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

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Introduction:

The opportunity to transform heat gradients in charge currents (and *vice versa*) became a largely pioneered field in recent years, as thermoelectricity, with the basic idea to improve the efficiency of standard devices recycling heat dispersions.

In 1996, Mahan and Sofo [1], proposed the ideal shape of the transport distribution function to optimize the figure of merit of a thermoelectric material:

$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_l} = \frac{\mathrm{PF}}{\kappa_e + \kappa_l}$$

S: Seebeck coefficient
σ: electronic conductivity
κ_e: electronic thermal conductivity
κ_l: lattice thermal conductivity

a) the carrier energy distribution as narrow as possible (FLAT BANDS), and
b) high carrier velocities in the direction of the field (HIGHLY DISPERSIVE BANDS).

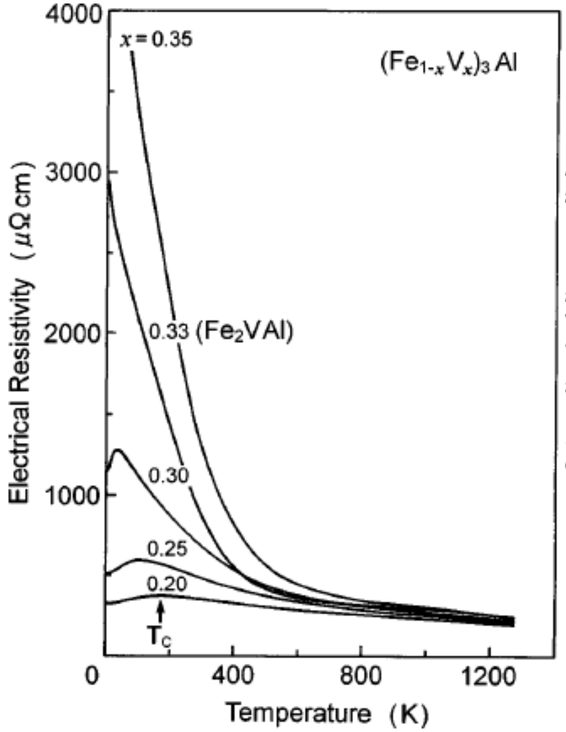
Actually, these conflicting requirements can be achieved in low dimensional transport.

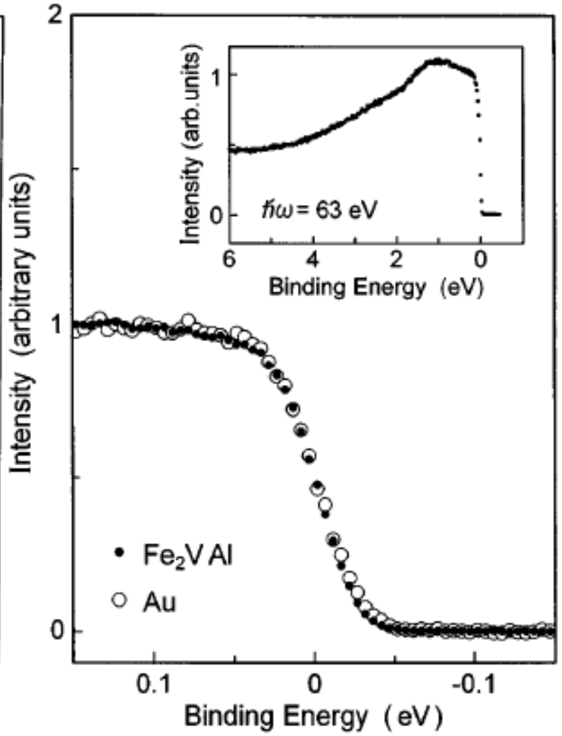
We show that in Fe_2YZ full Heusler bulk compounds we can exploit the highly directional character of certain orbitals to allow for low dimensional transport on bulk.

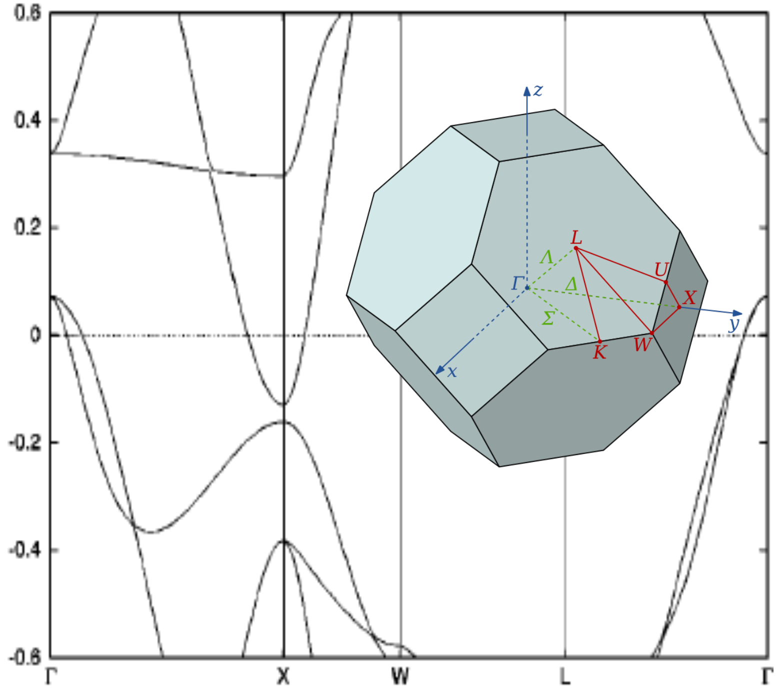
Fe_2VAl : an “electronically” debated compound

PRL **79** 1909 (1997)

PRB **57**, 14352 (1998)







Semiconductor-like

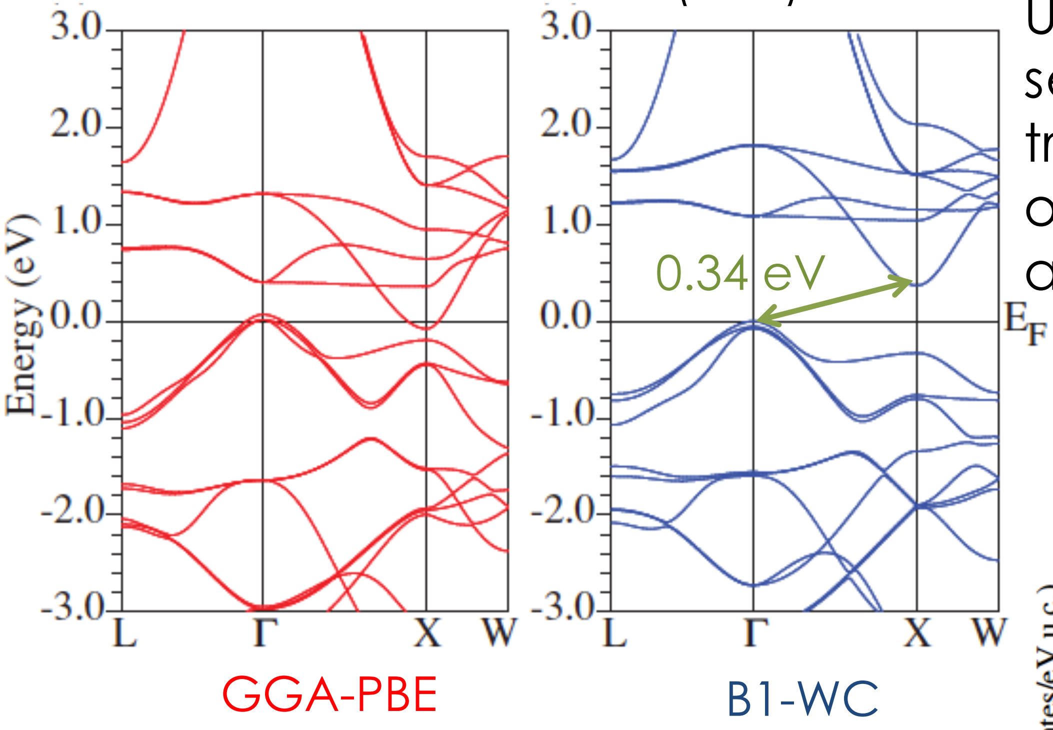
Metal-like

semimetal-like

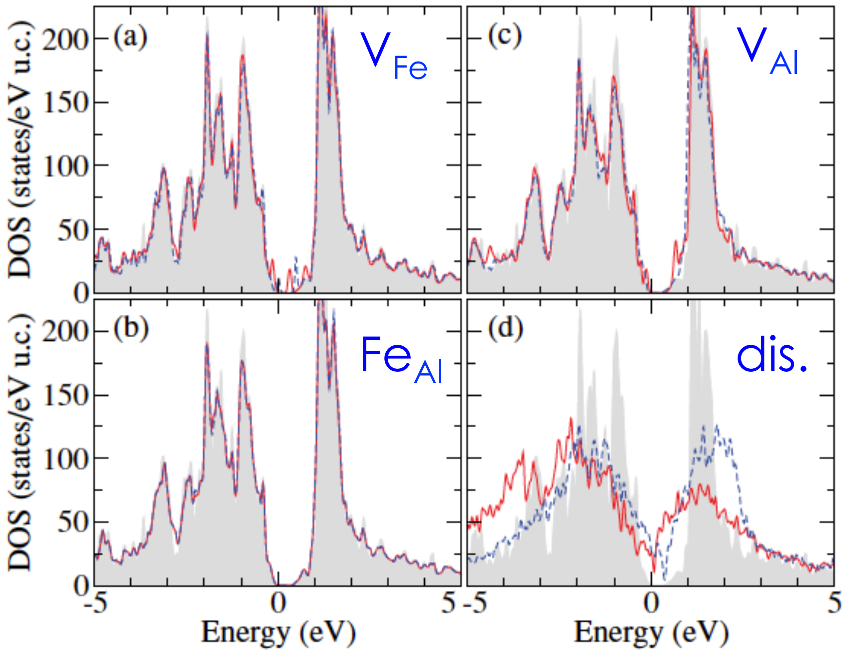
The resistivity decreases with temperature indicating a semiconducting character; on the contrary, the photoemission spectrum indicates a Fermi-edge and a clear absence of a gap. From standard DFT calculations it is shown to be a compensated semimetal with a pseudo gap ≈ 0.1 – 0.2 eV. This last result has been confirmed by later experiments [2,3] and contradicted by other ones [4].

Fe_2VAl : “electronically” reconciled?

PRB **83** 205204 (2011)

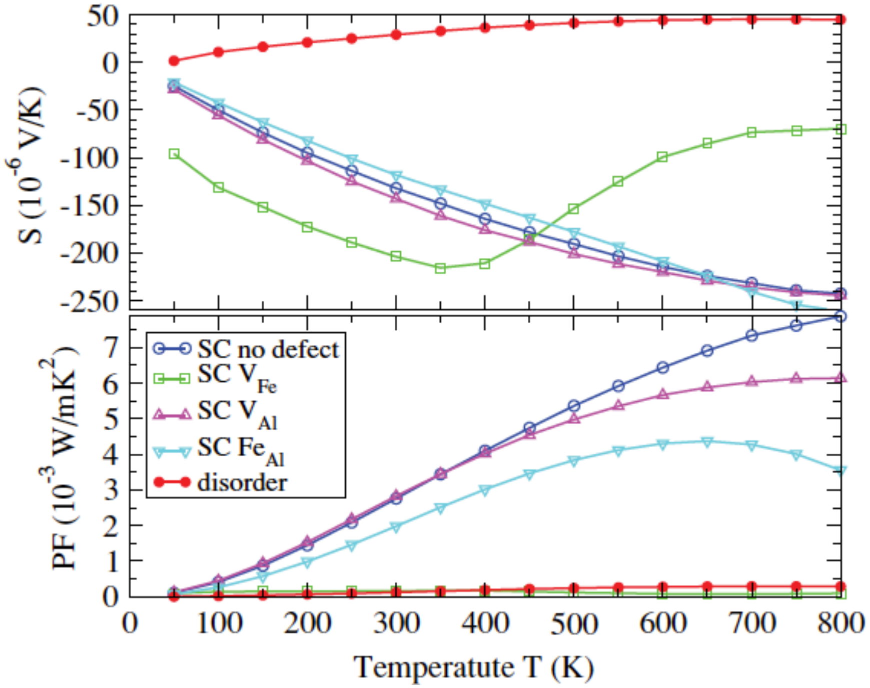


Using Hybrid-Functionals the semiconductor - semi-metallic transition is predicted to depend on antisite defects: V_{Fe}, V_{Al}, Fe_{Al} and for disordered configuration.

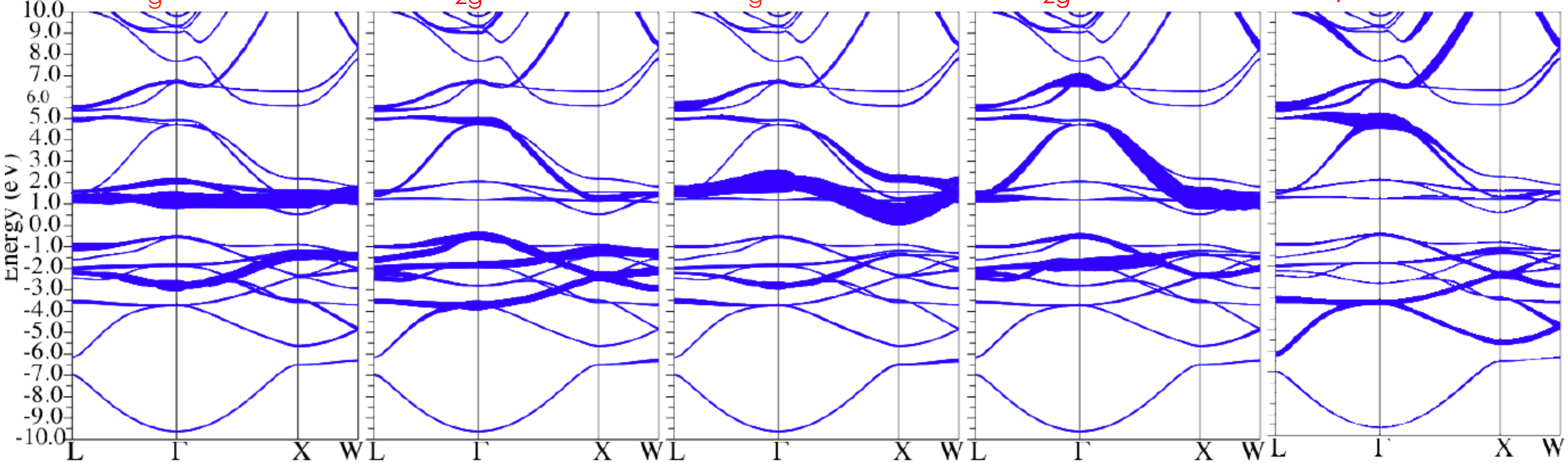


This system results to be very sensitive: its nature can be changed and its transport properties can be tuned with doping.

Fe_2VAl : tuning the Power Factor (PF)



For classical TE (PbTe or Bi_2Te_3) only nanostructures of thin films give PF > 3 [4].
The PF ($S^2\sigma$) at 300 K for Fe_2VAl is known to be between 4 – 6 mW/mK^2 [5]. However, these values are for "modest" thermoelectrics even if for low cost applications [6].
The Fe_2YZ bands sensitivity allows to engineer and enhance the PF of a factor larger than 2 - 3.



Thermodinamic stability:

Fe_2YZ → d^3 | d^2 ; ↓ p^1 | p^2

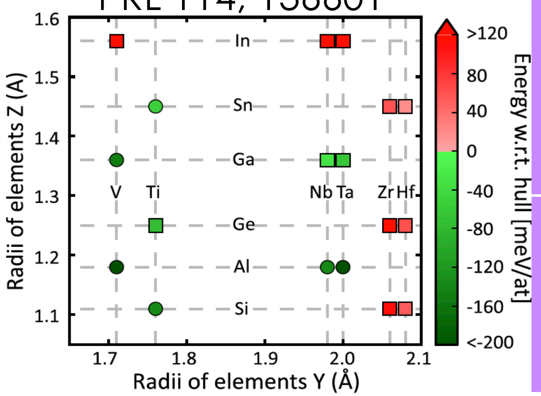
	d^3			d^2		
p^1	Fe_2VAl	Fe_2NbAl	Fe_2TaAl	Fe_2TiAl	Fe_2ZrAl	Fe_2HfAl
	Fe_2VGa	Fe_2NbGa	Fe_2TaGa			
	Fe_2VIn	Fe_2NbIn	Fe_2TaIn			
p^2	Fe_2VSi			Fe_2TiSi	Fe_2ZrSi	Fe_2HfSi
	Fe_2VGe			Fe_2TiGe	Fe_2ZrGe	Fe_2HfGe
	Fe_2VSn			Fe_2TiSn	Fe_2ZrSn	Fe_2HfSn

Slater-Pauling behaviour:

$$M_t = Z_t - 24$$

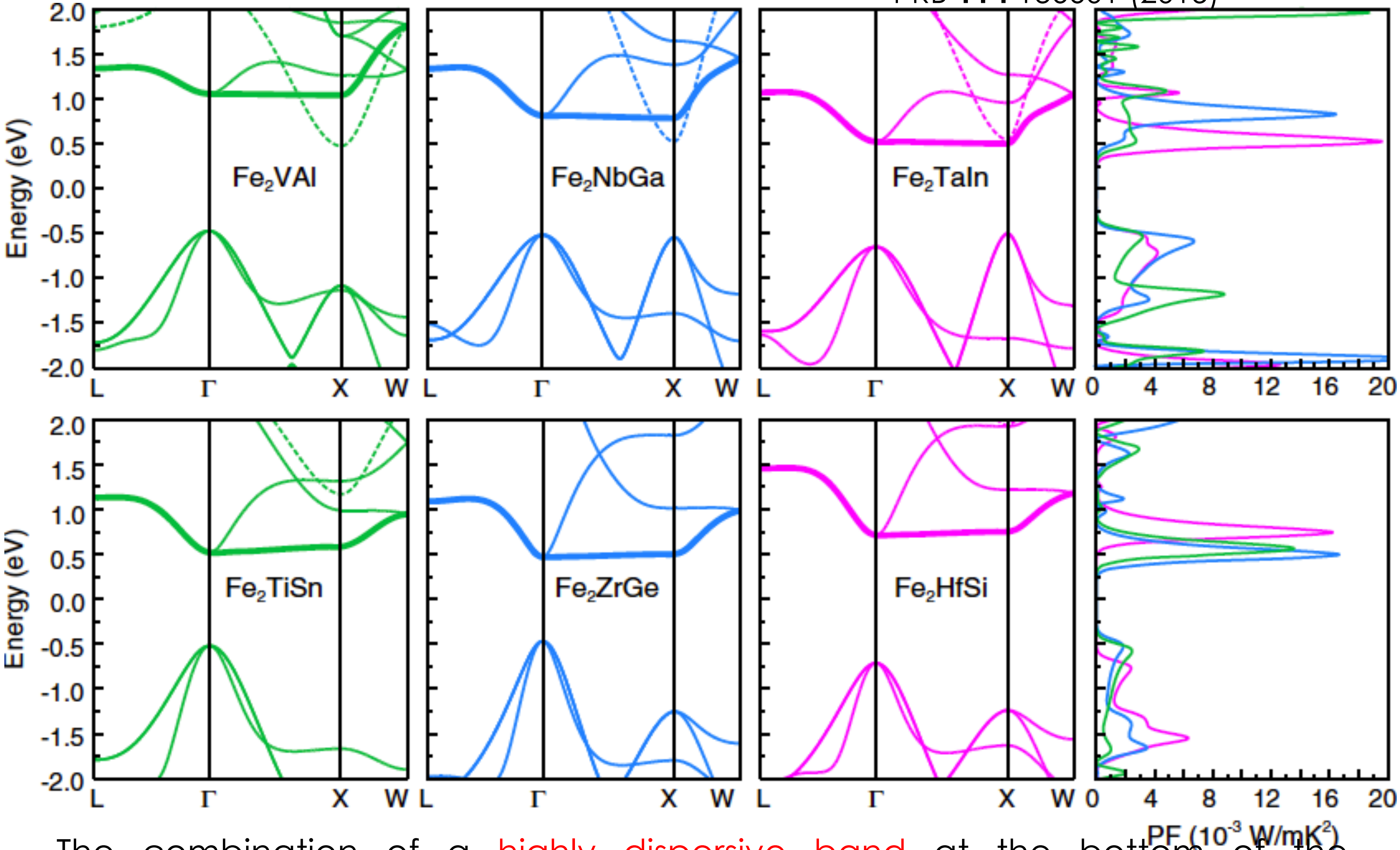
■ energetically unstable
■ energetically stable

PRL 114, 136601



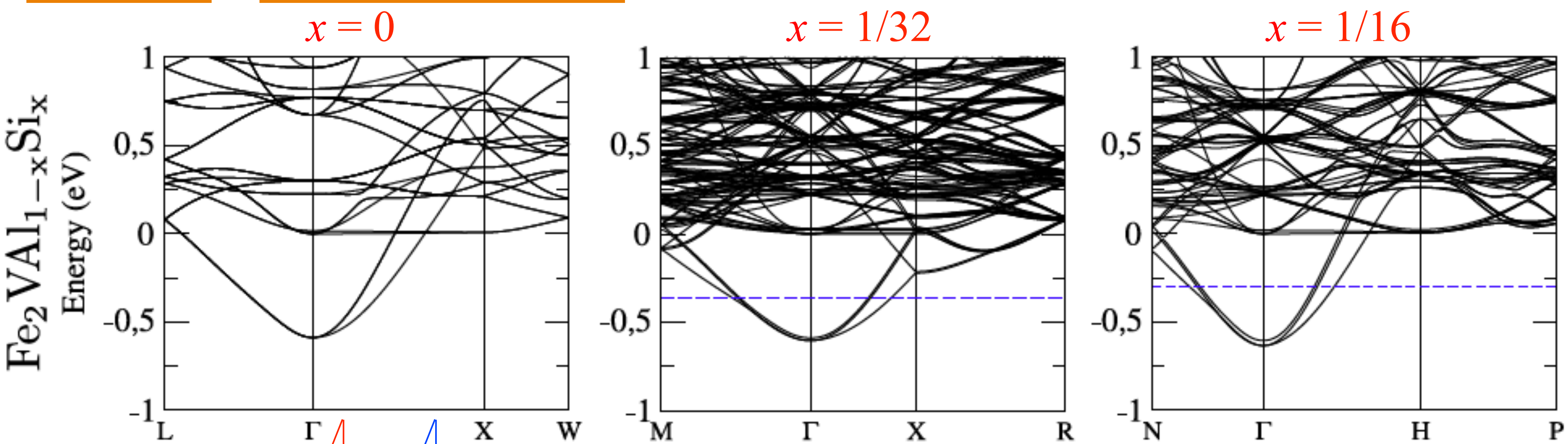
Huge PF in full-Heusler systems:

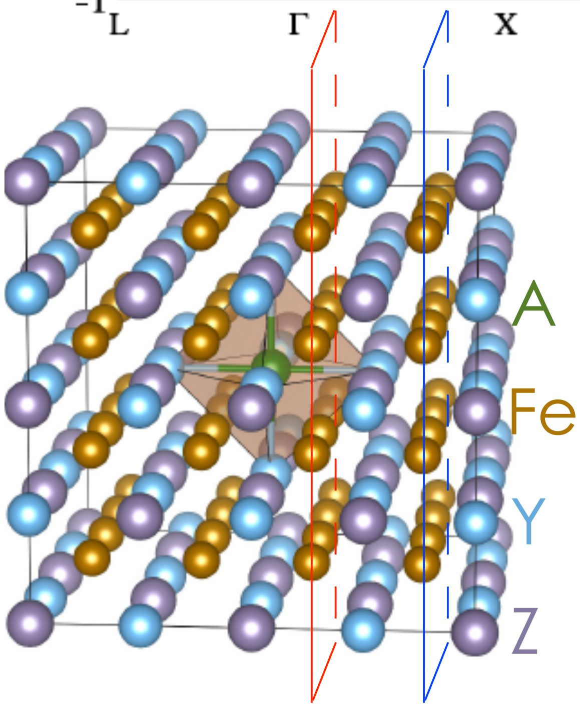
PRB **114** 136601 (2015)



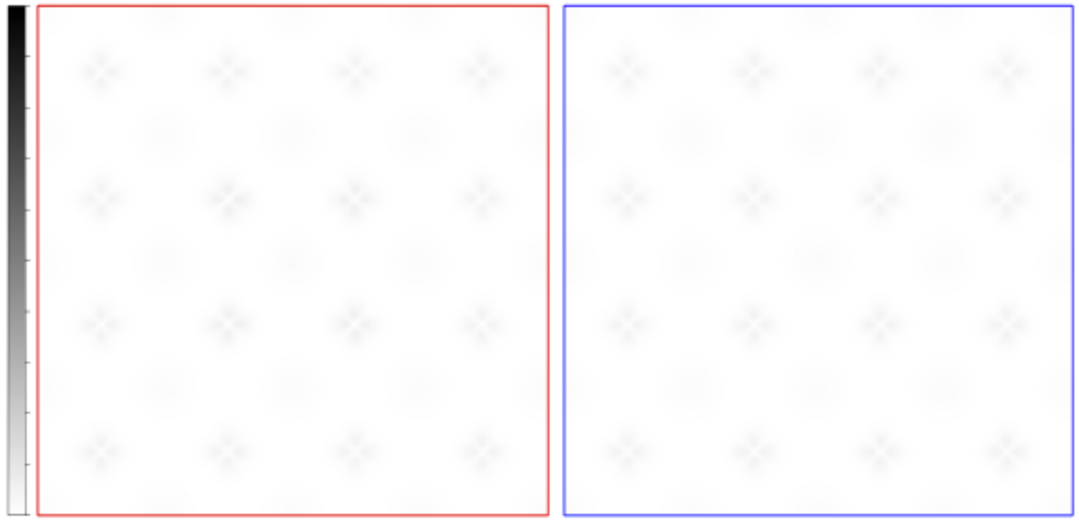
The combination of a highly dispersive band at the bottom of the conduction band (V e_g states) and along ΓL (Fe e_g) and a flat band along ΓX (Fe e_g) guarantees a huge PF.

Heavily *n*-doped alloys: $n \approx 1 \div 3\ 10^{21}$ e/cm^3



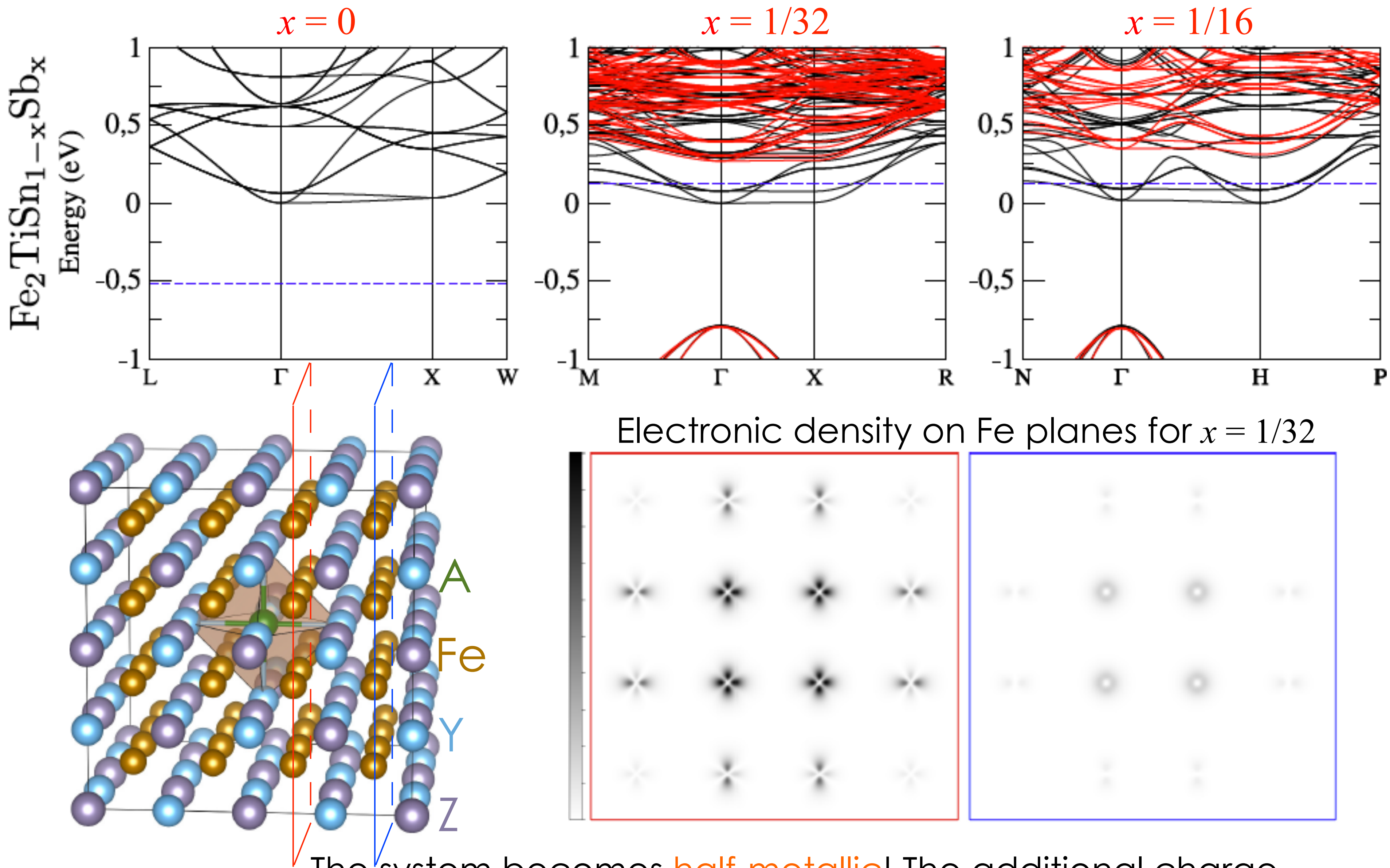


Electronic density on Fe planes for $x = 1/32$



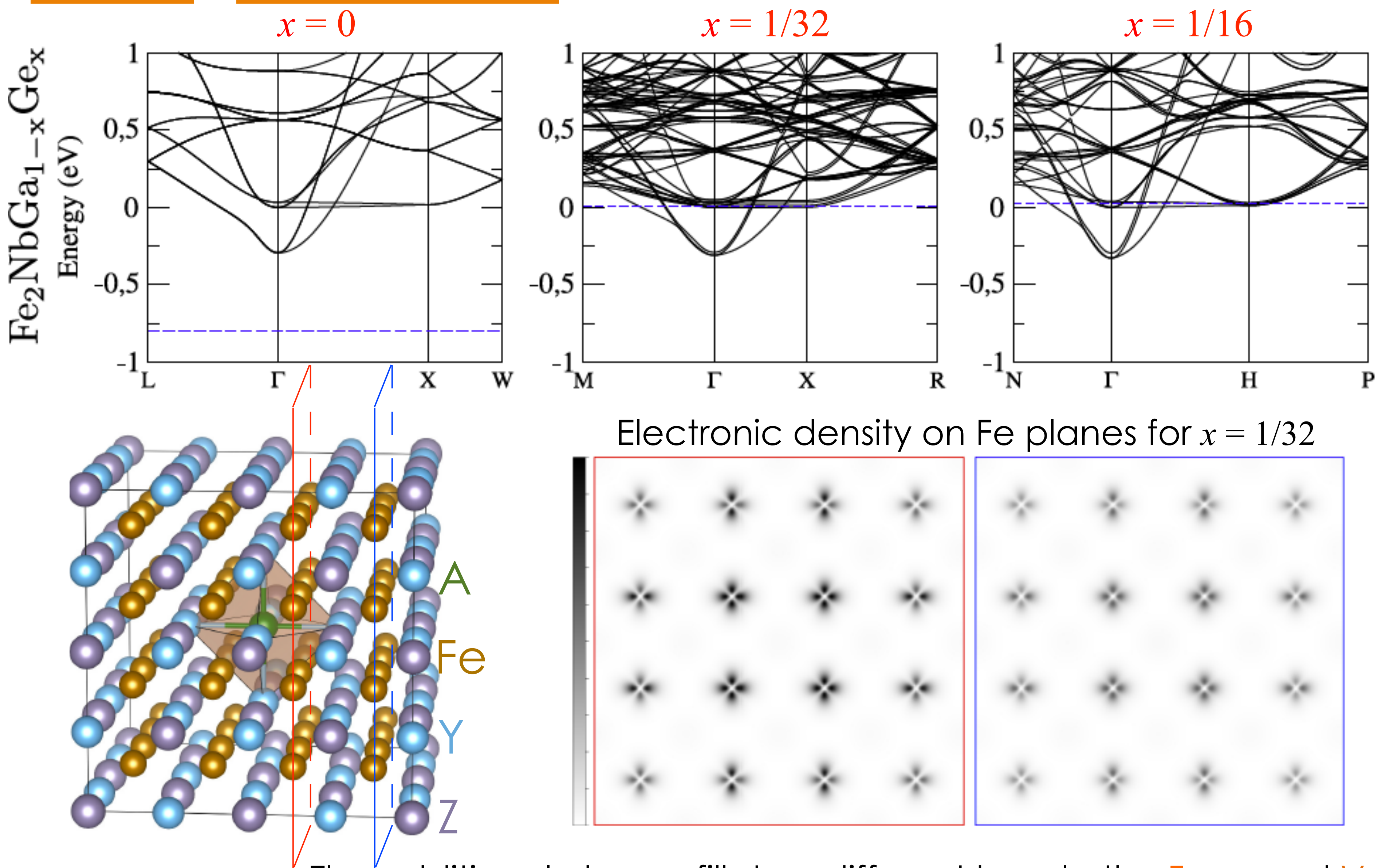
The system becomes metallic. Additional features are due to the band folding effect.

Heavily *n*-doped alloys: $n \approx 1 \div 3\ 10^{21}$ e/cm^3



The system becomes half-metallic! The additional charge induces a local magnetization (Stoner Instability) and a spin-polarization. It is a pure electronic effect that lowers PF.

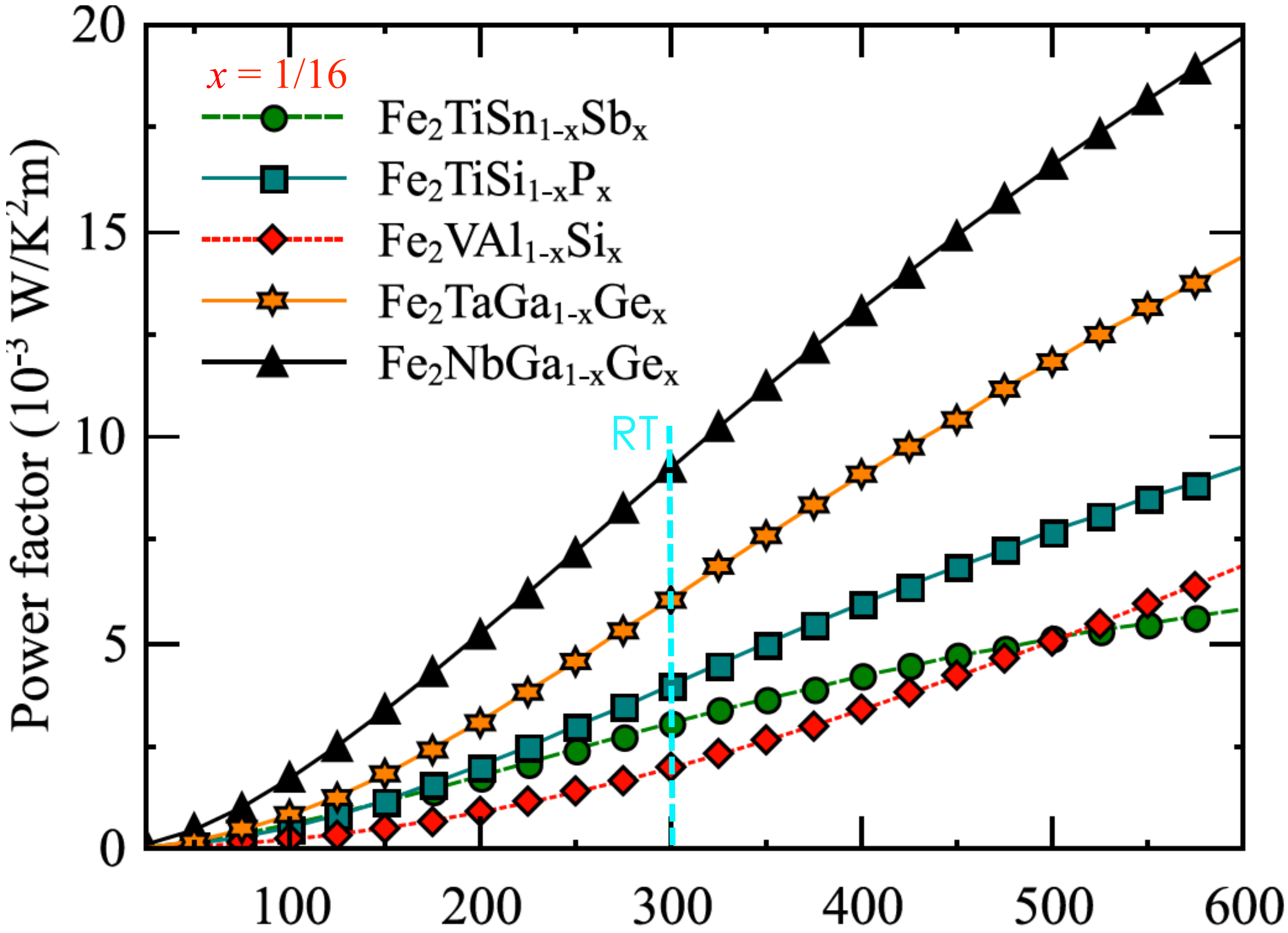
Heavily *n*-doped alloys: $n \approx 1 \div 3\ 10^{21}\ e/cm^3$



The additional charge fills two different bands: the Fe e_g and V e_g moving up to E_F, increasing the number of available states for transport.

Transport properties:

The *n*-doped compounds show an increase of the PF when there is not the magnetic instability. On the contrary, the presence of the Stoner instability inhibits part of carriers for transport reducing PF.



Conclusions:

The *n*-doped Fe_2YZ show a very interesting behavior for high-dopant concentrations. In some cases, $Fe_2TiSn_{1-x}Sb_x$, $Fe_2TaGa_{1-x}Ge_x$, $Fe_2TiSi_{1-x}P_x$, the additional charge localizes on Fe *d*-states and removes the spin degeneracy, causing the appearance of a net magnetization (accordingly to the Stoner model). Even if half-metallicity appears, the PF decreases, caused by a loss of charge carriers at E_F . In $Fe_2VAl_{1-x}Si_x$, the heavy doping brings the system to a metallic (non-magnetic) state due to the V e_g band crossing E_F .
The case of $Fe_2NbGa_{1-x}Ge_x$ shows a large enhancement of PF (up to 19.7 W/K^2). This trend is induced by the additional charge on the Fe e_g states that move at E_F keeping the spin degeneracy intact.

The opportunity to exploit the highly directional character of the charge carriers enhancing the thermoelectric properties of Fe_2YZ alloys, combined with their low-cost and wide availability, make them very attracting for large scale applications.

References:

[1] Proc. Natl. Acad. Sci. U. S. A. **93**, 7436 (1996).
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[3] Phys. Rev. B **58**, 9763 (1998).
[4] Angew. Chem. Int. Ed. **47**, 8618 (2008).
[5] Phys. Rev. B **74**, 115115 (2006).
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Electronic structure details: contributions projected DOS