First principles study of heavily doped full Heusler Fe$_2$YZ for high thermoelectric power factor

S. Lemal$^1$, D. Bilc$^2$, F. Ricci$^1$ & P. Ghosez$^1$

$^1$Physique Théorique des Matériaux, University of Liège, Belgium
$^2$National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

mail-to: fabio.ricci@ulg.ac.be
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:

\[ ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} = \frac{\text{PF}}{\kappa_e + \kappa_l} \]

- \( S \): Seebeck coefficient
- \( \sigma \): electronic conductivity
- \( \kappa_e \): electronic thermal conductivity
- \( \kappa_l \): 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\(_2\)YZ full Heusler bulk compounds we can exploit the highly directional character of certain orbitals to allow for low dimensional transport on bulk.
Fe$_2$VAI: 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 $\approx 0.1 - 0.2$ eV. This last result has been confirmed by later experiments [2,3] and contradicted by other ones [4].
Fe$_2$VAl: "electronically" reconciled?

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.
**Fe₂VAI : tuning the Power Factor (PF)**

For classical TE (PbTe or Bi₂Te₃) only nanostructures of thin films give PF > 3 [4].

The PF ($S^2\sigma$) at 300 K for Fe₂VAI is known to be between 4 – 6 mW/mK² [5]. However, these values are for “modest” thermoelectrics even if for low cost applications [6]. The Fe₂YZ bands sensitivity allows to engineer and enhance the PF of a factor larger than 2 - 3.
Thermodynamic stability:

Fe₂YZ → d³

Fe₂VAI Fe₂NbAl Fe₂TaAl
Fe₂VGa Fe₂NbGa Fe₂TaGa
Fe₂VIn Fe₂NbIn Fe₂TaIn

Fe₂VSi
Fe₂VGe Fe₂VSn

Slater-Pauling behaviour:

\[
M_t = Z_t - 24
\]

energetically unstable
energetically stable

PRL 114, 136601

Radii of elements Z (Å)
Radii of elements Y (Å)
Huge PF in full-Heusler systems:

The combination of a highly dispersive band at the bottom of the conduction band ($V_{e_g}$ states) and along $\Gamma L$ ($Fe_{e_g}$) and a flat band along $\Gamma X$ ($Fe_{e_g}$) guarantees a huge PF.
Heavily n-doped alloys: $n \approx 1 \div 3 \times 10^{21} \text{ e/cm}^3$

$x = 0$

$x = 1/32$

$x = 1/16$

The system becomes metallic. Additional features are due to the band folding effect.
Heavily n-doped alloys: \( n \approx 1 \div 3 \times 10^{21} \text{ e/cm}^3 \)

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: $n \approx 1 \div 3 \, 10^{21} \text{ e/cm}^3$

$x = 0$

$x = 1/32$

$x = 1/16$

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$_2$YZ show a very interesting behavior for high-dopant concentrations. In some cases, Fe$_2$TiSn$_{1-x}$Sb$_x$, Fe$_2$TaGa$_{1-x}$Ge$_x$, Fe$_2$TiSi$_{1-x}$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$_2$VAl$_{1-x}$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$_2$NbGa$_{1-x}$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$_2$YZ alloys, combined with their low-cost and wide availability, make them very attracting for large scale applications.

References:
Electronic structure details: contributions projected DOS

$Fe_2VAI_{1-x}Si_x$

$Fe_2TaGa_{1-x}Ge_x$

$Fe_2TiSn_{1-x}Sb_x$

$Fe_2NbGa_{1-x}Ge_x$

DOS (states/eV)

Energy (eV)