Study of electron transport properties in disordered half-Heusler semiconductors

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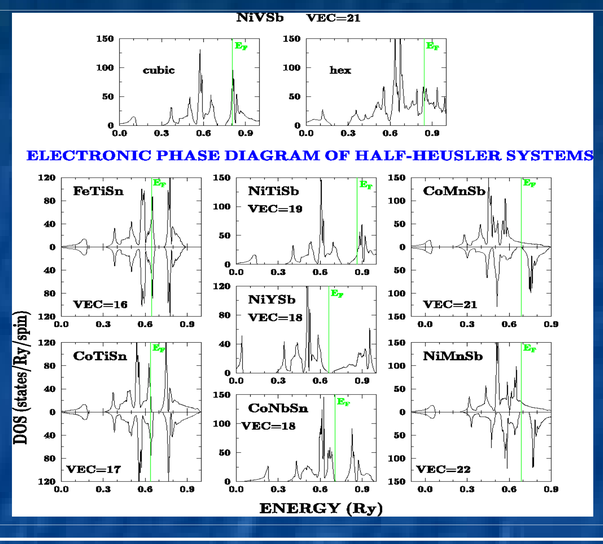
INTRODUCTION

Half-Heusler alloys exhibit a wide variety of physical behaviors in relatively simple crystal structure (MgAgAs-type). They are considered as promising materials for applications in different technological fields (e.g. spintronics, thermoelectricity, shape memory magnetism). It was also revealed that the **18 valence electron** half-Heusler semiconductors exhibit very attracting **thermoelectric properties** characterized by large thermopower and electrical conductivity easily tunable by doping. Accurate investigations of point defects influence on electronic structure and transport properties are essential not only to correctly interpret experimental results, but also to better control doping or substitution, to **optimize the figure of merit ZT**.

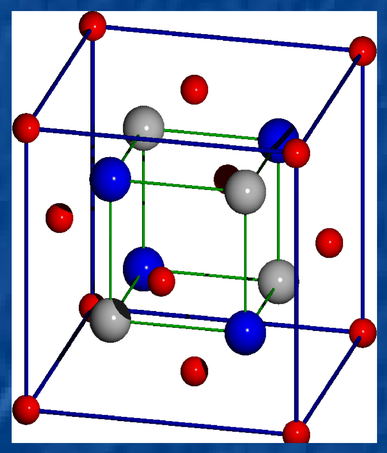


Physical properties of half-Heusler phases are strongly governed by the valence electron number (VEC). This is likely responsible for a wide variety of their behaviours :
- ferro-, antifferromagnets,
- Pauli paramagnets,
- metals, semiconductors,
- half-metallic ferromagnets, etc.

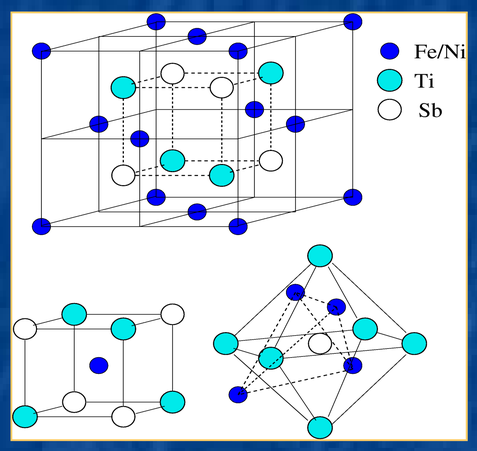
CRYSTAL STRUCTURE of "HALF-HEUSLER"

S.G. *F-43m* (MgAgAs-type), three interpenetrating *fcc* sublattices :
Mg (4a) 0,0,0 Ag (4b) ½, ½, ½ and As (4c) ¼, ¼, ¼
If a vacancy ¾ ¾ ¾ is occupied by the same atom as on (4c) ¼, ¼, ¼, one obtains a "true" Heusler structure (Cu_2MnAl-type),

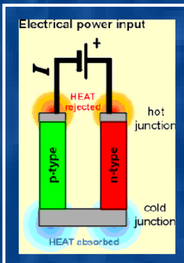
- "half-Heusler" can be seen as a 'filled' rocksalt structure or as a 'filled' zincblende structure



e.g. (Fe-Ni)TiSb



THERMOELECTRIC PROPERTIES



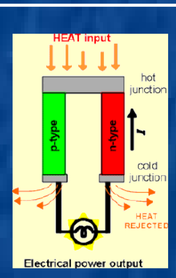
TE figure of merit

$$ZT = \frac{S^2}{\rho\,\kappa}$$

Seebeck coeffcient

Electrical conductivity

Thermal conductivity



TE Cooling

Power generation

Electron transport properties calculations

Using Korringa-Kohn-Rostoker method with Coherent Potential Approximation, the complex energy bands were calculated, allowing to deduce from the real and imaginary parts of E(**k**), the electron group velocity $v_k = \frac{1}{\hbar}\nabla_k\,[\mathrm{Re}\,E(k)]$ and the electron life-time $\tau_k = \frac{h}{\mathrm{Im}\,E(k)}$

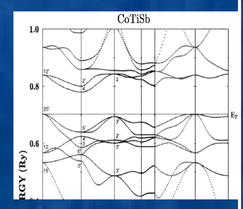
Electrical conductivity

$$\sigma(E) = \frac{2e^2}{3(2\pi)^3\hbar}\int_{\Sigma(E)} \mathrm{d}S_k\, v_k\, \tau_k$$

Thermopower (Seebeck coefficient)

$$\frac{S}{T} = -\frac{\pi^2}{3}\frac{k_B^2}{e}\left.\frac{\partial \ln\sigma(E)}{\partial E}\right|_{E_F}$$

Compound	S (μV/K) experim.	ρ (Ω cm) experim.	Energy gap E_g (eV) theory
FeVSb	-125/-70	2 x 10^{-2}	0.46 (L-X)
CoTiSb	-250	4 x 10^{-2}	0.95 (Γ-X)
CoZrSb	-130	5 x 10^{-2}	1.11 (L-X)
NiScSb	-	-	0.32 (Γ-X)
NiYSb	-	-	0.29 (L-X)
NiTiSn	-240/-142	1 x 10^{-2}	0.42 (Γ-X)
NiZrSn	-210/-175	2 x 10^{-2}	0.55 (Γ-X)
NiHfSn	-400/-124	2 x 10^{-1}	0.51 (Γ-X)
RhZrSb	-	-	1.14 (Γ-X)



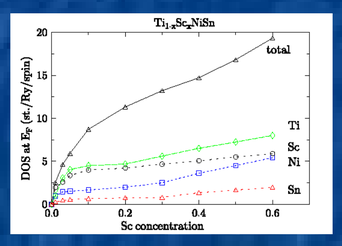
Tobola et al. J.Phys:CM (1998)

*Poon et al., Semicon. Semimetals **70** (2001)*

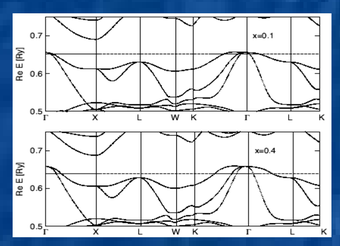
COMPUTATIONAL RESULTS (ILLUSTRATIVE EXAMPLES)

Metal-semiconductor crossover $Ti_{1-x}Sc_xNiSn$

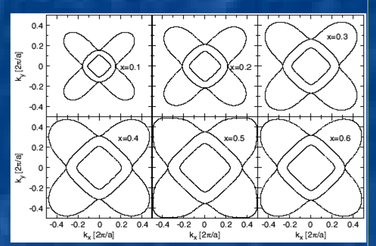
DOS at E_F



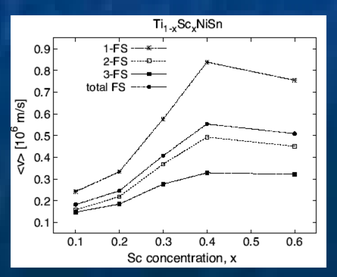
Real part of bands



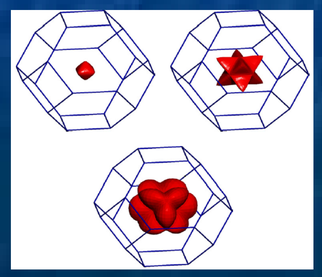
FS cross-sections



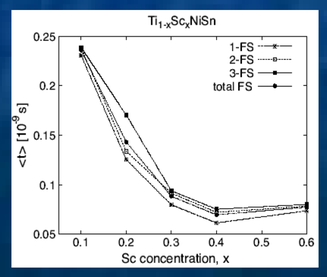
Electron velocities



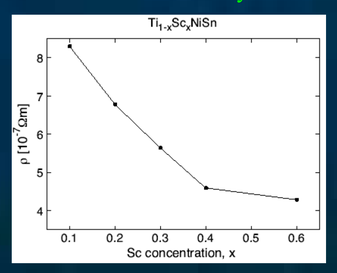
FS sheets



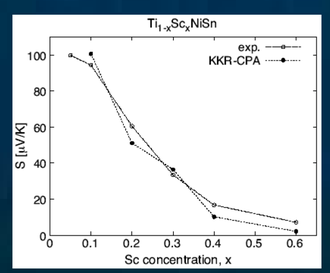
Electron life-times



Residual resistivity



Seebeck coefficient



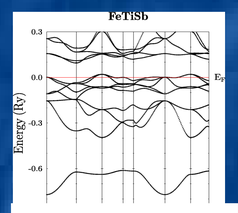
Comparison Theory-Experiment

Composition	$S^{90\,K}_{exp}$	$S^{90\,K}_{calc}$	$S^{300\,K}_{exp}$	$S^{300\,K}_{calc}$
$Ti_{0.9}Sc_{0.1}NiSn$	29.8	30.3	94.4	100.6
$Ti_{0.8}Sc_{0.2}NiSn$	12.6	15.3	60.5	51.1
$Ti_{0.7}Sc_{0.3}NiSn$	4.6	10.0	33.4	36.5
$Ti_{0.6}Sc_{0.4}NiSn$	4.0	3.1	16.7	10.2
$Ti_{0.4}Sc_{0.6}NiSn$	−0.4	0.6	7.1	2.1

Stopa et al., J. Phys. CM: 18 (2006) 63

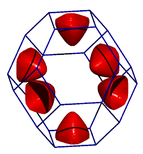
Metal-semiconductor-metal crossover $Fe_{1-x}Ni_xTiSb$

1-hole metal

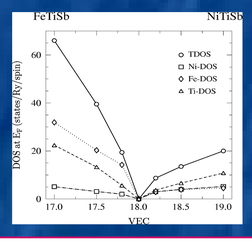


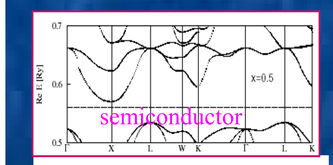
FS hole-like pockets

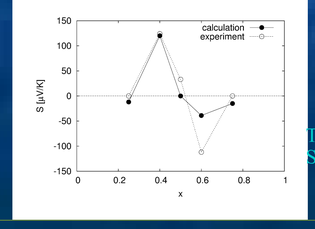
x=0.4



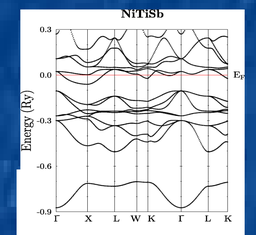
DOS vs. composition





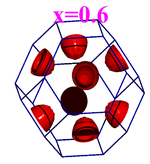


1-electron metal



FS electron-like pockets

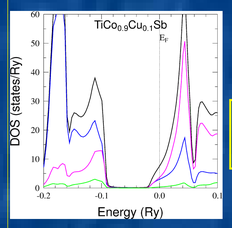
x=0.6



Tobola et al. Phys. Rev. B (2001),
Stopa et al. ETS Conference Proc. (2004)

Metal-semiconductor crossover $TiCo_{1-x}Cu_xSb$

DOS near E_F

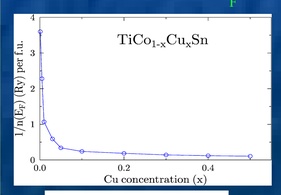


Simplified analysis of thermopower

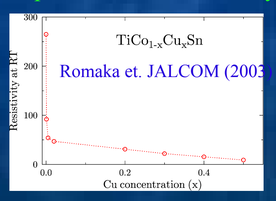
$\sigma(E) \sim N_{tot}(E)\,\mu(E)$

$S/T\ (\mu V/K^2) = 0.2877 \times 10^{-2}\ \mathrm{d}\ \ln N_{tot}(E)/\mathrm{d}E$
$N_{tot}(E)$ (in states/Ry) at $E=E_F$

Inverted DOS at E_F

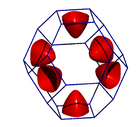


Experimental RT resistivity

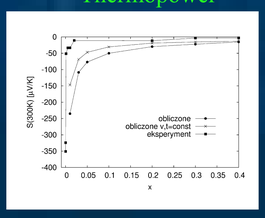


FS hole-like pockets

x = 0.1



Thermopower



Acknowlegements

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CONCLUSIONS A satisfying agreement with measured thermopower was found when calculating electron transport properties (electron velocities and life-times) directly from complex energy bands KKR-CPA computations. This result also shows that chemical disorder play a predominant role in electron scattering in the investigated half-Heusler systems. This gives us the confidence to use this methodology to study TE properties of more complex alloys (skutterudites, Zintl, Chevrel phases in progress). But phonons should also be accounted for to estimate ZT.

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