sigma$.

Technical details

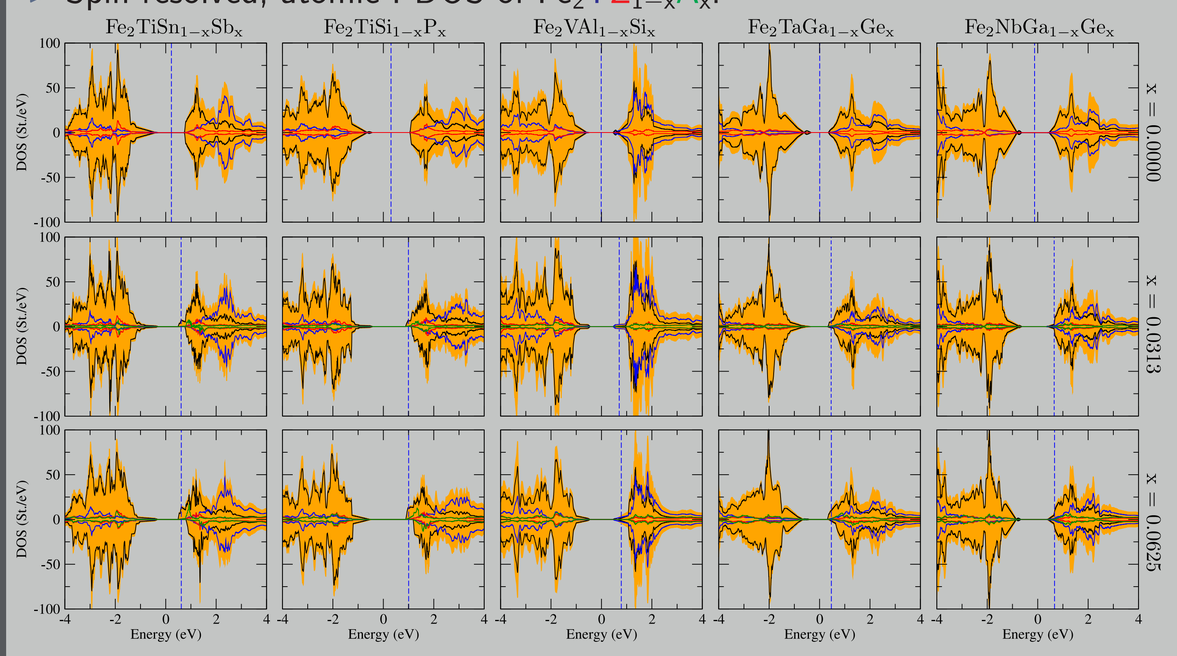
- Doping simulated by the $2 \times 2 \times 2$ cubic supercell method: 128 atoms, 1 or 2 Y atoms replaced by A $\longrightarrow\sim 0.6 \times 10^{21}$ cm^{-3} and $\sim 1.2 \times 10^{21}$ cm^{-3} n-type doping values. The following compounds are studied :
  - $Fe_2TiSn_{1-x}Sb_x$;
  - $Fe_2TiSi_{1-x}P_x$;
  - $Fe_2VAl_{1-x}Si_x$;
  - $Fe_2TaGa_{1-x}Ge_x$;
  - $Fe_2NbGa_{1-x}Ge_x$; each with x = 0.0000; 0.0313; 0.0625.



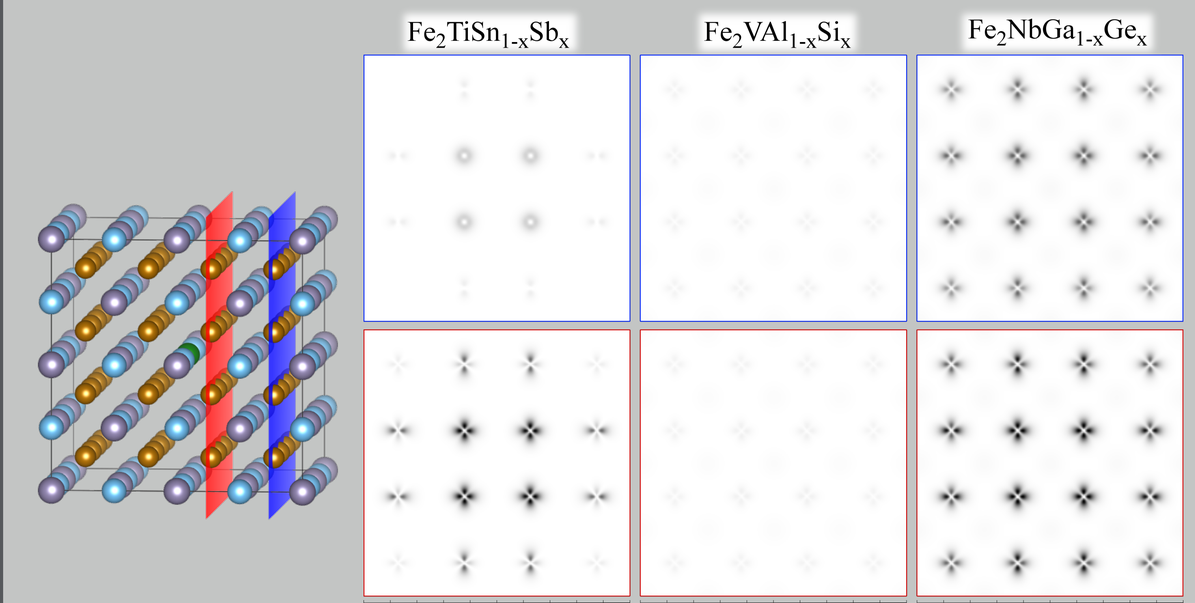
- Crystal14 package for the DFT calculations [2, 3], with **B1 Wu-Cohen** hybrid functional for E_{xc}.
- Thermoelectric properties computed with BoltzTraP [4]
- $9 \times 9 \times 9$ Monkhorst-Pack k-mesh for structural relaxation of conv. cell. (lattice para. + atomic positions).
- $5 \times 5 \times 5$ Monkhorst-Pack k-mesh for structural relaxation of SC (lattice para. + atomic positions).
- $10 \times 10 \times 10$ Monkhorst-Pack k-mesh for electronic properties.
- $32 \times 32 \times 32$ Monkhorst-Pack k-mesh for transport and TE properties.
- Energy convergence criterium fixed at 10^{-9} Ha.
- Relaxation time $\tau = 3.4 \times 10^{-14}$ s, from ref. [1].
- Basis sets, same as Ref. [1].

Electronic properties

- Spin-resolved, atomic PDOS of $Fe_2YZ_{1-x}A_x$:



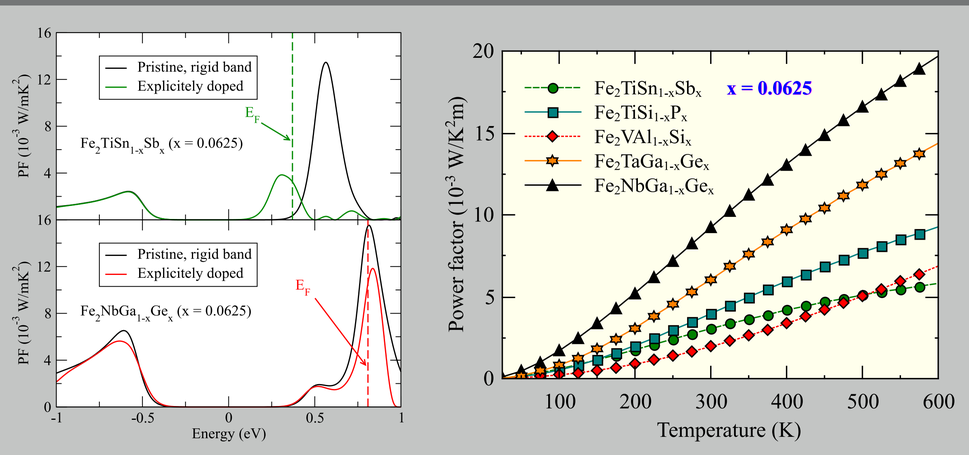
- Depending the matrix, **half-metallic** and **metallic** phases appear, previously associated with disorder [5].
- Electron density of the excess charge (x = 0.0313):



- Results consistent with a **Stoner instability** studied through a Jellium model (fixed geometry + 1 e$^-$ + charged background):$\Delta E_{ex} \times g^{NM}(E_F) > 1$

X_2YZ	ΔE_{ex} [eV]	$g^{NM}(E_F)$ [St./eV]	$\Delta E_{ex} \times g^{NM}(E_F)$
Fe_2TiSn	0.200	35.31	7.1
Fe_2TiSi	0.154	37.84	5.8
Fe_2VAl	0.000	8.07	0.0
Fe_2TaGa	0.097	25.14	2.4
Fe_2NbGa	0.060	13.76	0.8

Thermoelectric properties



Despite spin-splitting a wide array of good **PF** can be achieved.

Conclusions

- n-type doping shifts the Fermi level toward the $Fe - e_g$ band.
- Spin-splitting of the $Fe - e_g$ band occurs in $Fe_2TiSn_{1-x}Sb_x$, $Fe_2TiSi_{1-x}P_x$, and $Fe_2TaGa_{1-x}Ge_x$.
- A **wide array of good power factors** can be achieved at higher temperatures, ranging from 5 to 20 $\times 10^{-3}$ W/K^{2}m.
- n-type doped Fe_2NbGa is the most promising candidate !

References

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