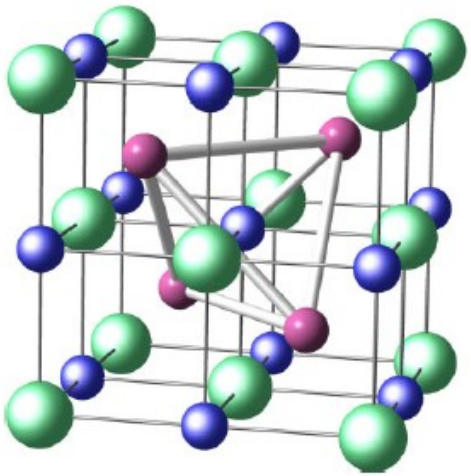
# Stopy Heuslera

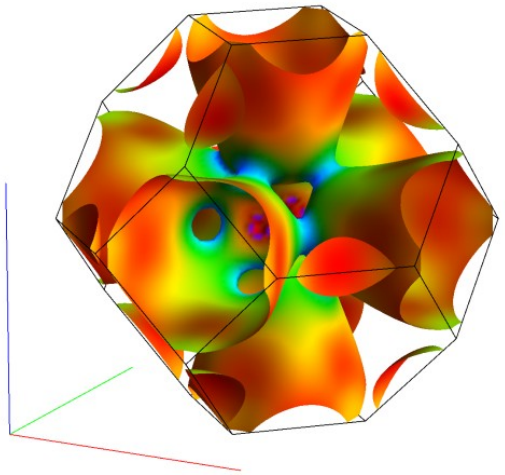
## laboratorium własności fizycznych “na życzenie”

Janusz TOBOLA

*Katedra Fizyki Materii Skondensowanej*
*WFIS AGH*

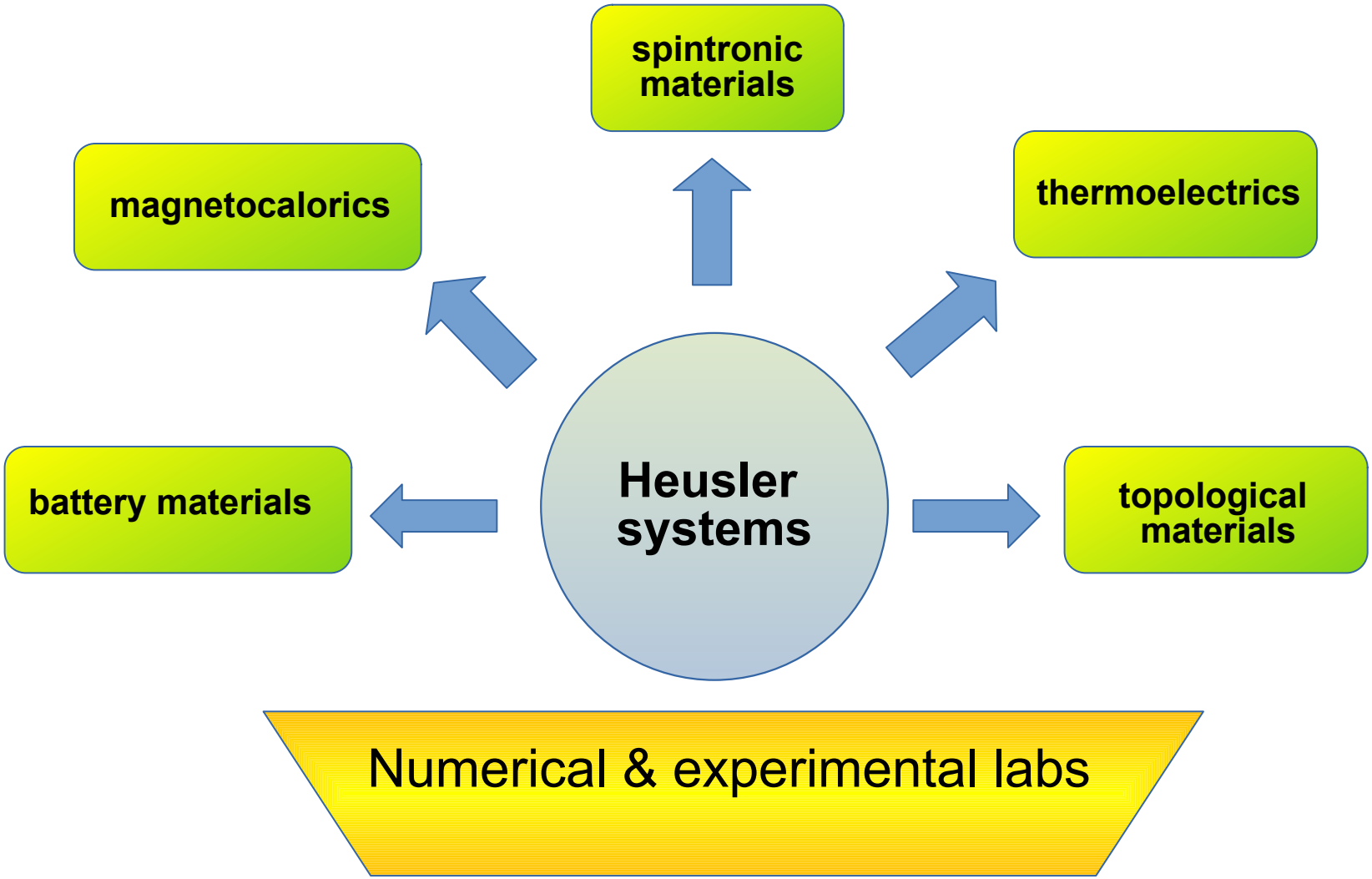


$$G = G_0 + G_0 V G$$



Seminarium WFIS, 21 maja 2021, Kraków

# PLAN


spintronic materials
magnetocalorics
thermoelectrics
Heusler systems
battery materials
topological materials
Numerical & experimental labs

# Discovery of Heusler phases

**1903 – Friedrich Heusler** (mining engineer and chemist) accidentally discovers $Cu_2MnAl$ as a new ferromagnetic compound from "non-ferromagnetic" elements, when mixing Mn with Zn,Cu, As, Sb, Bi and B, but good ferromagnetic properties was obtained when adding Al.


**Verhandlungen**

der

**Deutschen Physikalischen Gesellschaft**

Im Auftrage der Gesellschaft herausgegeben

von

**Karl Scheel**

5. Jahrg. 30. Juni 1903. Nr. 12.


**Sitzung vom 12. Juni 1903.**

Vorsitzender: Herr M. PLANCK.

Vor Eintritt in die Tagesordnung verliest Hr. **H. Starke** auf Wunsch des Hrn. **Fr. Heusler** eine von diesem durch Vermittelung des Hrn. **F. Richarz** am 18. Juni 1901 bei der Gesellschaft niedergelegte Notiz:

Über magnetische Manganlegierungen

und macht weiter Mitteilung über zwei im Zusammenhang hiermit stehende Arbeiten von Hrn. **Fr. Heusler, W. Starck** und **E. Haupt**:

Magnetisch-chemische Studien:

I. Über die Synthese ferromagnetischer Manganlegierungen; von Hrn. FR. HEUSLER

und

II. Über die magnetischen Eigenschaften von eisenfreien Manganlegierungen; von Hrn. W. STARCK und E. HAUPT.

Alle drei Mitteilungen gelangen weiter unten zum Abdruck.

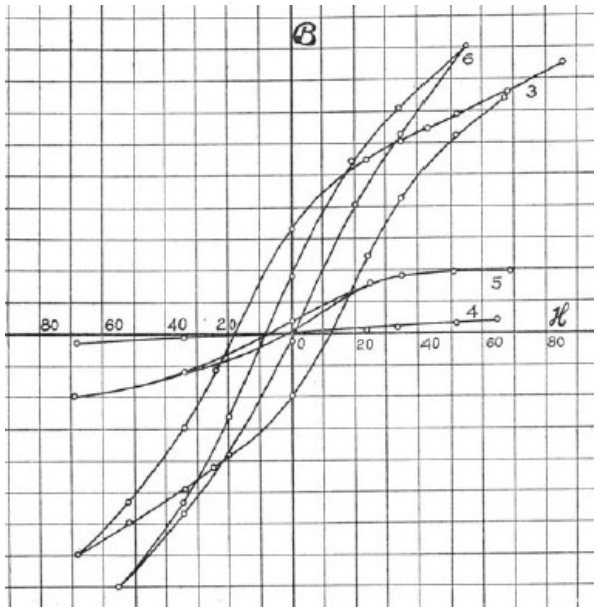

UNIVERSITY OF ILLINOIS

ENGINEERING EXPERIMENT STATION

BULLETIN NO. 47 DECEMBER 1910


MAGNETIC PROPERTIES OF HEUSLER ALLOYS


BY EDWARD B. STEPHENSON, FORMERLY ASSISTANT IN PHYSICS


$T_C$ = **630 K** (high)

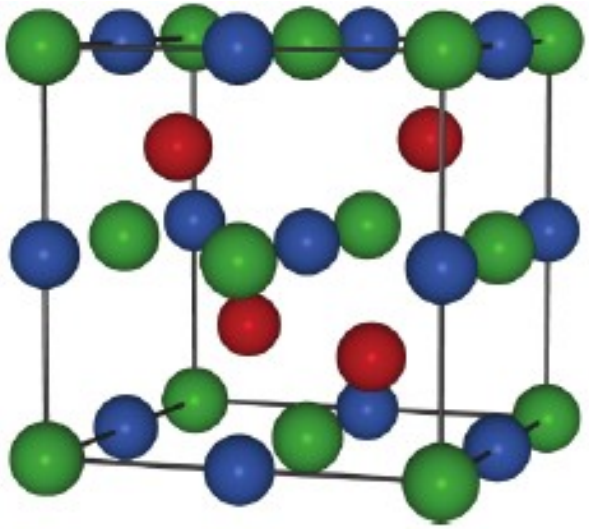
$M = 3.7\ \mu_B$

attributed to Mn atoms

RT sat. magnetization strongly depends on heat treatment
6.1 kGs for Ni < 8kGs < 23 kGs for Fe

# Crystal structure of Heusler phases

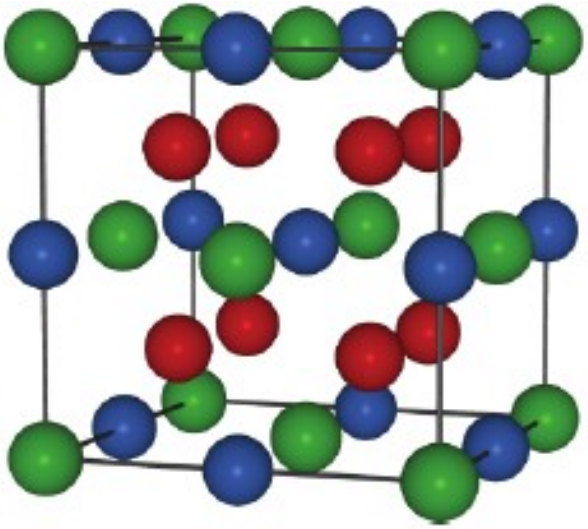
**1934 –** A.J. Bradley & J.W. Rogers and independently O. Heusler (son of FH) describe **$Cu_2MnAl$** as fully ordered crystal structure of $L2_1$ type



No. 216, F-43m, $C1_b$

**XYZ**

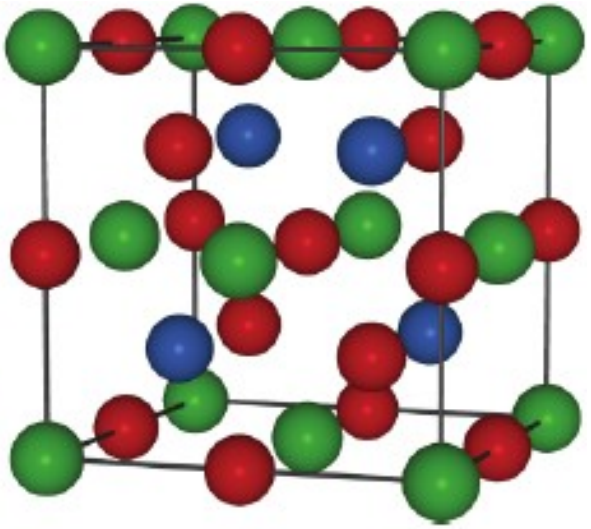
Half-Heusler structure
LiMgAs(Nowotny) & CuMgAs(Juza)



No. 225, Fm3m, $L2_1$

**$X_2YZ$**

Full-Heusler structure



No. 225, $X_A$

**XYXZ or XYUZ**

Inverse Heusler structure

L Wollmann, A K Nayak, S. S. P. Parkin, C Felser, Heusler 4.0: Tunable Materials (2017)

Heusler O. 1934. Kristallstruktur und Ferromagnetismus der Mangan-Aluminium- Kupferlegierungen. Adv. Phys. 411, 155- 201

Bradley AJ, Rodgers JW. 1934. The crystal structure of the Heusler alloys. Proc. Roy. Soc. (London) A 144, 340- 359

# Heusler phases $X_2YZ$, $XYZ$

**structure $DO_3$**

***Fm3m*** (type $Fe_3Al$)

*X :* (0,0,0), (1/2,1/2,1/2)

*X :* (3/4,3/4,3/4)

*Z:* (1/4,1/4,1/4)

**Normal Heusler $L2_1$**

***Fm3m*** (type $Cu_2MnAl$)

*X :* (0,0,0), (1/2,1/2,1/2)

*Y :* (3/4,3/4,3/4)

*Z:* (1/4,1/4,1/4)

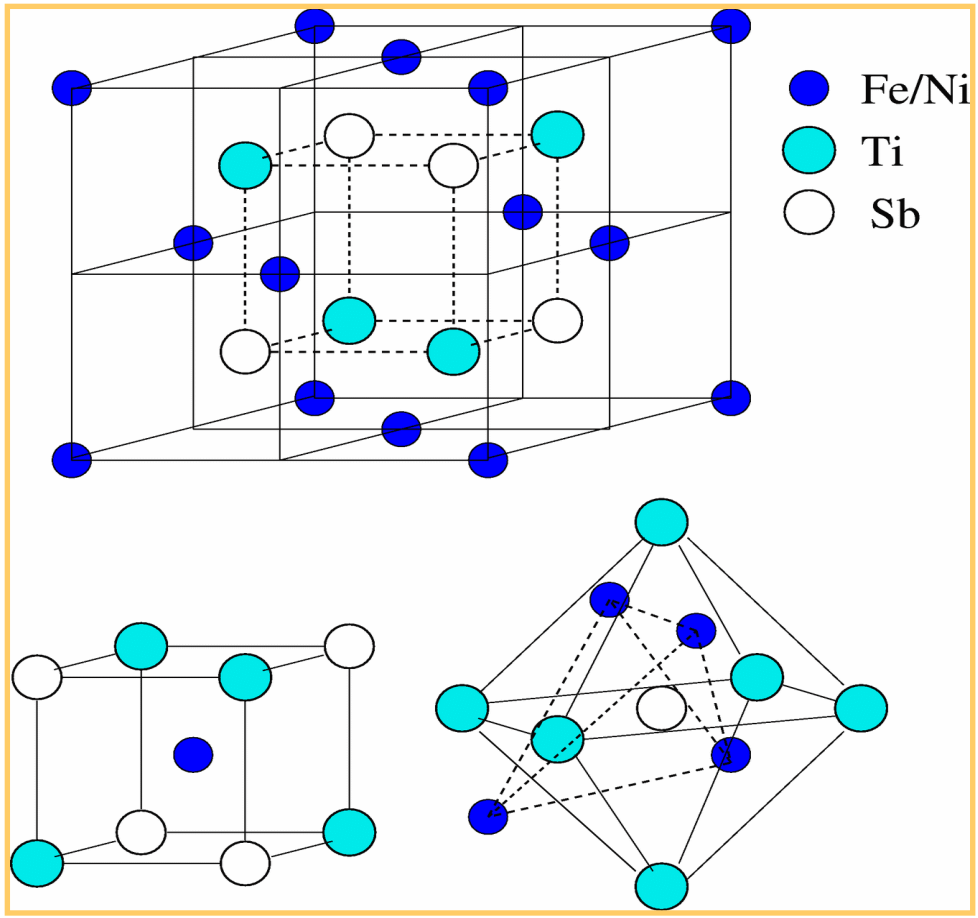
**Half-Heusler $C1_b$**

***F-43m*** (type AgMgAs)

*X :* (0,0,0) 4a

*Y :* (3/4,3/4,3/4) 4d

*Z:* (1/4,1/4,1/4) 4c



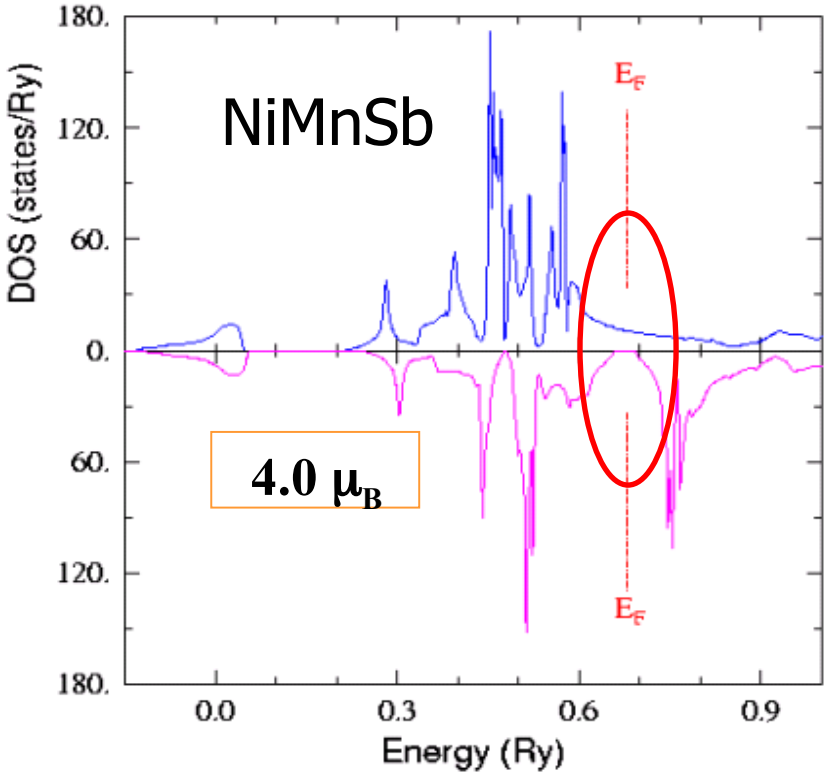

**Crystal stability**

**orbitals *sp³*, *d***

# Half-Heusler phases

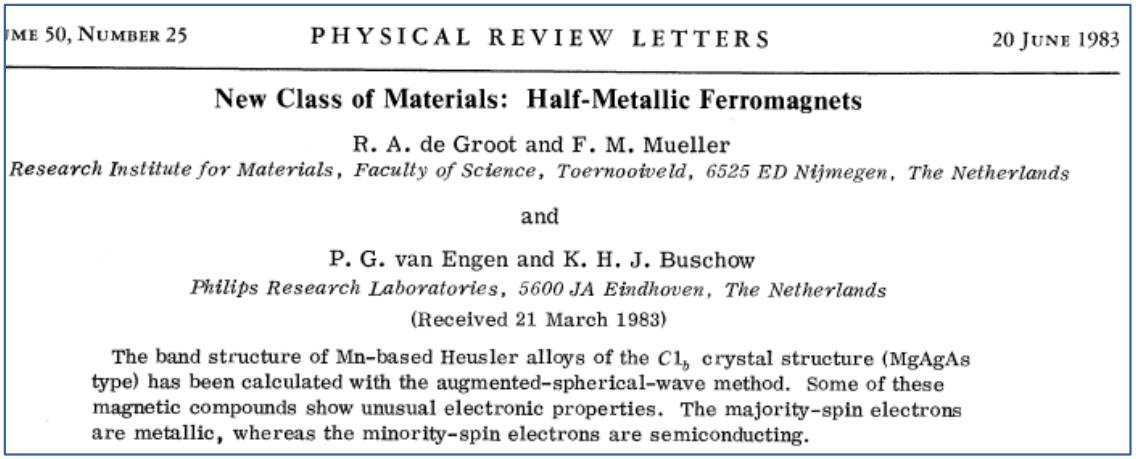
Wide variety of physical behaviours

* metals, semiconductors, semimetals
* strong and weak FM, AFM (high $T_C$ / $T_N$)
* Pauli paramagnets, Curie-Weiss PM
* half-metallic ferromagnets (HFM)
* strong thermoelectrics




Half-metallic ferromagnetism

* lack of FS for one spin direction
* integer magnetic moment value
* anomalous $\rho$(T) dependence
* giant magneto-optic Kerr effect
* predictions of HM-AF (1993)
* HFM : $CrO_2$, (La-Sr)$MnO_3$, spinels
* spintronic materials



VOLUME 50, NUMBER 25 PHYSICAL REVIEW LETTERS 20 JUNE 1983

**New Class of Materials: Half-Metallic Ferromagnets**

R. A. de Groot and F. M. Mueller
*Research Institute for Materials, Faculty of Science, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

and

P. G. van Engen and K. H. J. Buschow
*Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands*

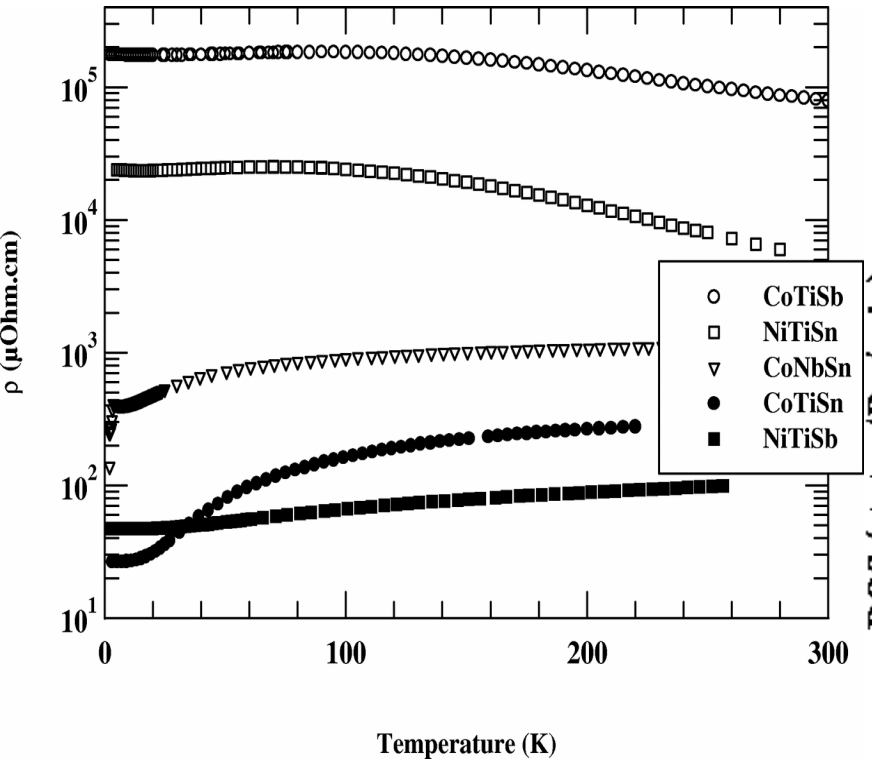
(Received 21 March 1983)

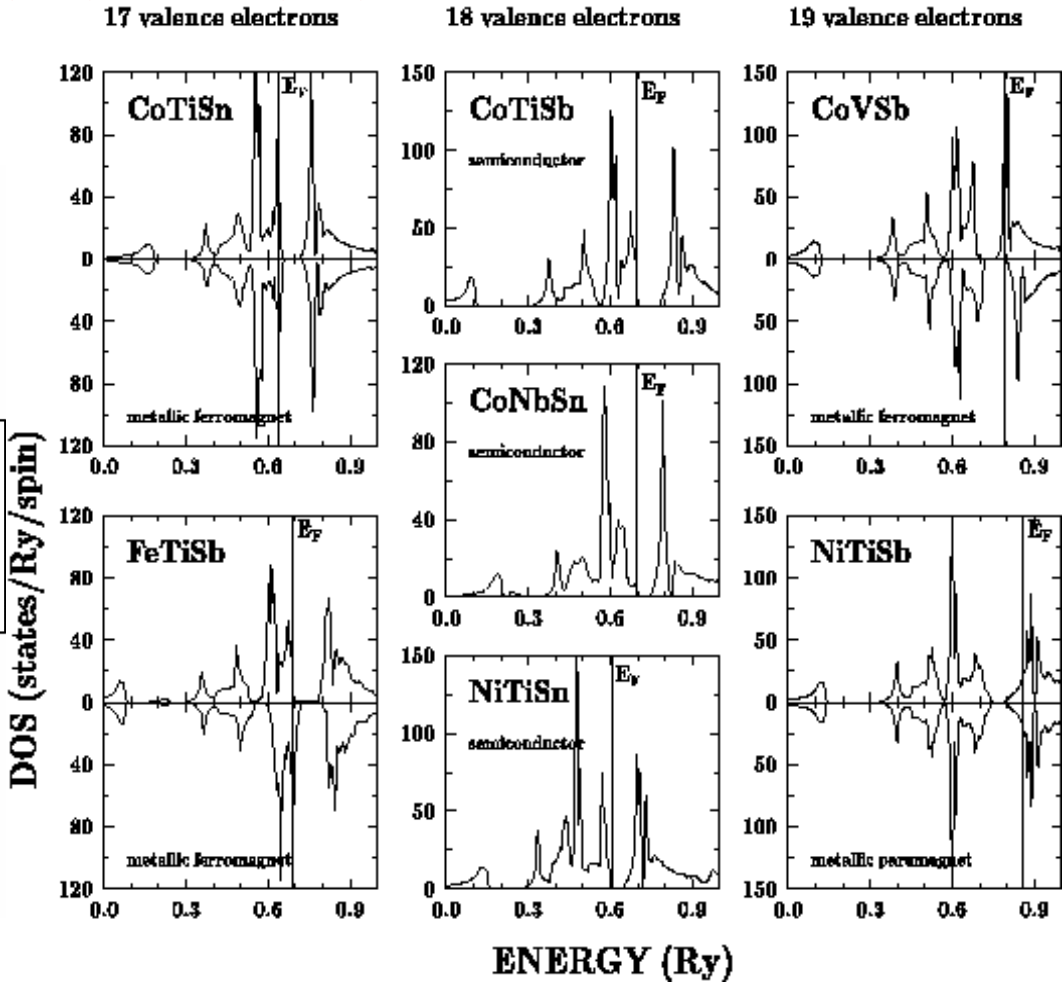
The band structure of Mn-based Heusler alloys of the $C1_b$ crystal structure (MgAgAs type) has been calculated with the augmented-spherical-wave method. Some of these magnetic compounds show unusual electronic properties. The majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting.

# Electron phase diagram of half-Heusler systems

*JT et al., JMMM (1996), J. Phys. CM (1998), JALCOM (2000)* ~ 650 citations

## Electrical resitivity




| CoTiSn | | | FeVSb | | | NiMnSb | | |
|---|---|---|---|---|---|---|---|---|
| $^{27}$Co : | $^{18}$Ar 4 s$^2$ 3 d$^7$ | (9) | $^{26}$Fe: | $^{18}$Ar 4 s$^2$ 3 d$^6$ | (8) | $^{28}$Ni: | $^{18}$Ar 4 s$^2$ 3 d$^8$ | (10) |
| $^{22}$Ti : | $^{18}$Ar 4 s$^2$ 3 d$^2$ | (4) | $^{23}$V : | $^{18}$Ar 4 s$^2$ 3 d$^3$ | (5) | $^{25}$Mn: | $^{18}$Ar 4 s$^2$ 3 d$^5$ | (7) |
| $^{50}$Sn: | [$^{36}$Kr4d$^{10}$] 5s$^2$5p$^2$ | (4) | $^{51}$Sb: | [$^{36}$Kr4d$^{10}$] 5s$^2$5p$^3$ | (5) | $^{51}$Sb: | [$^{36}$Kr4d$^{10}$] 5s$^2$5p$^3$ | (5) |
| **VEC =** | | **17** | **VEC =** | | **18** | **VEC =** | | **22** |

# Variety of physical properties of HH

EVIER

Journal of Alloys and Compounds 262–263 (1997) 101–107

## Properties on request in semi-Heusler phases

J. Pierre[a,*], R.V. Skolozdra[b], J. Tobola[c], S. Kaprzyk[c], C. Hordequin[a], M.A. Kouacou[a], I. Karla[a], R. Currat[d], E. Lelièvre-Berna[d]

[a] *Laboratoire L.NEEL, CNRS, 166X, 38042 Grenoble, France*
[b] *Dept of Inorganic Chemistry, I.FRANKO University, 290005 Lviv, Ukraine*
[c] *Faculty of Physics and Nuclear Techniques, Academy of Mining and Metallurgy, 30-073 Krakow, Poland*
[d] *Institut Laue Langevin, 156X, 38042 Grenoble, France*

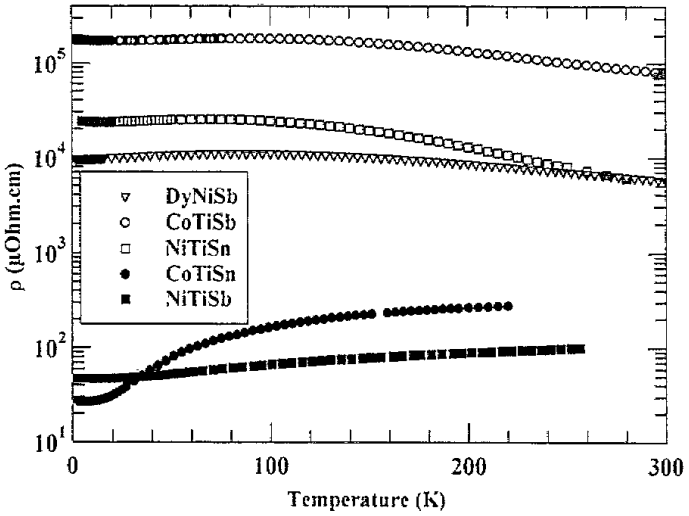
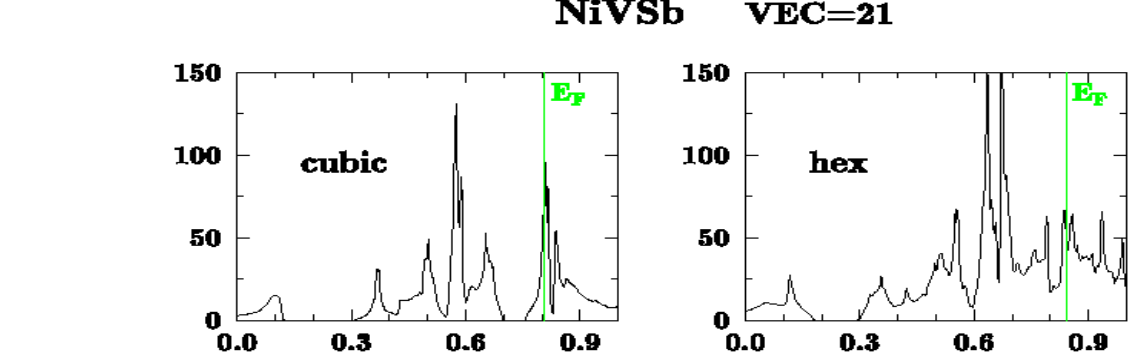



Fig. 1. Resistivity for some semi-Heusler phases.

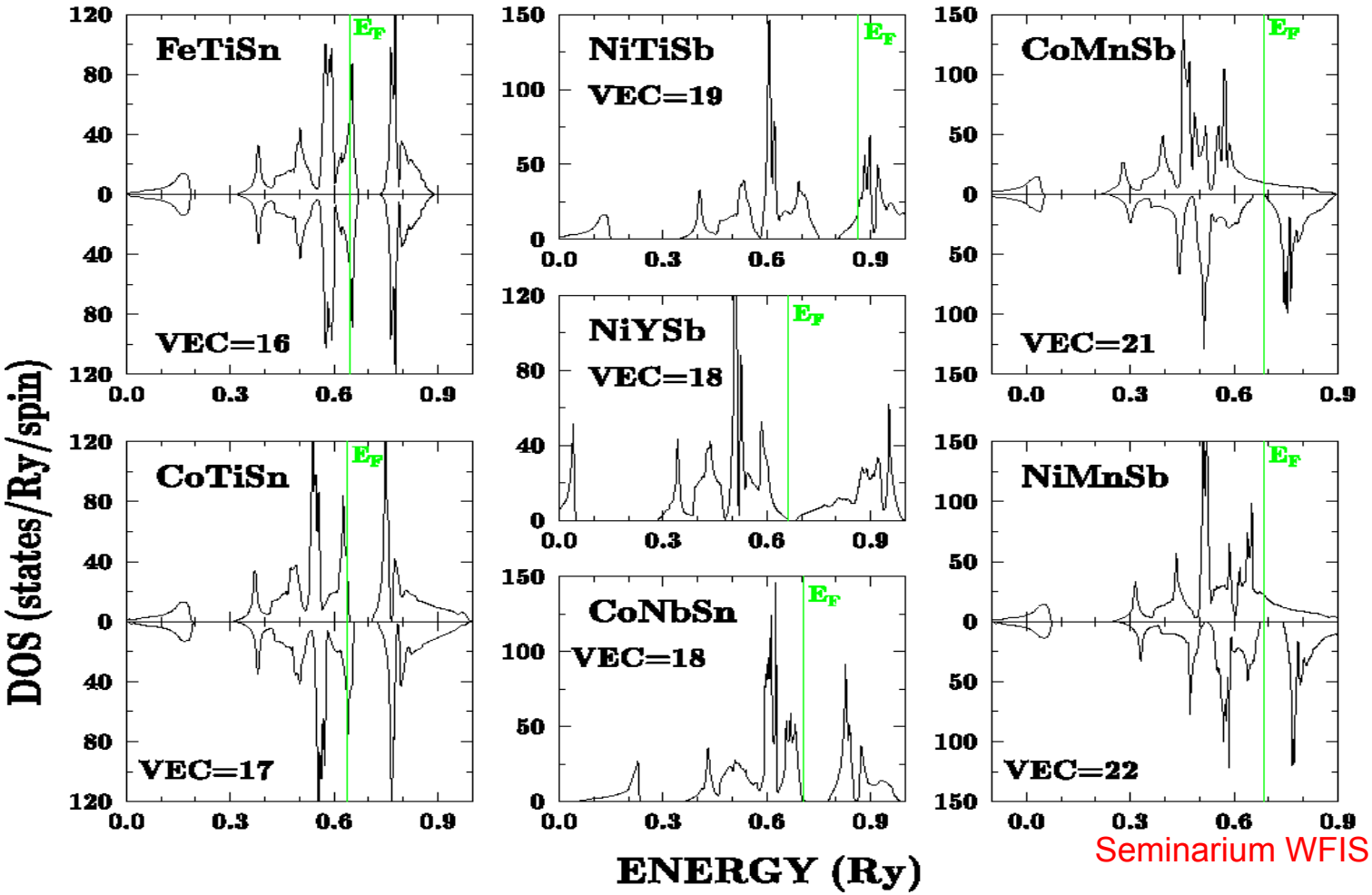
Lattice parameter (300 K), Curie, Néel and Curie–Weiss temperatures, ordered and paramagnetic moments for some semi-Heusler phases

| Phase | $a$ (Å) | $T_c$, $T_N$ (K) | $M(0)$ ($\mu_B$) | $\theta p$ (K) | $M_{eff}$ ($\mu_B$) | $10^4\,\chi$ (emu mol$^{-1}$) |
|---|---|---|---|---|---|---|
| CoTiSn | 5.997 | $T_c = 135$ | 0.357 | 158 | 1.35 | — |
| CoTiSb | 5.884 | — | — | — | — | 1.7 |
| CoNbSn | 5.947 | — | — | — | — | 0.53 |
| NiTiSn | 5.947 | — | — | — | — | 1.3 |
| CoVSb | 5.791 | $T_c = 11$–$58$ | 0.04–0.18 | 15–75 | 0.9–1.26 | — |
| NiTiSb | 5.872 | — | — | — | — | 1.4 |
| NiTbSb | 6.310 | $T_N = 5.5$ | 5.6 | −17 | 9.7 | — |
| NiDySb | 6.305 | 3.5 | — | −8 | 10.9 | — |
| NiHoSb | 6.286 | 2.5 | — | −7.5 | 10.7 | — |
| NiMnSb | 5.930 | $T_c = 730$ | 4.02 | ~ 900 | 4.5–2.9 | — |




# Properties "on request"

## ELECTRONIC PHASE DIAGRAM OF HALF-HEUSLER SYSTEMS




Phase transitions

- FM-PM
- FM-HMF
- FM-SC
- PM-SC
- PM-SC-PM
- FM-SC-PM

# Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals

L. P. Bouckaert,* R. Smoluchowski and E. Wigner, *The Institute for Advanced Study Princeton University, Princeton, New Jersey and the University of Wisconsin*

Table I. *Characters of small representations of* Γ, *R*, *H*.

| Γ, *R*, *H* | *E* | $3C_4^2$ | $6C_4$ | $6C_2$ | $8C_3$ | *J* | $3JC_4^2$ | $6JC_4$ | $6JC_2$ | $8JC_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $\Gamma_2$ | 1 | 1 | −1 | −1 | 1 | 1 | 1 | −1 | −1 | 1 |
| $\Gamma_{12}$ | 2 | 2 | 0 | 0 | −1 | 2 | 2 | 0 | 0 | −1 |
| $\Gamma_{15}'$ | 3 | −1 | 1 | −1 | 0 | 3 | −1 | 1 | −1 | 0 |
| $\Gamma_{25}'$ | 3 | −1 | −1 | 1 | 0 | 3 | −1 | −1 | 1 | 0 |
| $\Gamma_1'$ | 1 | 1 | 1 | 1 | 1 | −1 | −1 | −1 | −1 | −1 |
| $\Gamma_2'$ | 1 | 1 | −1 | −1 | 1 | −1 | −1 | 1 | 1 | −1 |
| $\Gamma_{12}'$ | 2 | 2 | 0 | 0 | −1 | −2 | −2 | 0 | 0 | 1 |
| $\Gamma_{15}$ | 3 | −1 | 1 | −1 | 0 | −3 | 1 | −1 | 1 | 0 |
| $\Gamma_{25}$ | 3 | −1 | −1 | 1 | 0 | −3 | 1 | 1 | −1 | 0 |

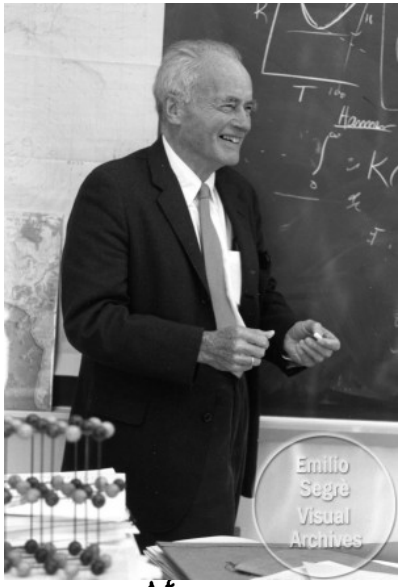
Table XIV. *Characters of small representations of W.*

| *W* | *E* | $C_4^2$ | $2C_2$ | $2JC_4$ | $2JC_4^2$ |
|---|---|---|---|---|---|
| $W_1$ | 1 | 1 | 1 | 1 | 1 |
| $W_1'$ | 1 | 1 | 1 | −1 | −1 |
| $W_2$ | 1 | 1 | −1 | 1 | −1 |
| $W_2'$ | 1 | 1 | −1 | −1 | 1 |
| $W_3$ | 2 | −2 | 0 | 0 | 0 |

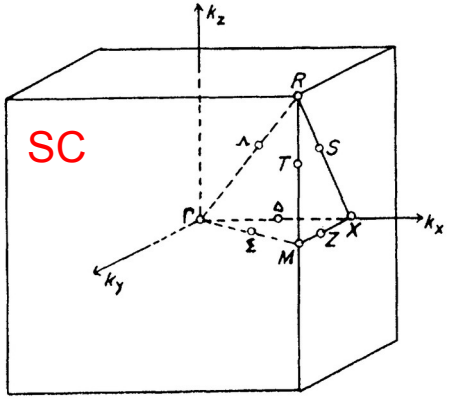
Table XV. *Characters of small representations of L.*

| *L* | *E* | $2C_3$ | $3C_2$ | *J* | $2JC_3$ | $3JC_2$ |
|---|---|---|---|---|---|---|
| $L_1$ | 1 | 1 | 1 | 1 | 1 | 1 |
| $L_2$ | 1 | 1 | −1 | 1 | 1 | −1 |
| $L_3$ | 2 | −1 | 0 | 2 | −1 | 0 |
| $L_1'$ | 1 | 1 | 1 | −1 | −1 | −1 |
| $L_2'$ | 1 | 1 | −1 | −1 | −1 | 1 |
| $L_3'$ | 2 | −1 | 0 | −2 | 1 | 0 |

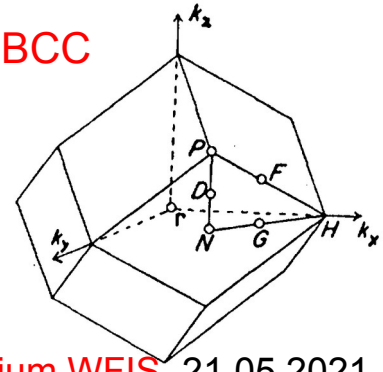
notation BSW for energy dispersion bands in BZ derived from Bloch states in crystals with basic structures SC, BCC & FCC (symmetry theory and characters of representations)



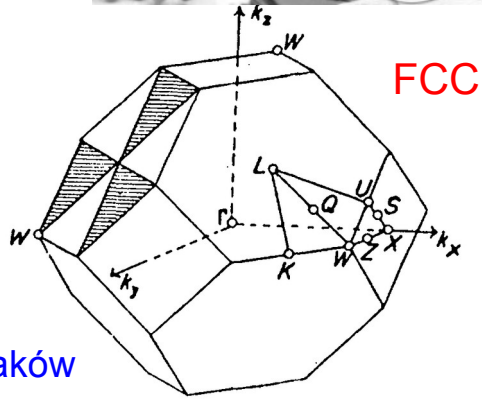

SC



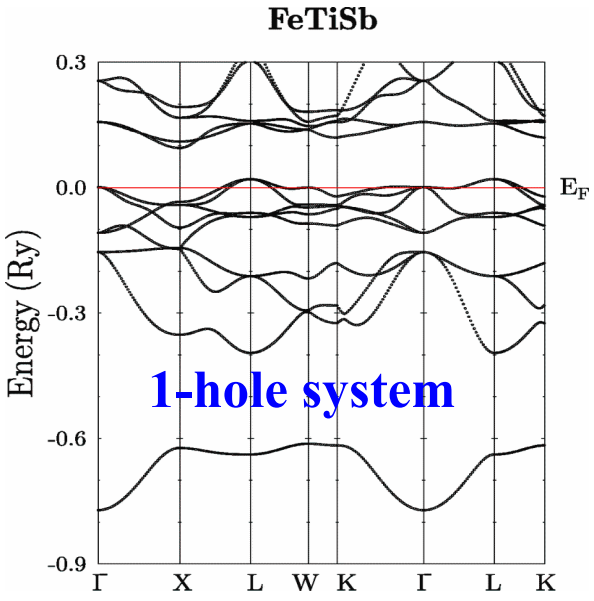

BCC




FCC



# Metal–semiconductor-metal crossovers



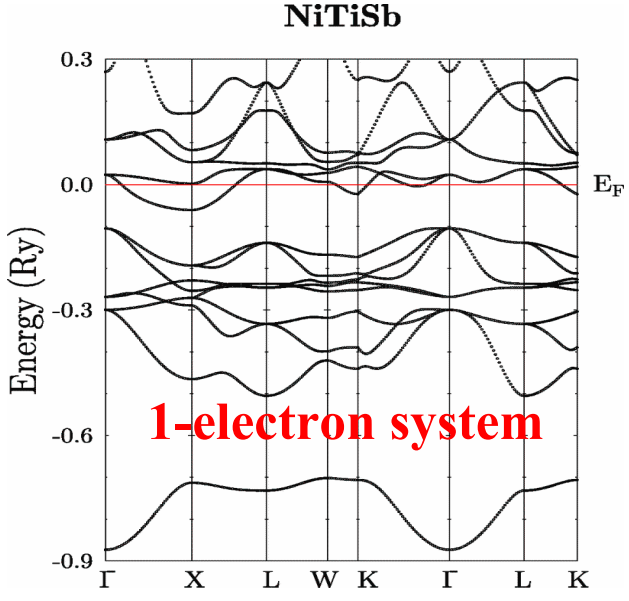

FeTiSb (VEC=17)

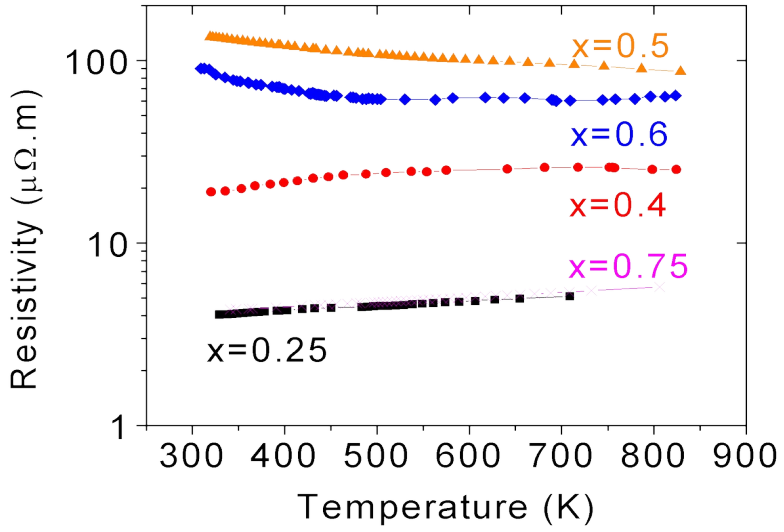
Curie-Weiss PM (~0.9$\mu_B$)

NiTiSb (VEC=19)

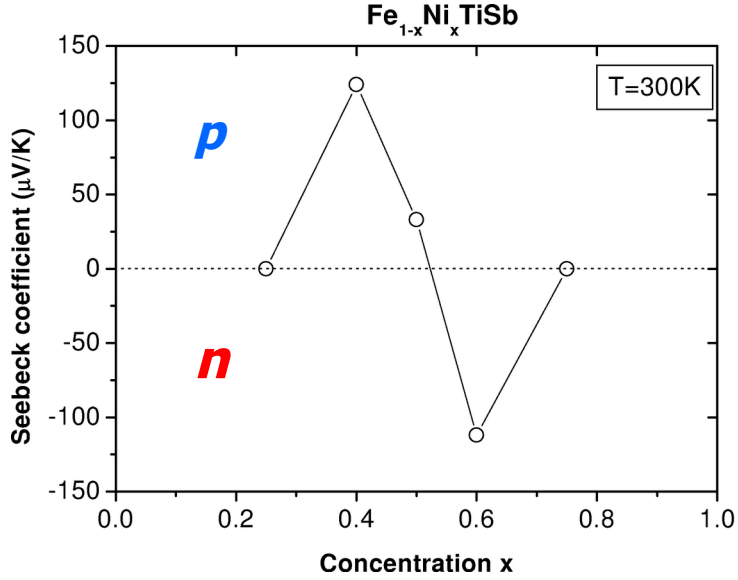
Pauli PM

*JT et al., PRB **64**, 155103 (2001)*



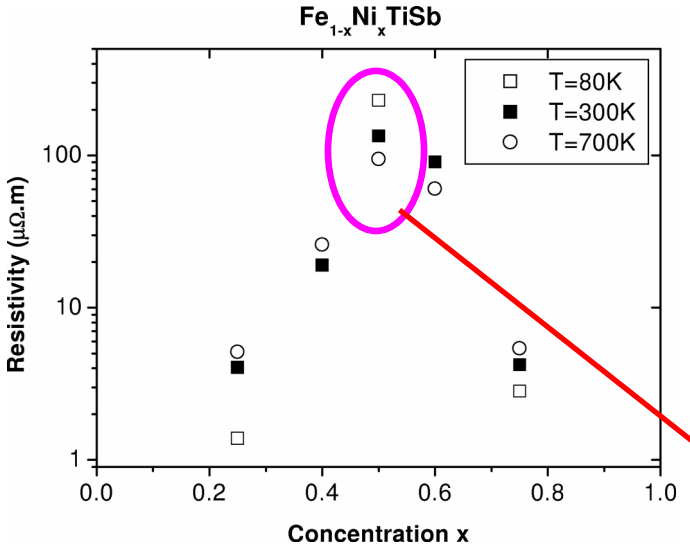




**Resistivity (experiment)**

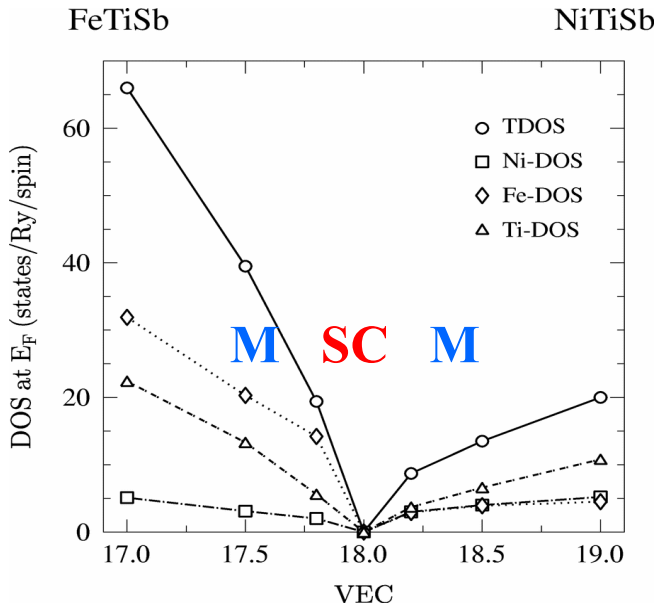



**Thermopower (experiment)**

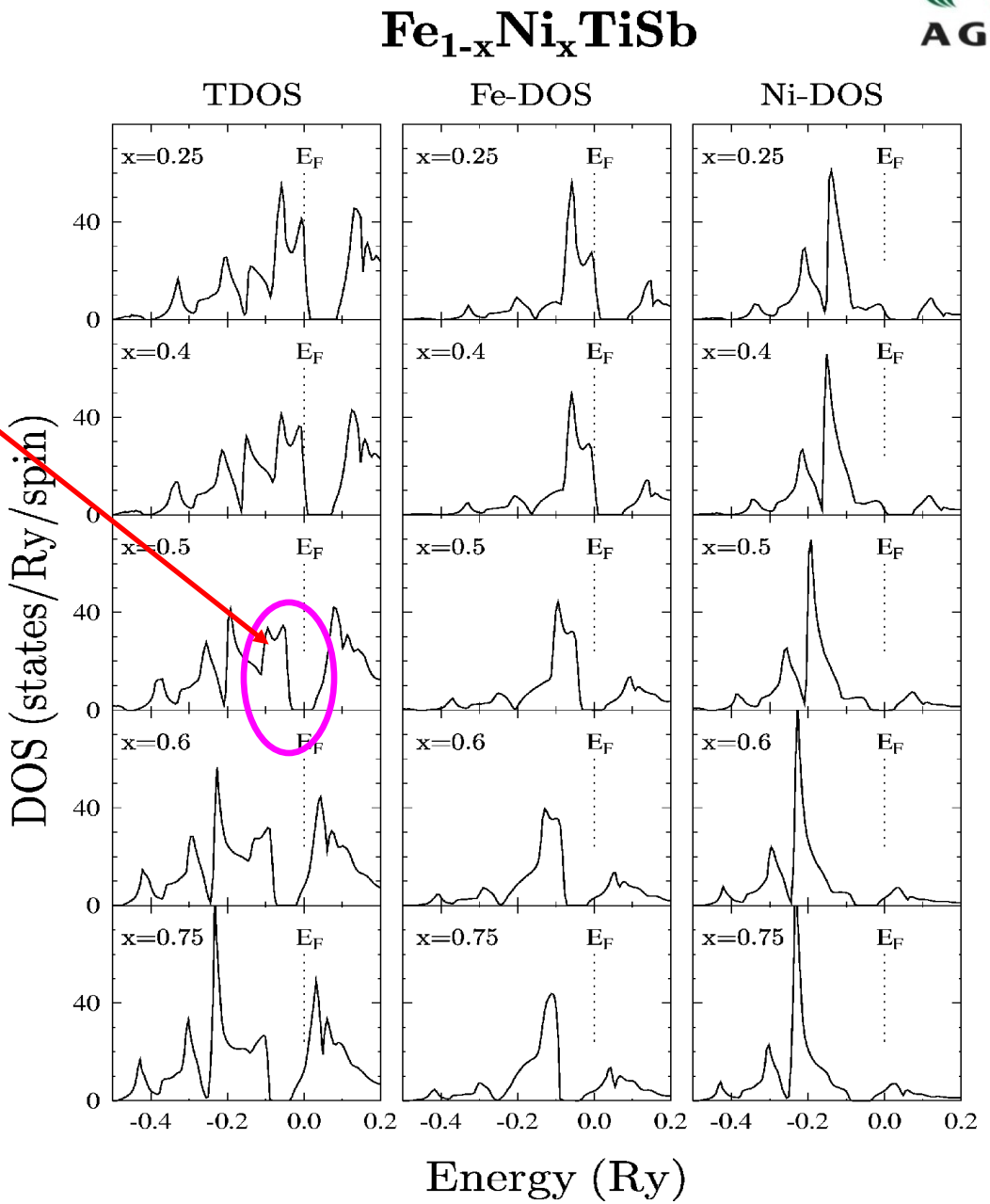
# Semiconductor from alloyed metals




Resistivity

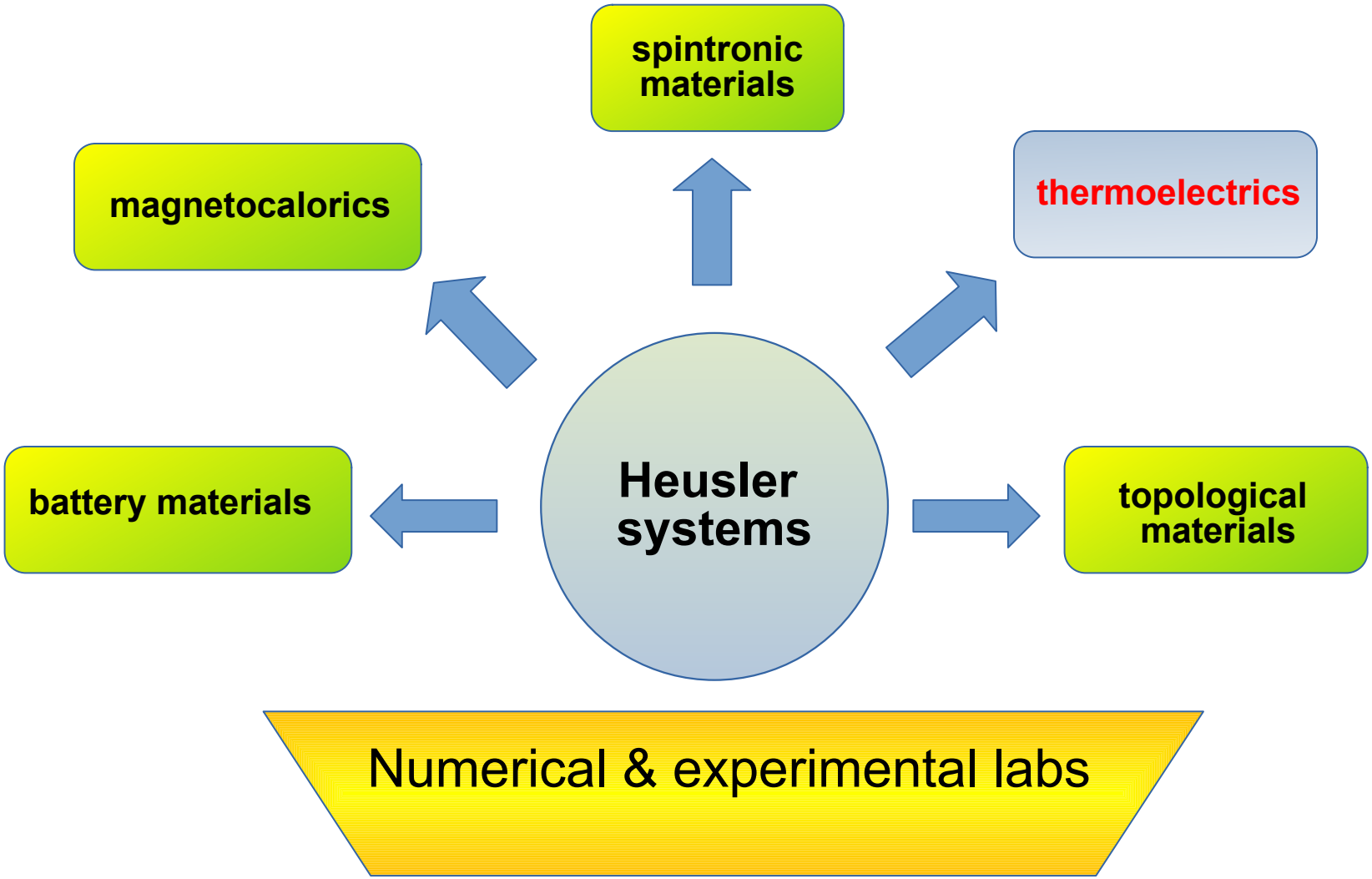



Density of states at $E_F$

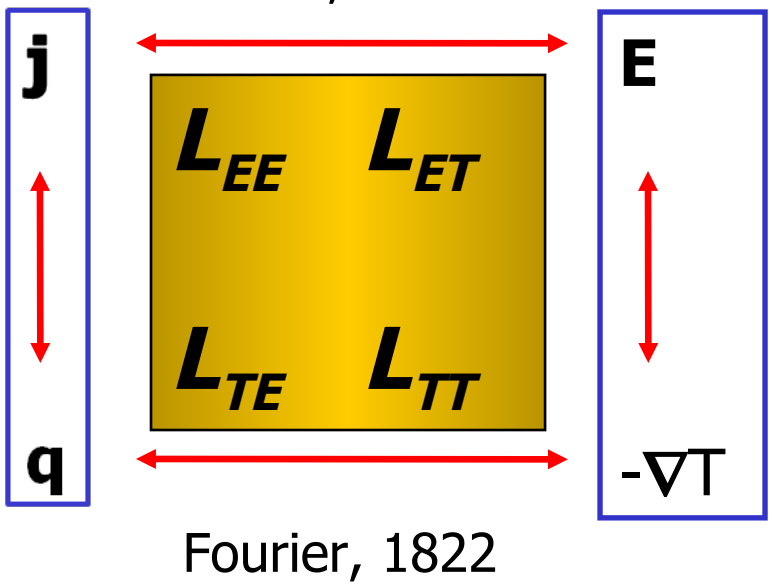



*JT et al., PRB **64**, 155103 (2001)*

# PLAN


spintronic materials
magnetocalorics
thermoelectrics
Heusler systems
battery materials
topological materials
Numerical & experimental labs

# Thermoelectric „tetragon”




$S\,T = \Pi$ (Thomson-Kelvin-Onsager) $L_{ET} = L_{TE}/T$

$\kappa/\sigma \approx L_0\,T$ (Wiedemann-Franz, $L_0$ Lorentz number) $\kappa \approx -L_{TT}$

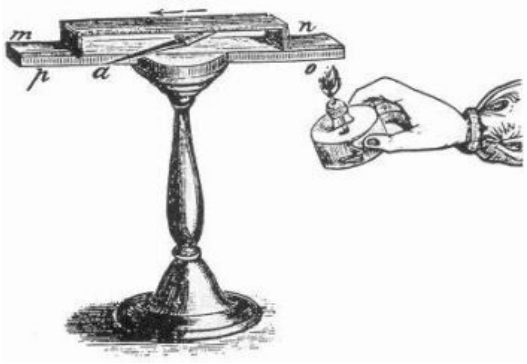
Volta (1800), Ampere (1820) , Faraday (1831), Gauss (1832), …

# Thermoelectric properties

## search for optimum

Improvement of figure of merit

Geometry of the devices



Physical properties of the system

*Carnot limit*

COOLING ELEMENTS

$COP = (T_H - T_C)(\gamma - 1)(T_C + \gamma T_H)^{-1}$

POWER GENERATORS

$\eta = (\gamma T_C - T_H)[(T_H - T_C + (\gamma+1)]^{-1}$

$\gamma = (1+ZT)^{1/2}$

A.F. Ioffe

$$ZT = \frac{S^2\sigma}{\kappa} T = \underbrace{\frac{S^2}{L}}_{calculated} \frac{1}{1+\frac{\kappa_L}{\kappa_e}}$$

Lorentz factor

Thermal conductivity (phonons /electrons)

# Thermoelectric properties

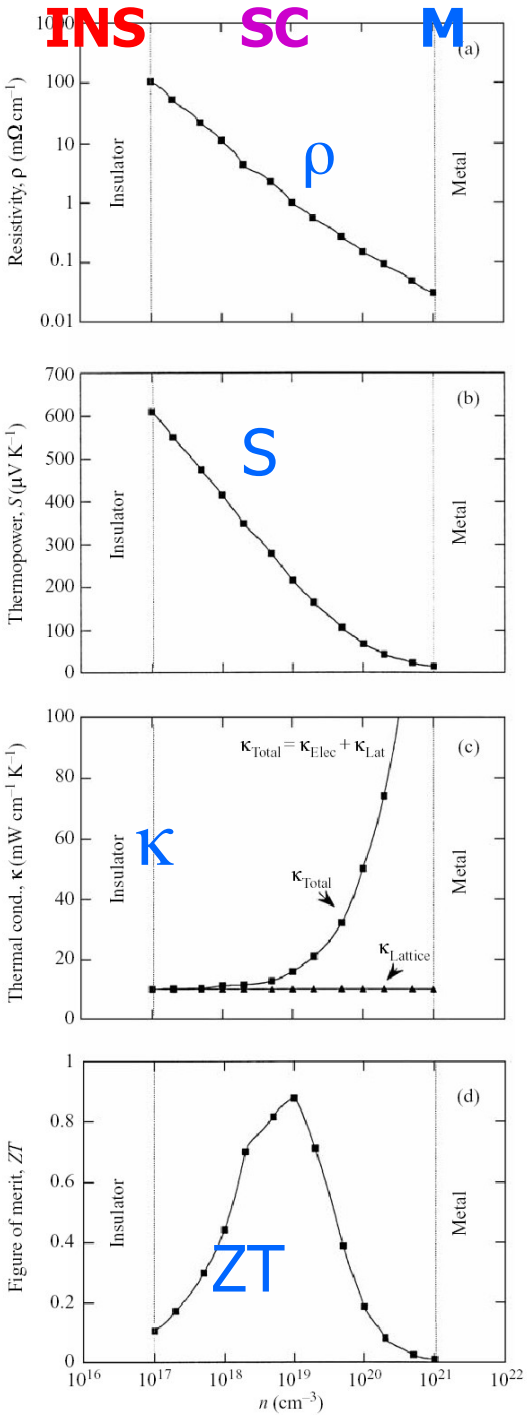
$$ZT = \frac{S^2\sigma}{\kappa}T$$

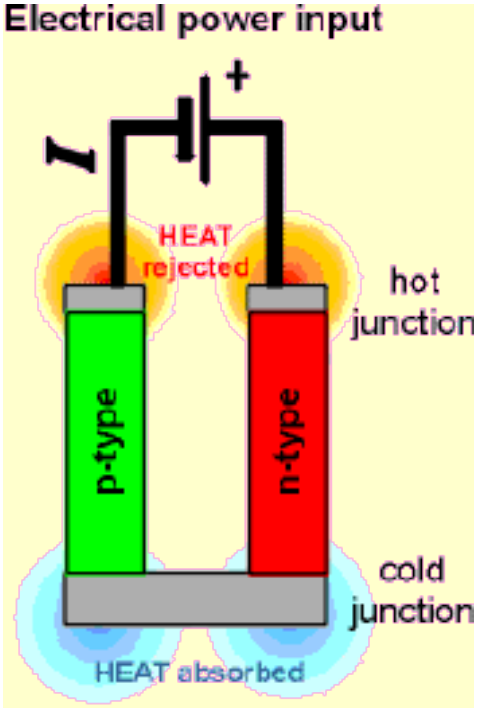
**Resitivity**

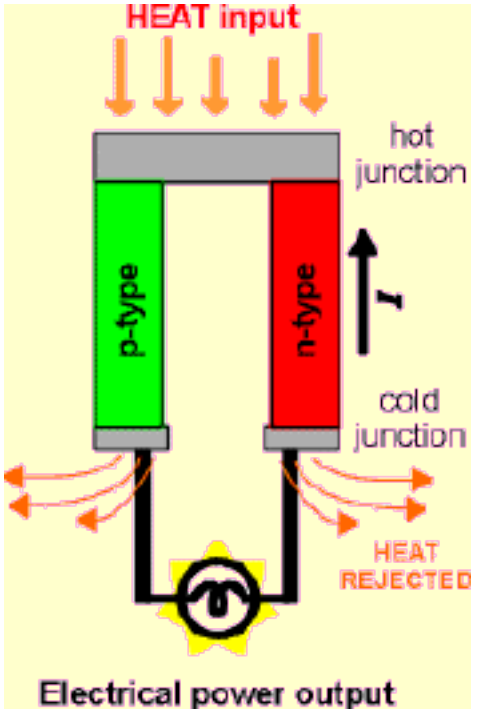
**Thermopower**

**Thermal conductivity**

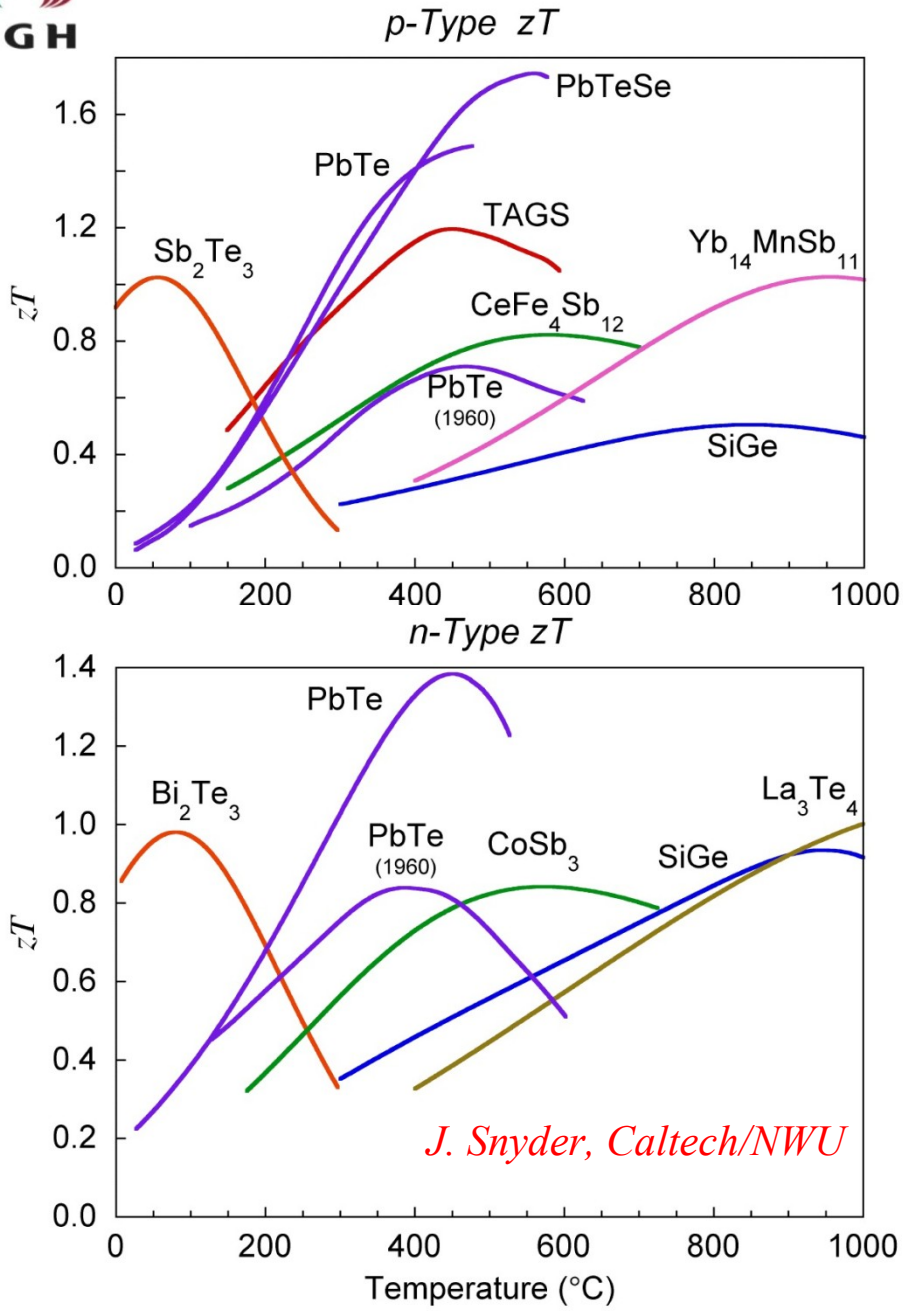
**ZT**
**Figure of merit**

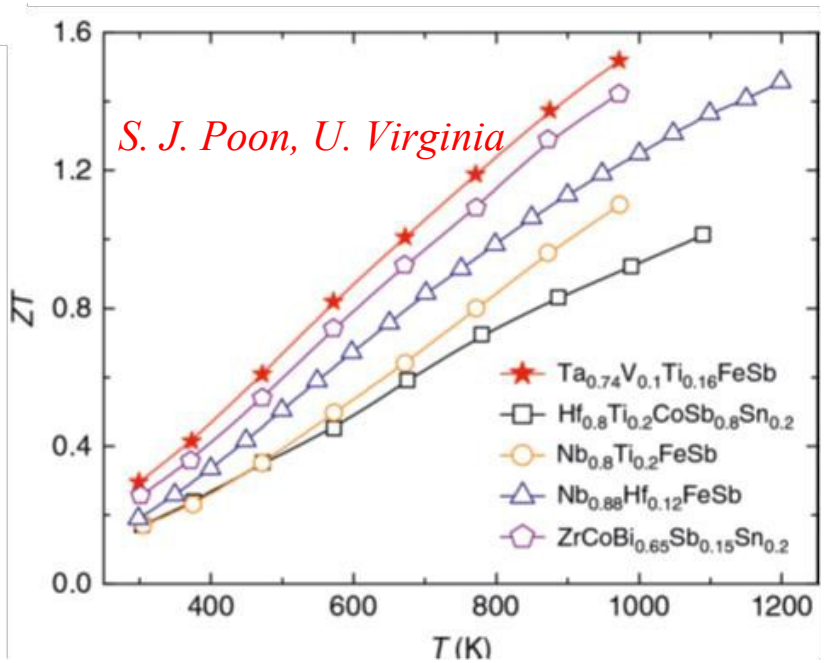


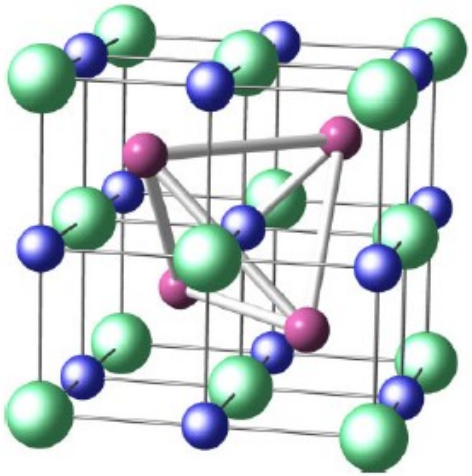



# Thermoelectric materials

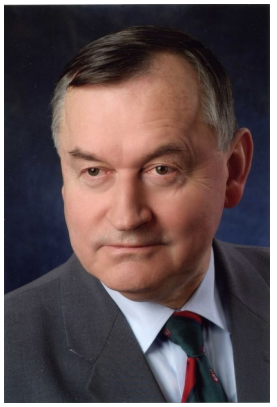



**Half-Heusler phases**

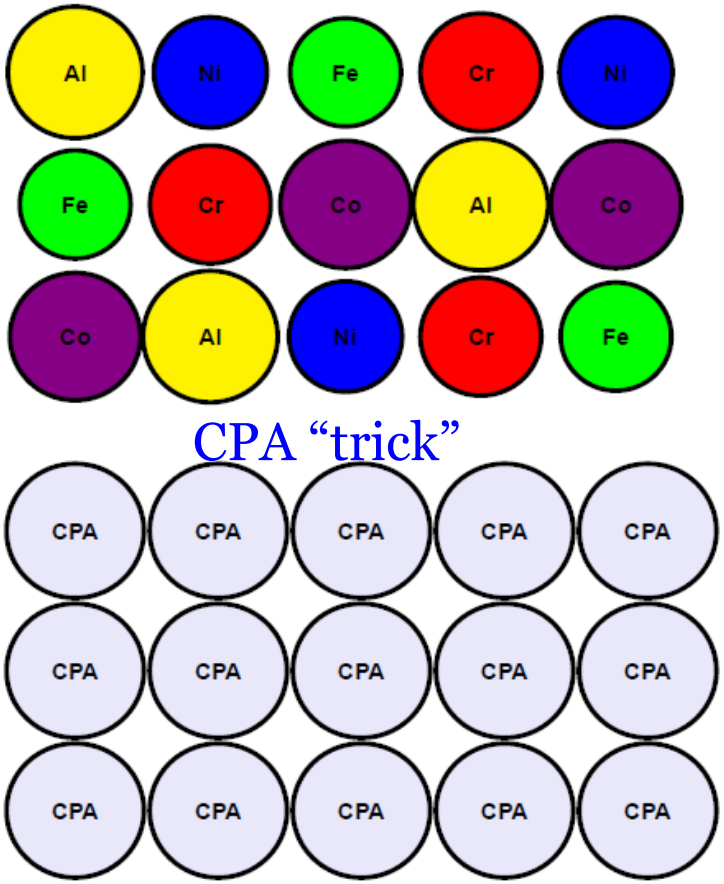


# KKR-CPA method



S. Kaprzyk

Disordered alloys: ~~periodic~~ - Coherent Potential Approximation (CPA):




**CPA condition**

$$G^{CP} = c_A G_A + c_B G_B + c_C G_C + \ldots + c_N G_N$$

**CPA crystal consists of ‘disordered’ nodes arranged with translation symmetry of cell and mimics alloys, defects, etc.**

KKR-CPA code allows for treat many atoms on disordered sites (N>10) solved self-consistently.

*Muffin-tin* potential is used due to CPA condition, defined for spherical potentials.

$$T^{CP}_{k'\sigma'L',k\sigma L} = \frac{1}{N}\sum_{\mathbf{k}\in BZ}\left[\tau^{-1}_{CP} - B(E,\mathbf{k})\right]^{-1}_{k'\sigma'L',k\sigma L}$$

# KKR-CPA method for disordered alloys

Korringa-Kohn-Rostoker with coherent potential approximation

$$G(E)=\sum_{s=(+,-)}\sum_{k=1}^{K}\int_{V_k} d^3r\langle s,\mathbf{r}+\mathbf{a}_k|G(E)|s,\mathbf{r}+\mathbf{a}_k\rangle.$$

*Bansil, Kaprzyk, Mijnarends, JT, Phys. Rev. B (1999)* conventional KKR

Full GF

*Stopa, Kaprzyk, JT, J.Phys.CM (2004)* novel formulation of KKR

$$\langle s',\mathbf{r}'+\mathbf{a}_{k_{CP}}|G^{A(B)}(E)|s,\mathbf{r}+\mathbf{a}_{k_{CP}}\rangle$$

$$=-\sum_{\sigma L} J^{A(B)}_{\sigma L}(s'\mathbf{r}')Z^{A(B)}_{\sigma L}(s\mathbf{r})$$

$$+\sum_{\sigma' L',\sigma L} Z^{A(B)}_{\sigma' L'}(s'\mathbf{r}')T^{A(B)}_{k_{CP}\sigma' L',k_{CP}\sigma L}Z^{A(B)}_{\sigma L}(s\mathbf{r})$$

$$G(E)=-\frac{d}{dE}\left\{\frac{1}{N}\sum_{\mathbf{k}\in BZ}\mathrm{Tr}\ln[G_0^{-1}(E,\mathbf{k})+D^{(j)}-D_{CP}]^{-1}\right\}$$

$$-\frac{d}{dE}\{c_A\mathrm{Tr}\ln[\Psi_A^{-1}G^A]+c_B\mathrm{Tr}\ln[\Psi_B^{-1}G^B]$$

$$-\mathrm{Tr}\ln G^{CP}\}+\frac{d}{dE}\left\{\sum_{k\neq k_{CP}}\mathrm{Tr}\ln[\Psi^{(k)}]\right\},\qquad(2.22)$$

Lloyd formula *Kaprzyk et al. Phys. Rev. B (1990)*

$$\langle s',\mathbf{r}'+\mathbf{a}_{k'}|G(E)|s,\mathbf{r}+\mathbf{a}_k\rangle$$

$$=-\sum_{\sigma L} J^{(k)}_{\sigma L}(s'\mathbf{r}')Z^{(k)}_{\sigma L}(s\mathbf{r})\delta_{kk'}$$

$$+\sum_{\sigma' L',\sigma L} Z^{(k')}_{\sigma' L'}(s'\mathbf{r}')T^{CP}_{k'\sigma' L',k\sigma L}Z^{(k)}_{\sigma L}(s\mathbf{r})$$

$$T^{CP}_{k'\sigma' L',k\sigma L}=\frac{1}{N}\sum_{\mathbf{k}\in BZ}[\tau_{CP}^{-1}-B(E,\mathbf{k})]^{-1}_{k'\sigma' L',k\sigma L}$$

CPA $\quad c_A T^A+c_B T^B=T^{CP}.$

Density of states $\quad N(E)=-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{E}dE\,G(E)$

Fermi energy $\quad N(E_F)=Z$

# Electron transport coefficients

$$\boldsymbol{\sigma}_e = \mathscr{L}^{(0)},$$

**Electrical conductivity**

$$\boldsymbol{S} = -\frac{1}{eT}\frac{\mathscr{L}^{(1)}}{\mathscr{L}^{(0)}},$$

**Seebeck coefficient (thermopower)**

$$\boldsymbol{\kappa_e} = \frac{\mathscr{L}^{(2)}}{e^2T} - \frac{\mathscr{L}^{(1)}\mathscr{L}^{(1)}}{e^2T\mathscr{L}^{(0)}}$$

**Electronic thermal conductivity**

$$L(T) = \frac{\kappa_e(T)}{\sigma(T)T}$$

Wiedemman-Franz-Lorenz

$$L = \frac{\kappa_e}{\sigma T}$$

$$PF = S^2\sigma$$

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

**Onsager-related functions**

$$\mathscr{L}^{(\alpha)} = \int d\mathscr{E}\left(-\frac{\partial f}{\partial \mathscr{E}}\right)(\mathscr{E}-\mu)^{\alpha}\boldsymbol{\sigma}(\mathscr{E})$$

$L(T,n)$

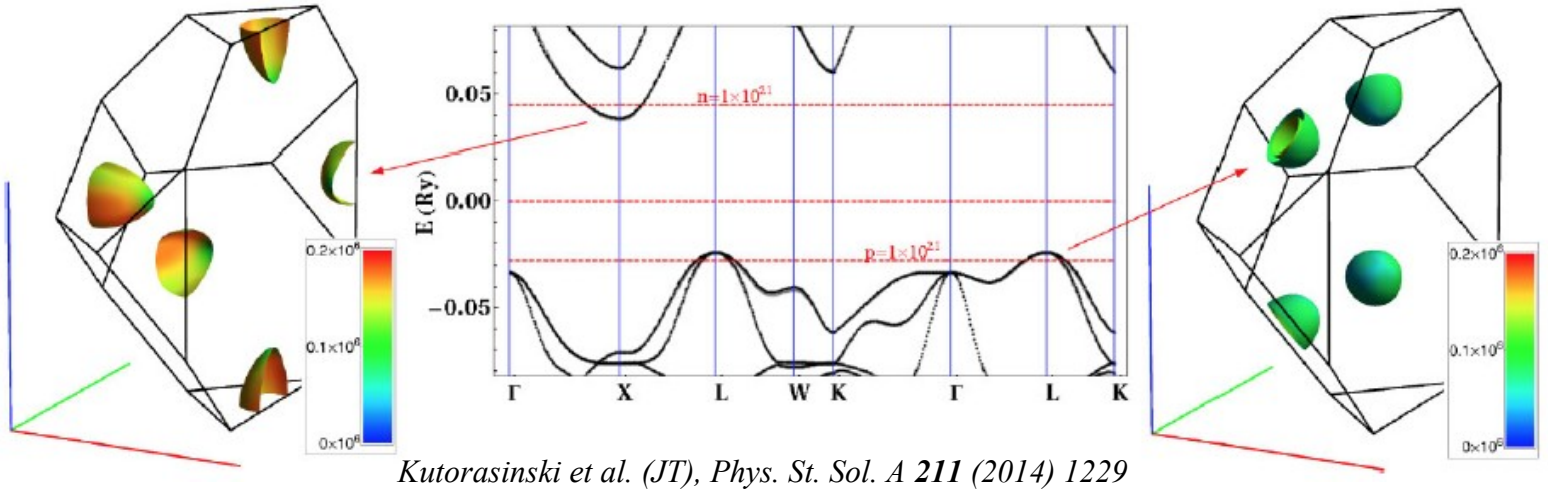
$PF(T,n)$

$ZT(T,n)$

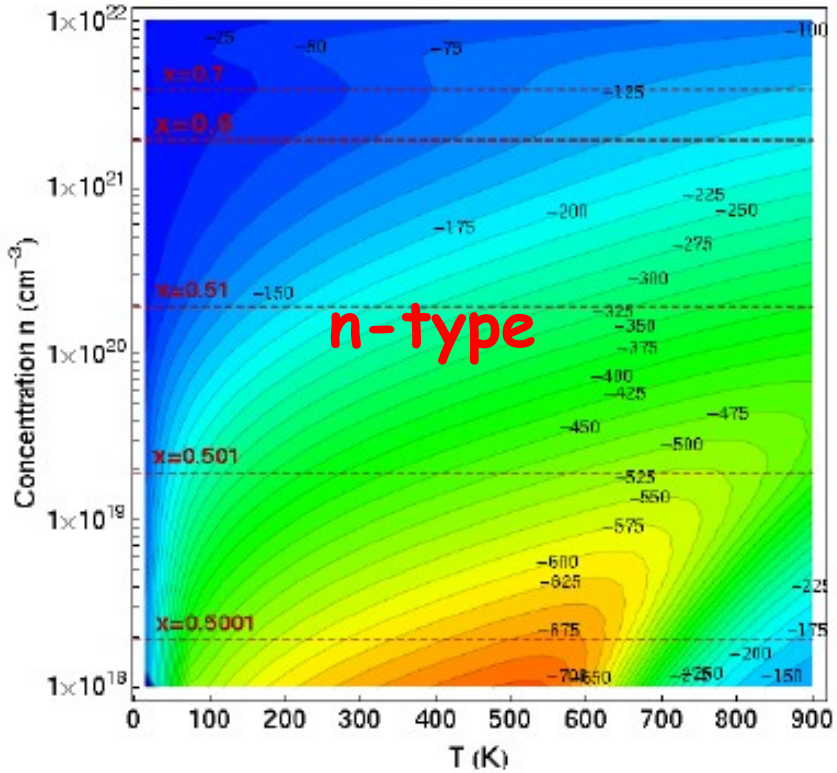
**Transport functions (in general tensors)**

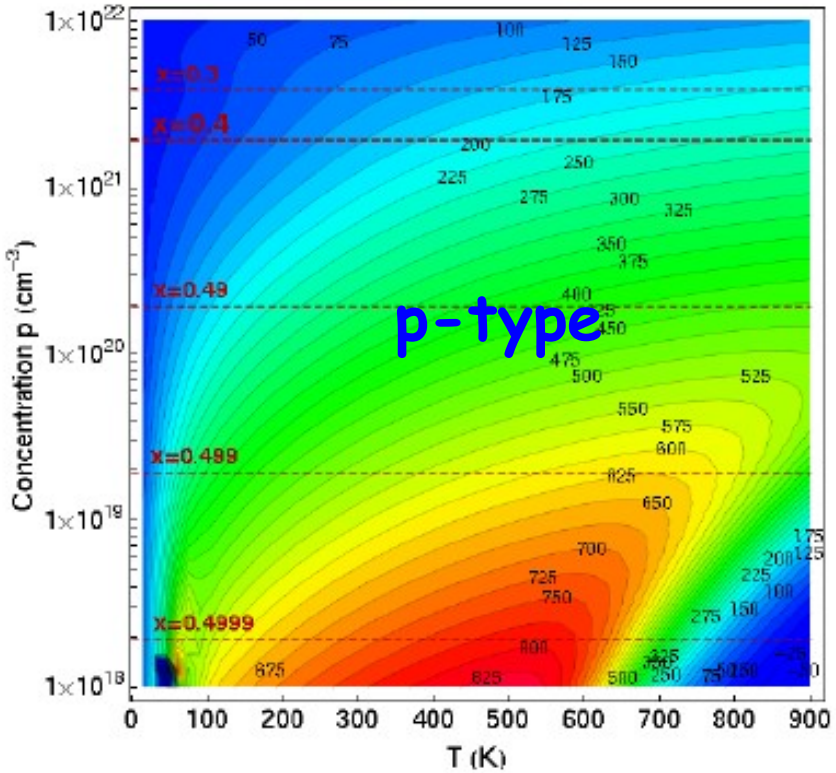
$$\boldsymbol{\sigma}(\mathscr{E}) = e^2\sum_n \int \frac{d\mathbf{k}}{4\pi^3}\tau_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\otimes\mathbf{v}_n(\mathbf{k})\delta(\mathscr{E}-\mathscr{E}_n(\mathbf{k}))$$

# Seebeck coefficient vs.temperature & carrier concentration



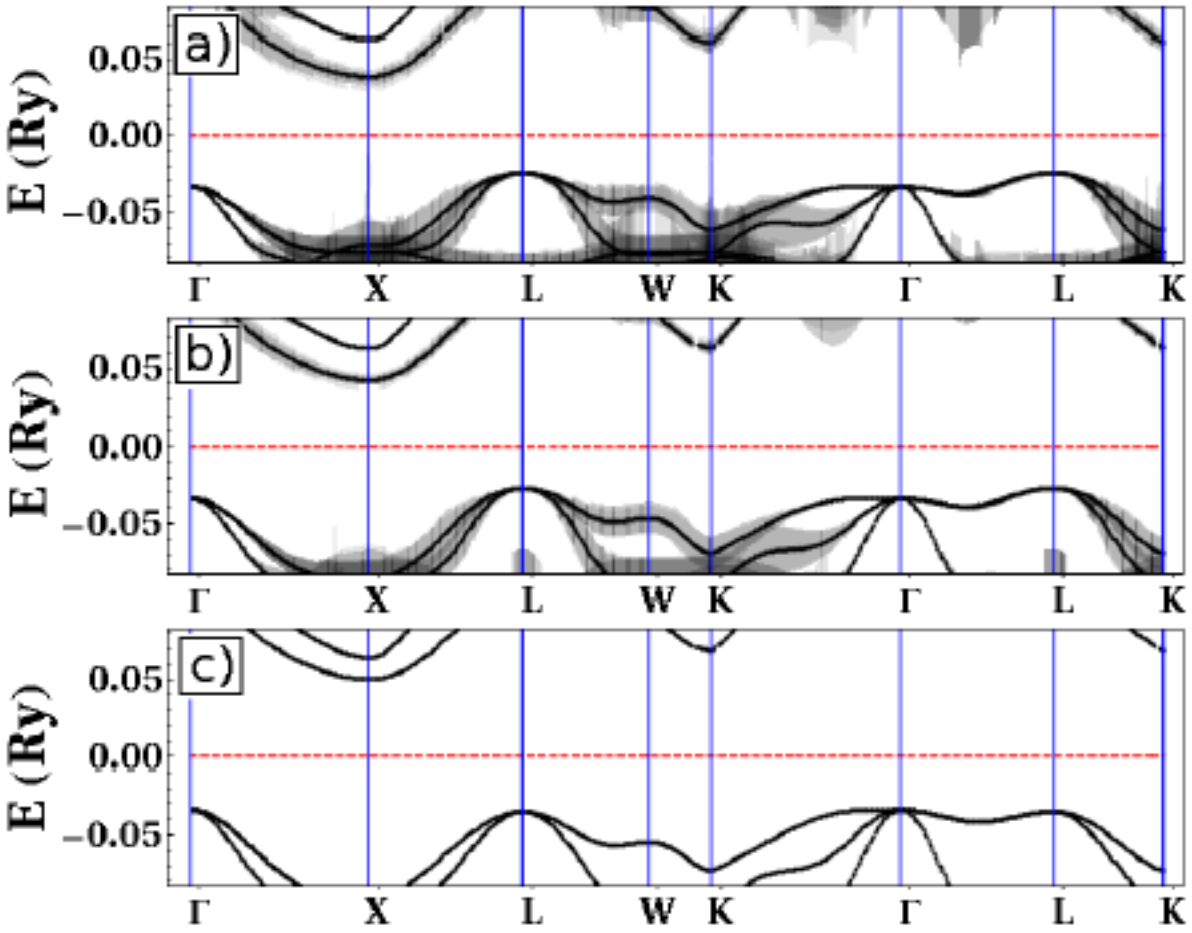

*Kutorasinski et al. (JT), Phys. St. Sol. A **211** (2014) 1229*




AGH

# Complex energy band „engineering”




$TiFe_{0.5}Ni_{0.5}Sb$

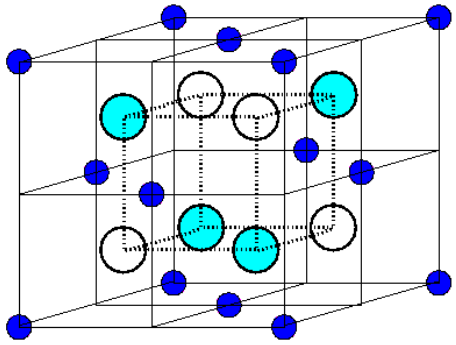
$TiFe_{0.3}Co_{0.4}Ni_{0.3}Sb$

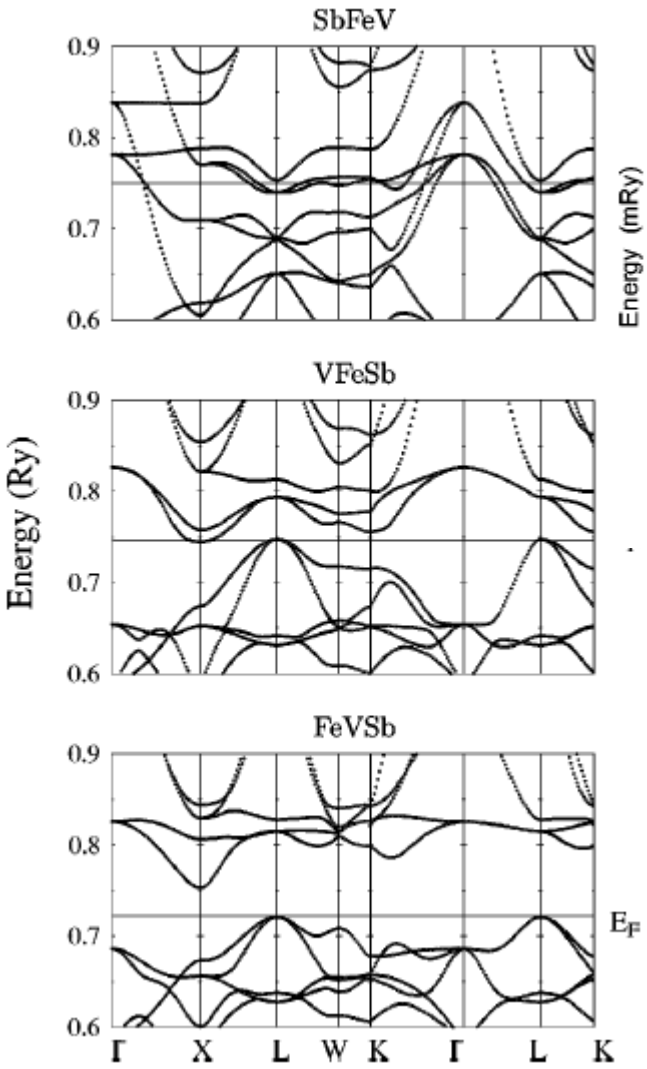
TiCoSb

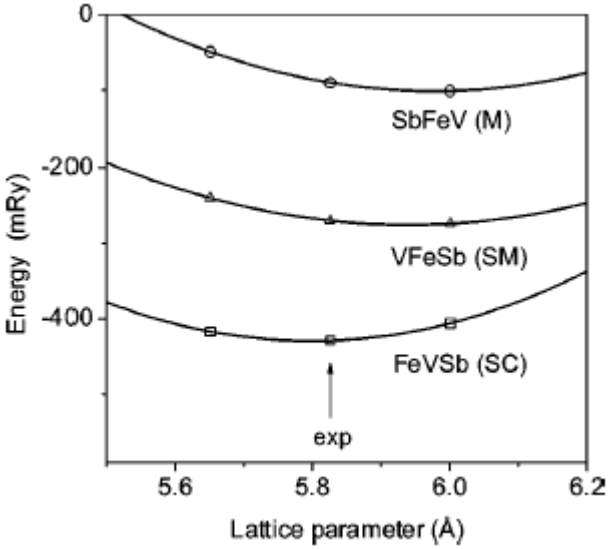
Tendency to alignment of bands near Fermi energy
BUT it needs experimental proof whether TE properties are really improved

*Kutorasinski et al. (JT), Phys. St. Sol. A* ***211*** *(2014) 1229*

# Role of point defects
# FeVSb – “dirty” semiconductor



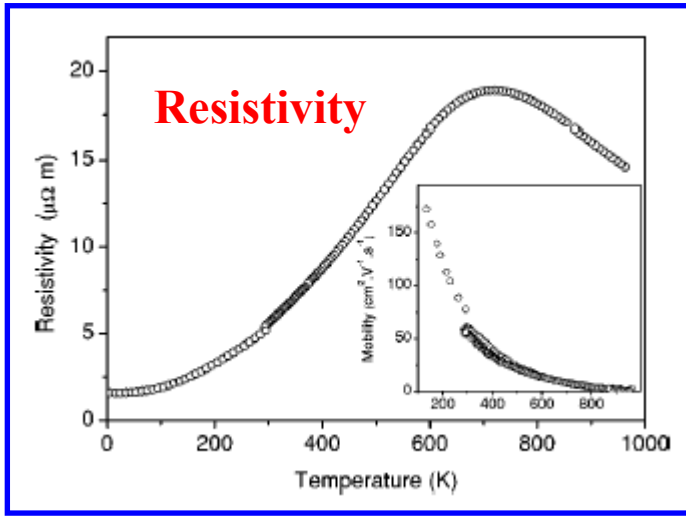


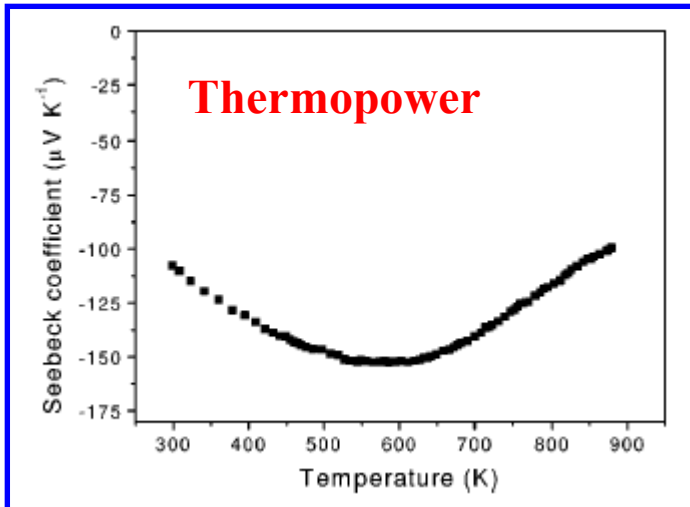




**KKR-CPA – total energy**

**Defects should be accounted :**
to interpret metallic electron conductivity + large Seebeck coefficient
FeVSb - rather semiconductor

*Jodin, JT, ..., PRB (2004)*



# Defects in Heusler alloys

| Nominal | EMPA |
|---|---|
| FeVSb | $Fe_{0.98}V_{0.99}Sb_{1.03}$ |
| $Fe_{0.995}Co_{0.005}VSb$ | $Fe_{0.97}Co_{0.006}V_{0.99}Sb_{1.03}$ |
| $Fe_{0.98}Co_{0.02}VSb$ | $Fe_{0.95}Co_{0.02}V_{1.02}Sb_{1.01}$ |
| $FeV_{0.90}Ti_{0.10}Sb$ | $Fe_{0.96}V_{0.9}Ti_{0.1}Sb_{1.04}$ |
| $FeV_{0.85}Ti_{0.15}Sb$ | $Fe_{0.98}V_{0.86}Ti_{0.15}Sb_{1.01}$ |
| $FeV_{0.80}Ti_{0.20}Sb$ | $Fe_{0.99}V_{0.77}Ti_{0.22}Sb_{1.02}$ |
| $FeV_{0.95}Zr_{0.05}Sb$ | $Fe_{0.95}V_{0.98}Zr_{0.02}Sb_{1.05}$ |
| $FeV_{0.90}Zr_{0.10}Sb$ | $Fe_{0.96}V_{0.97}Zr_{0.03}Sb_{1.04}$ |
| $FeV_{0.85}Zr_{0.15}Sb$ | $Fe_{0.95}V_{0.93}Zr_{0.07}Sb_{1.05}$ |

**EPMA data**

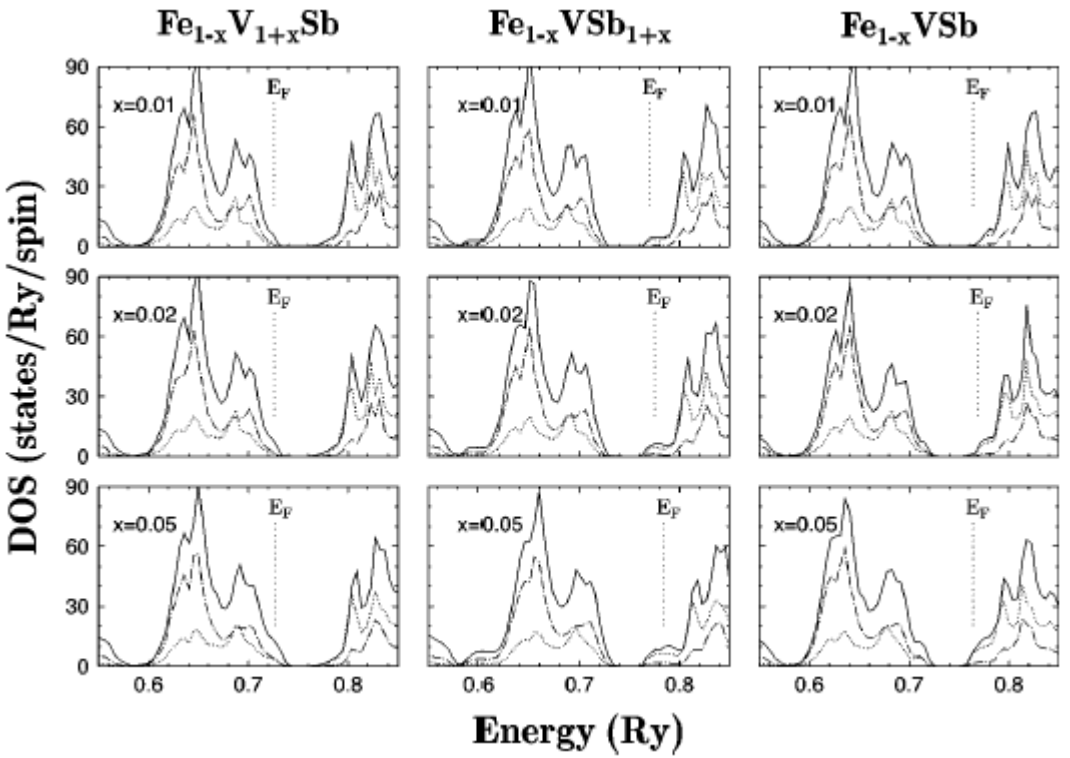
## Doping of n and p types

TABLE IV. Room temperature Seebeck coefficient $S$ and resistivity $\rho$ in pure and substituted FeVSb half-Heusler phases.

| Composition | $\rho$ ($\mu\Omega$ m) | $S$ ($\mu$V K$^{-1}$) | $n\times10^{20}$(cm$^{-3}$) |
|---|---|---|---|
| FeVSb | 5.1 | −110 | ≈1 |
| $Fe_{0.995}Co_{0.005}VSb$ | 4.2 | −130 | ≈1 |
| $Fe_{0.98}Co_{0.02}VSb$ | 2.3 | −80 | ≈5 |
| $FeV_{0.95}Ti_{0.05}Sb$ | 13 | +180 | ≈5 |
| $FeV_{0.90}Ti_{0.10}Sb$ | 15.5 | +145 | ≈5 |
| $FeV_{0.85}Ti_{0.15}Sb$ | 68.7 | +125 | ≈2 |
| $FeV_{0.80}Ti_{0.20}Sb$ | 20 | +70 | ≈20 |
| $FeV_{0.95}Zr_{0.02}Sb$ | 46 | −20 | ≈1 |
| $FeV_{0.90}Zr_{0.03}Sb$ | 43 | +20 | ≈3 |
| $FeV_{0.85}Zr_{0.07}Sb$ | 23 | +30 | ≈4 |

**KKR-CPA density of states upon inclusion Fe/Sb vac/Fe defects**

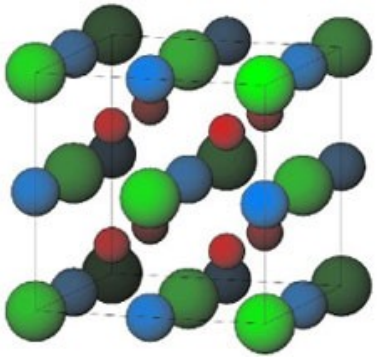
**Vacancy on Fe-site & Sb on Fe-site behaves as a HOLE donor**




*Jodin, JT, ..., PRB (2004)*

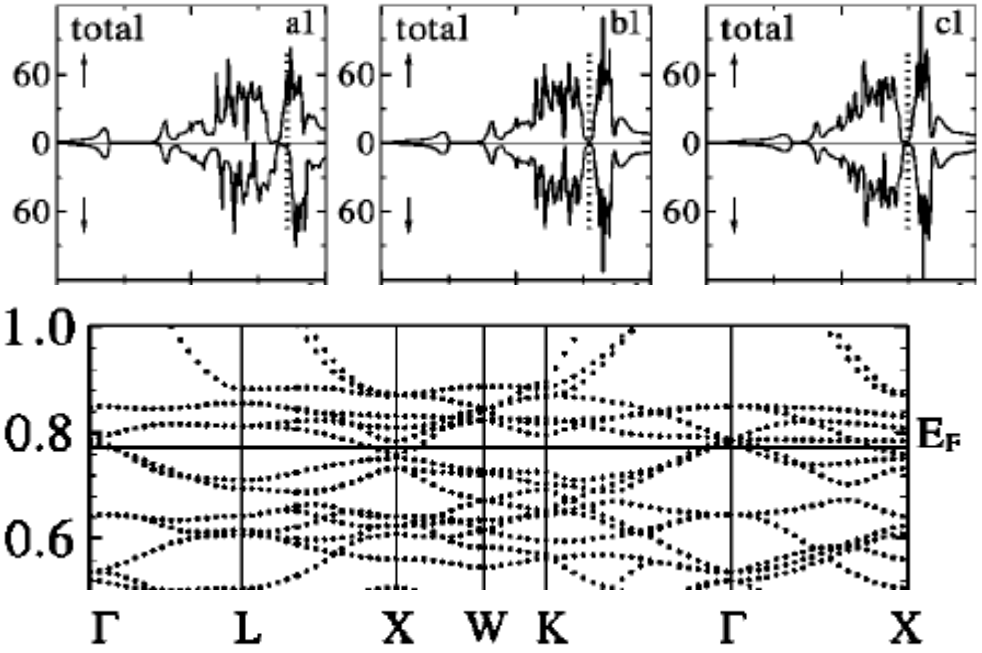
# $Fe_2VAl$ i $Fe_2VGa$ semimetals

theory

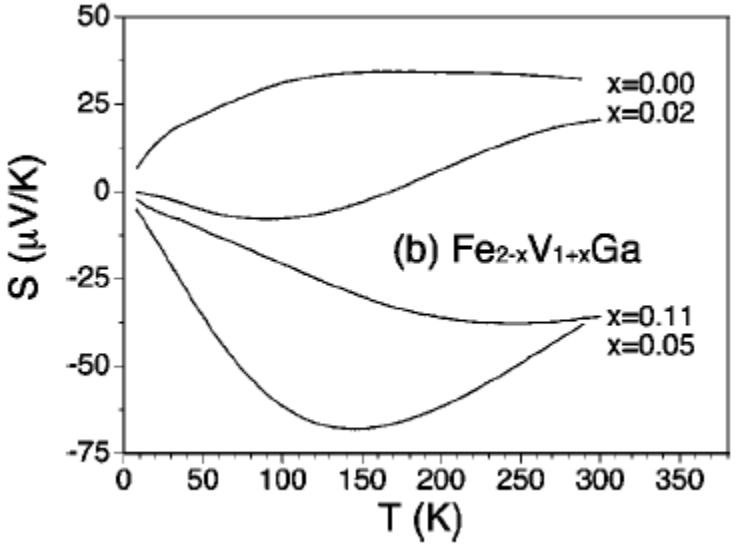


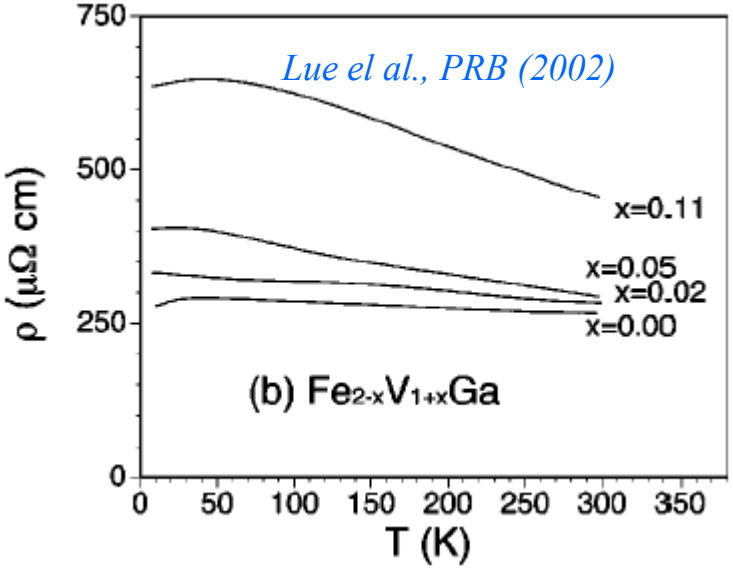
*Bansil,...JT, PRB 60(1999) 13397*

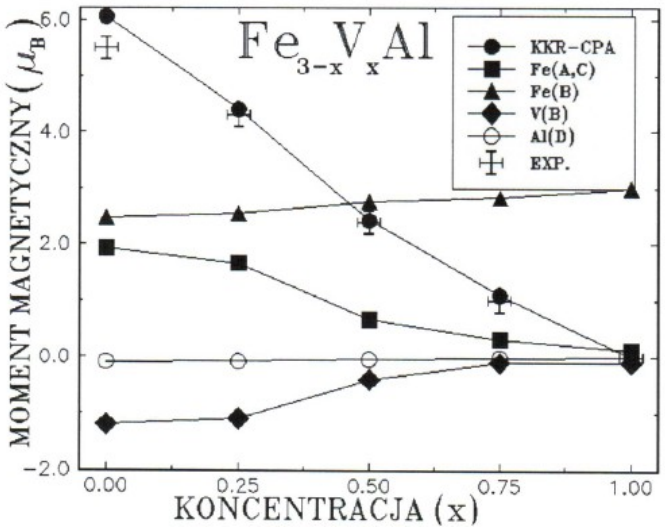
$Fe_2VSi$ $Fe_2VGa$ $Fe_2VAl$




experiments



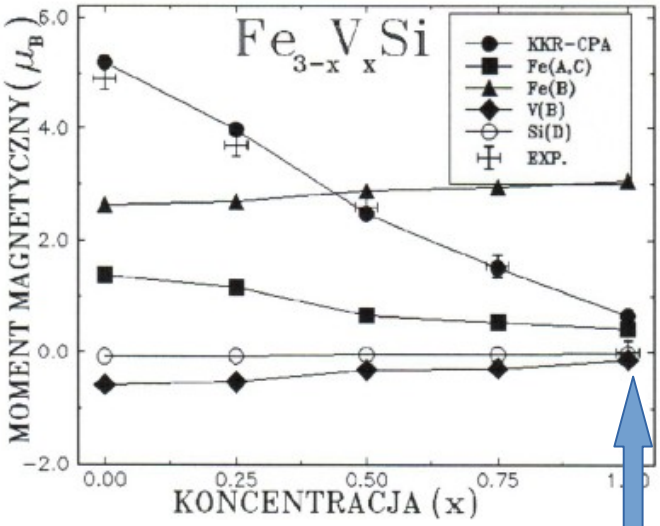


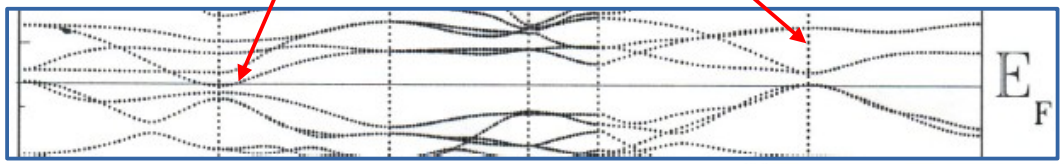

**$Fe_2VSi$**
weak ferromagnet

VEC=25

**$Fe_2VAl$**
pseudogap

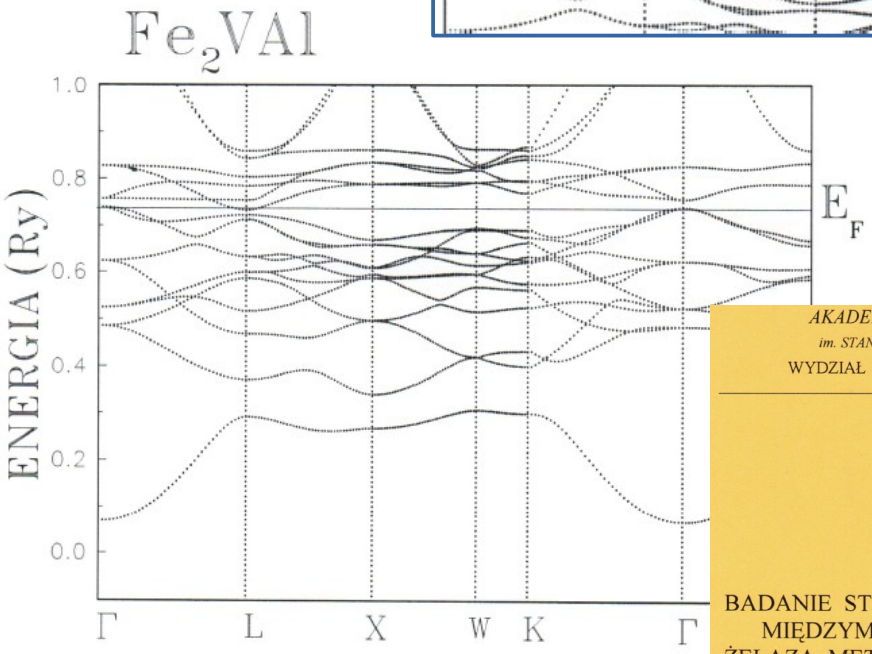
VEC=24

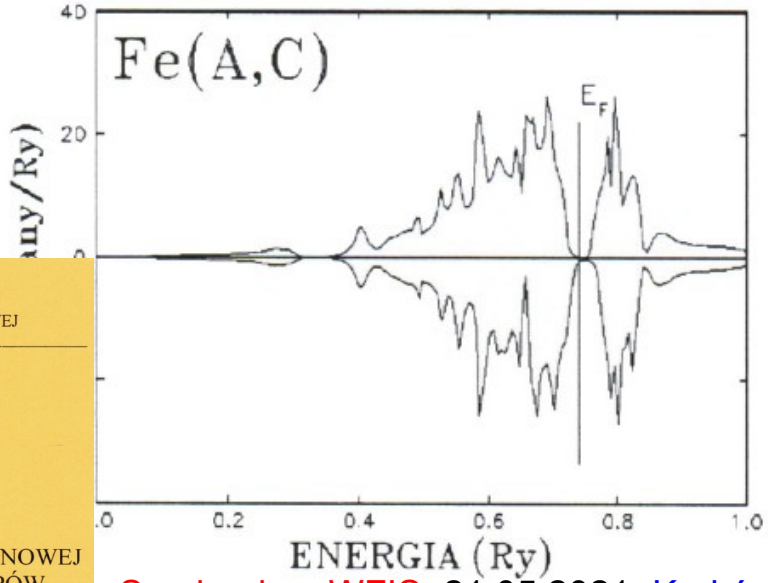



$0.37\mu_B$ (exp)

$0.42\mu_B$ (theory)




AKADEMIA GÓRNICZO-HUTNICZA
im. STANISŁAWA STASZICA w KRAKOWIE
WYDZIAŁ FIZYKI I TECHNIKI JĄDROWEJ

*Praca doktorska*

1994

Janusz Toboła

BADANIE STRUKTURY ELEKTRONOWEJ MIĘDZYMETALICZNYCH STOPÓW ŻELAZA METODAMI TEORII PASMOWEJ

Nature | Vol 576 | 5 December 2019 | 85

B. Hinterleitner[1,2,9], I. Knapp[1,2,9], M. Poneder[1,2,9], Yongpeng Shi[3,4,9], H. Müller[1], G. Eguchi[1], C. Eisenmenger-Sittner[1], M. Stöger-Pollach[1,5], Y. Kakefuda[6], N. Kawamoto[6], Q. Guo[6,7], T. Baba[6,7], T. Mori[6,7,8], Sami Ullah[3], Xing-Qiu Chen[3,4] & E. Bauer[1,2,9]*

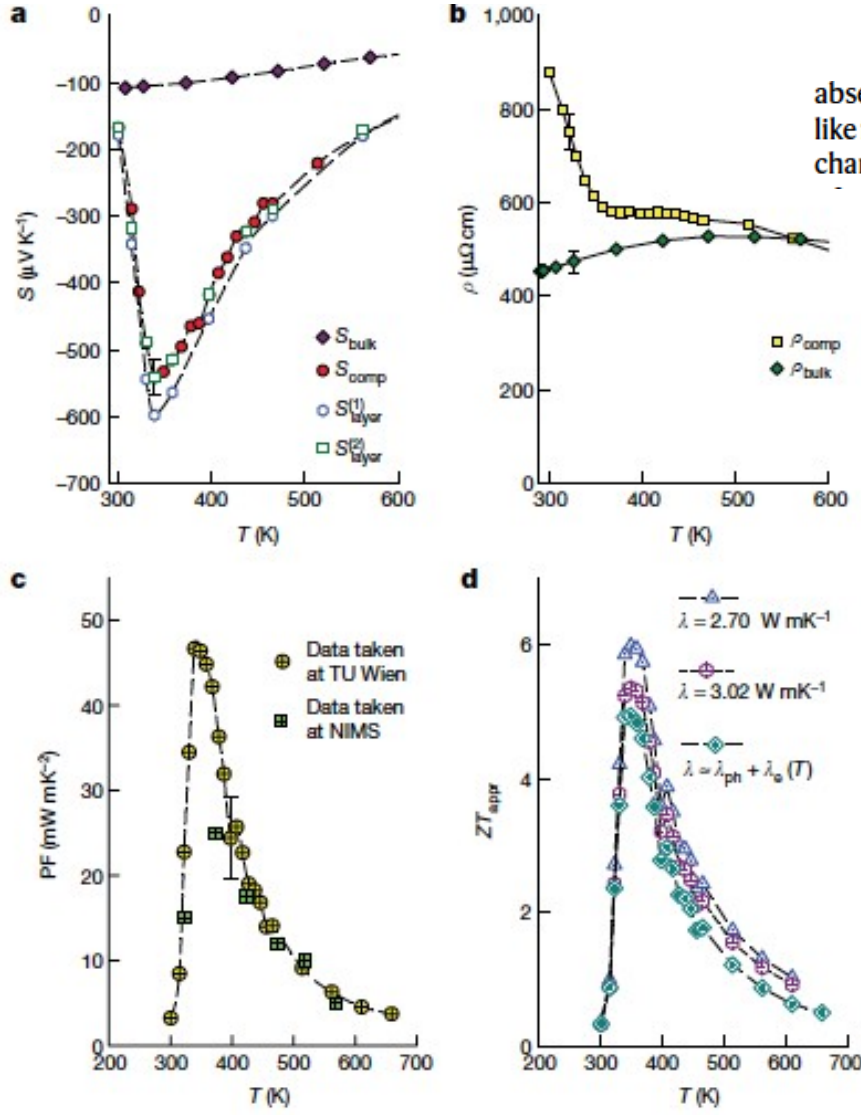
Article

# Thermoelectric performance of a metastable thin-film Heusler alloy

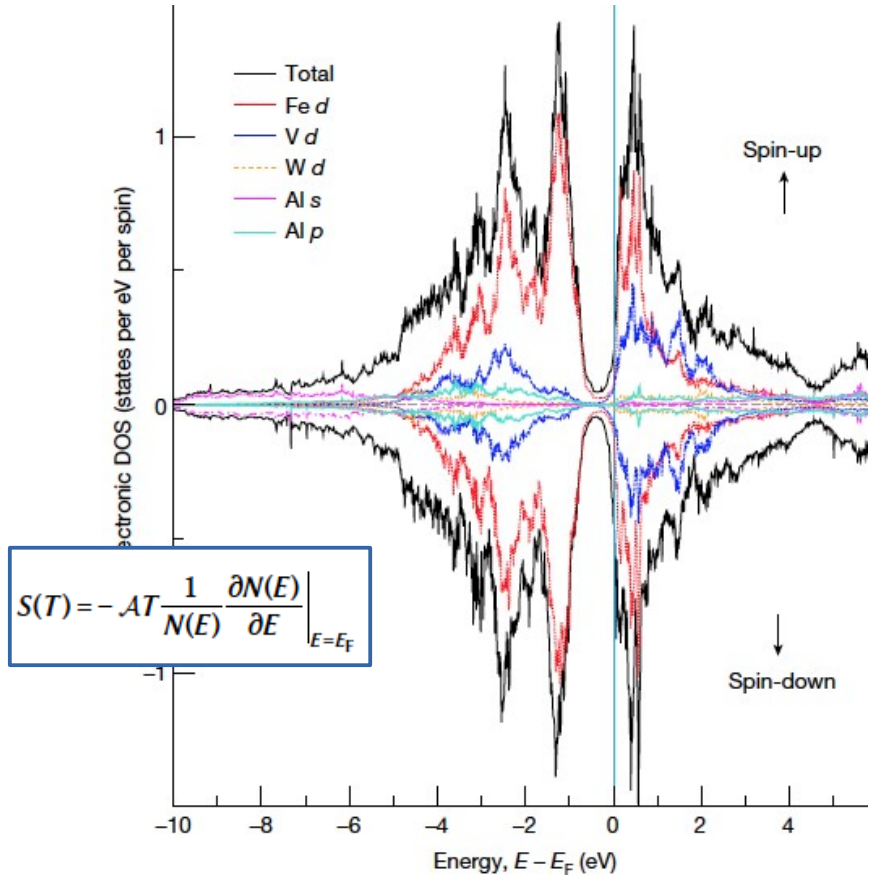
$Fe_2(V\text{-}W)Al$

**ZT ~ 6 !!!**

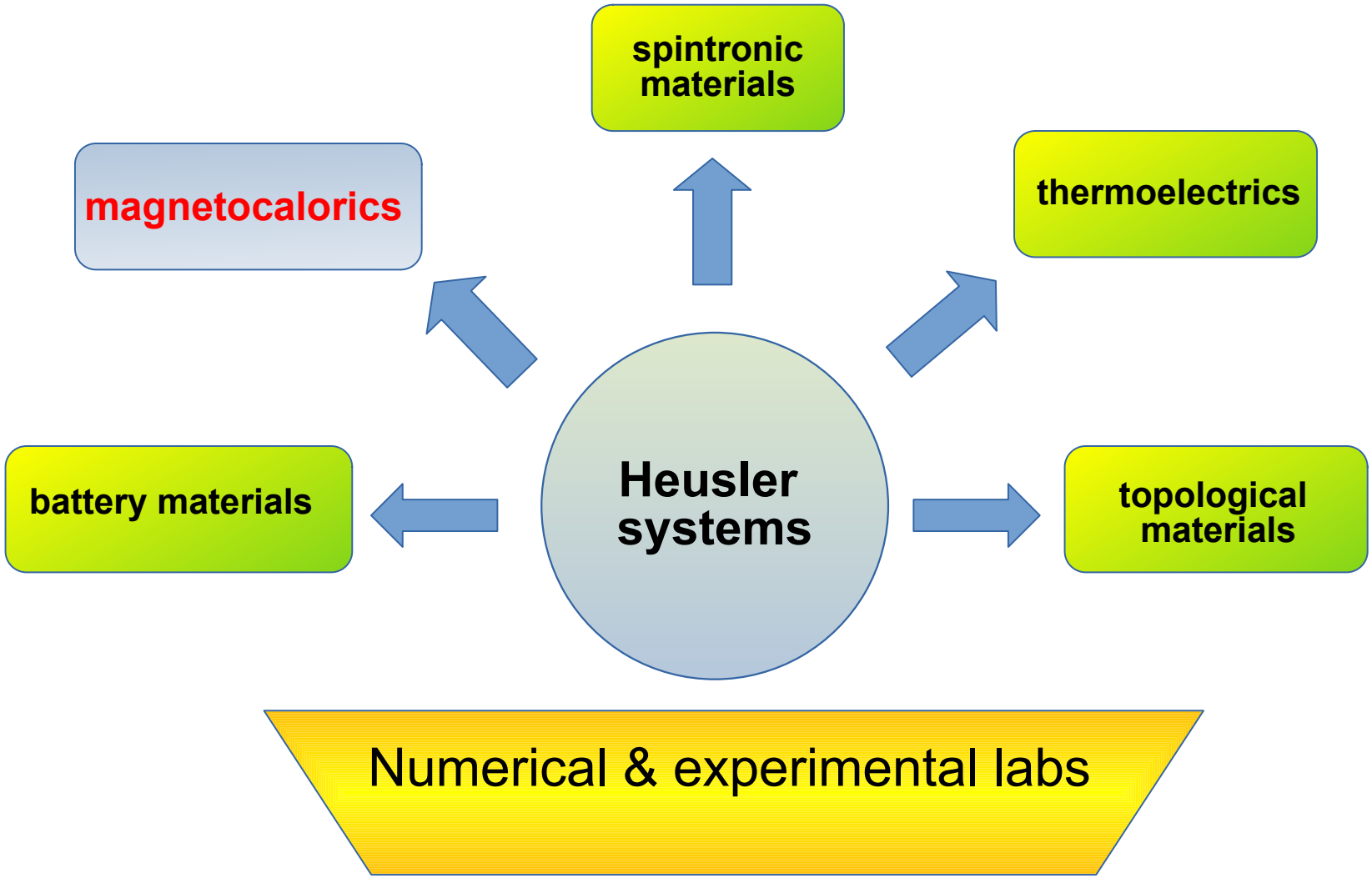
**the largest ZT ever measured**




absent. In other words, bcc-type $Fe_2V_{0.8}W_{0.2}Al$ exhibits potential Weyl-like fermions around the Fermi level for both the spin-up and spin-down channels, thereby leading to a possible profound, non-trivial topology




$$S(T) = -\mathcal{A}T\frac{1}{N(E)}\frac{\partial N(E)}{\partial E}\bigg|_{E=E_F}$$


spintronic materials
magnetocalorics
thermoelectrics
Heusler systems
battery materials
topological materials
Numerical & experimental labs

# Brief history of MCE discovery

1881 E. Warburg, iron heats up in magnetic field ~0.5-2 K/1T, Ann. Phys. (1881)

1926 P. Debye (Nobel 1936, chemistry)

1927 W. Giauque (Nobel 1949, chemistry)

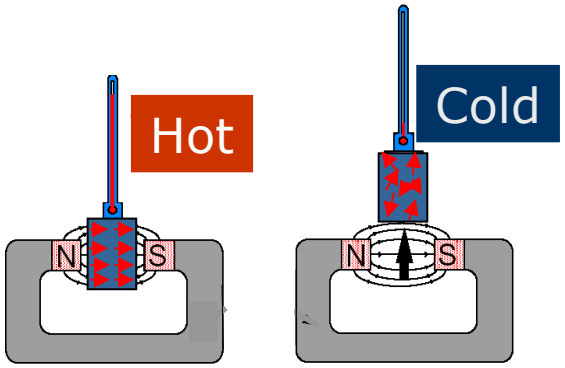
cooling via adiabatic demagnetization (order-disorder transition of magnetic moments in presence (or not) of magnetic field; for cryogenic purposes, down to 0.25 K (MacDougall, 1933).

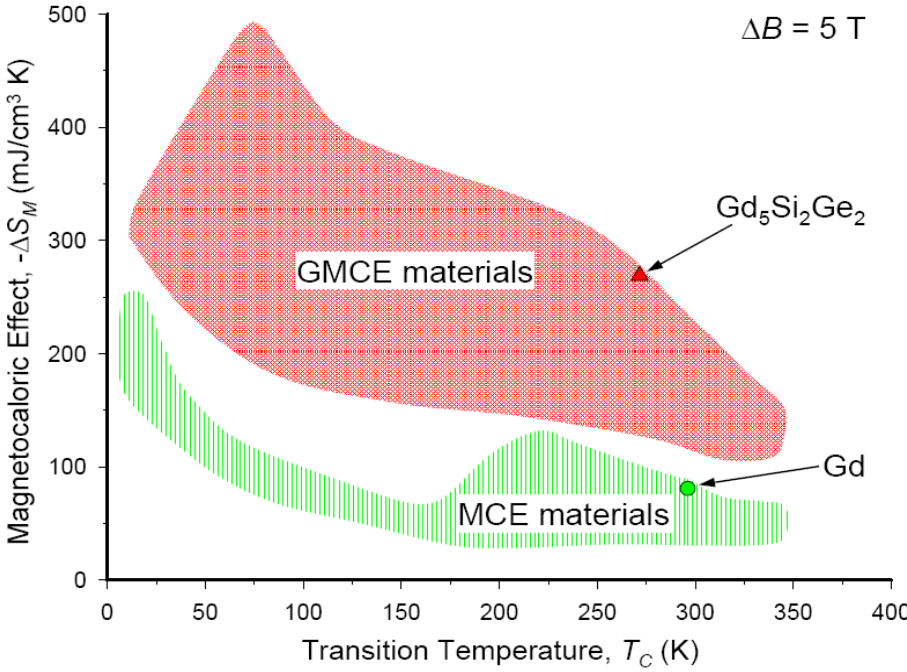
1997 K. A. Gschneider & V. Pecharsky (Ames Lab., USA), PRL (1997) - discovery of giant magnetocaloric effect :

MCE: an intrinsic property of magnetic materials;

MCE : the largest at the transition temperature, e.g. ferro-para

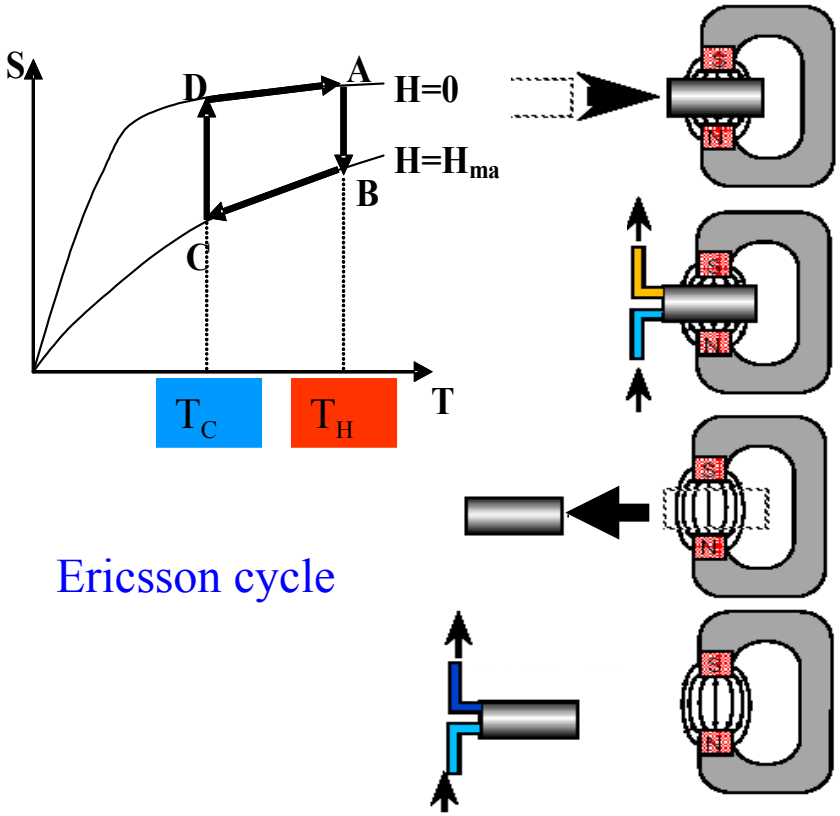
Adiabatic magnetization / demagnetisation



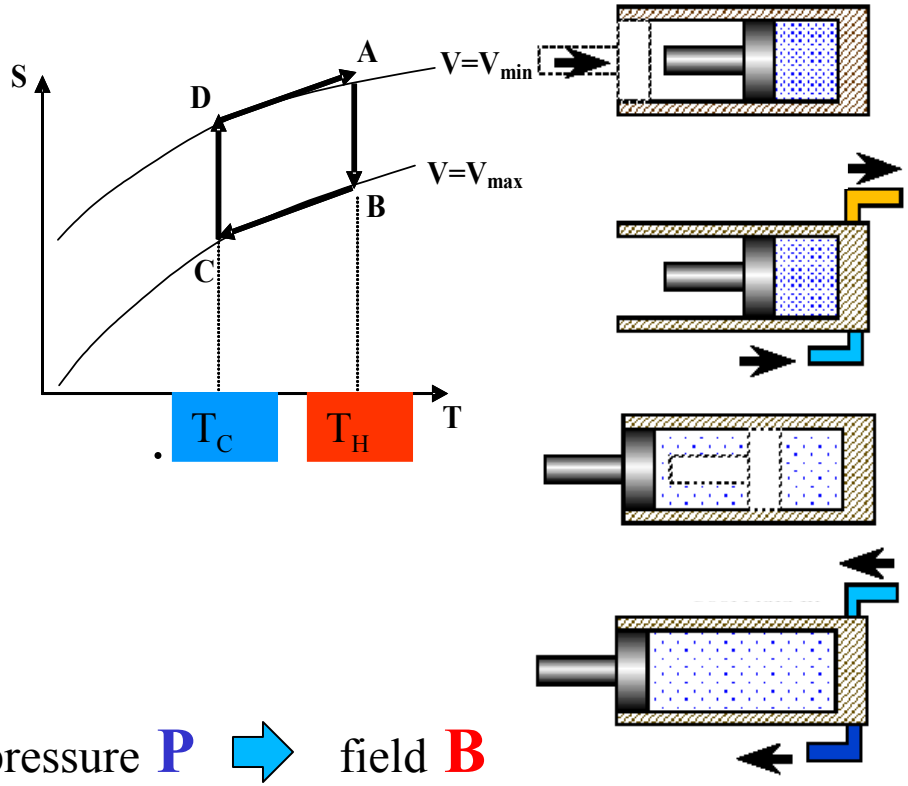



# Analogy to thermodynamic cycle

## Adiabatic magnetization/demagnetization




Ericsson cycle




pressure **P** ⇨ field **B**

volume **V** ⇨ magnetization **M**

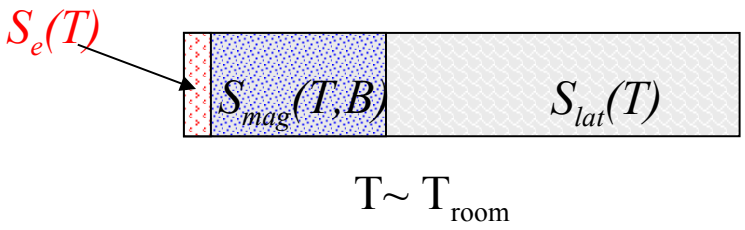
$$B \cdot (M_1 - M_2) = \Delta S \cdot \Delta T = -\mathrm{RCP}$$

Ideal Carnot cycle :

$$\eta = \frac{\Delta W}{\Delta Q_H} = 1 - \frac{T_C}{T_H} \qquad \Delta W = \oint P dV = (T_H - T_C)(S_B - S_A)$$

$$\Delta Q_C = T_C(S_B - S_A)$$
$$\Delta Q_H = T_H(S_B - S_A)$$

# Entropy




$$S_{tot} = S_{el} + S_{mag} + S_{lat}$$

$$\Delta S_{mag} + \Delta S_{lat} = 0$$

**Adiabatic Process**

$$\Delta S_{mag}(T,\Delta B) = \int_0^B \left( \frac{\partial M}{\partial T} \right)_B dB$$

$$\Delta S_{lat} = C_p(B,T) \frac{\Delta T}{T}$$

$$\Delta T_{max} = \frac{-T\Delta S_{mag}}{C_p(B,T)}$$

Calorific Capacity $C_p(B,T)$

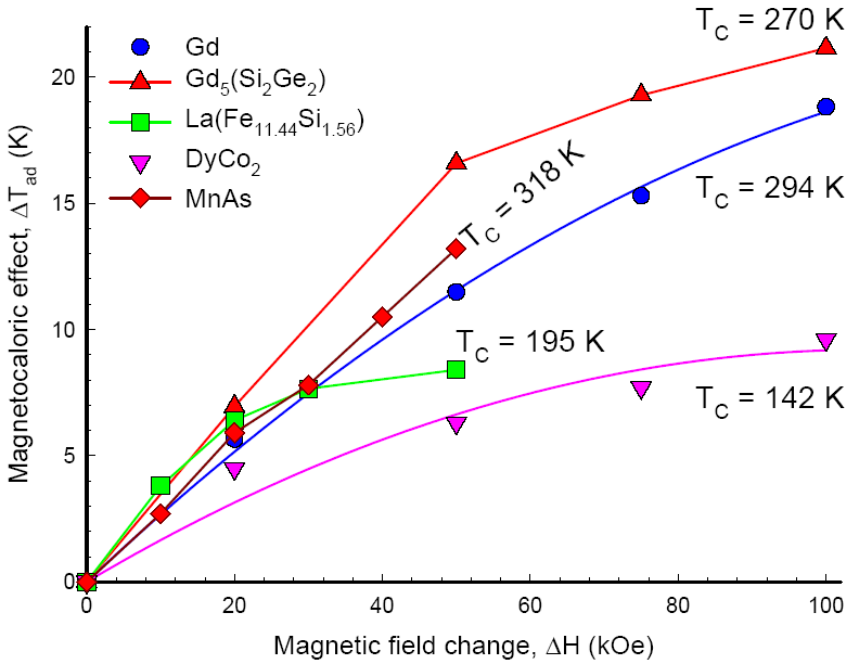
↓

Magnetic Entropy $\Delta S_{mag}$

↓

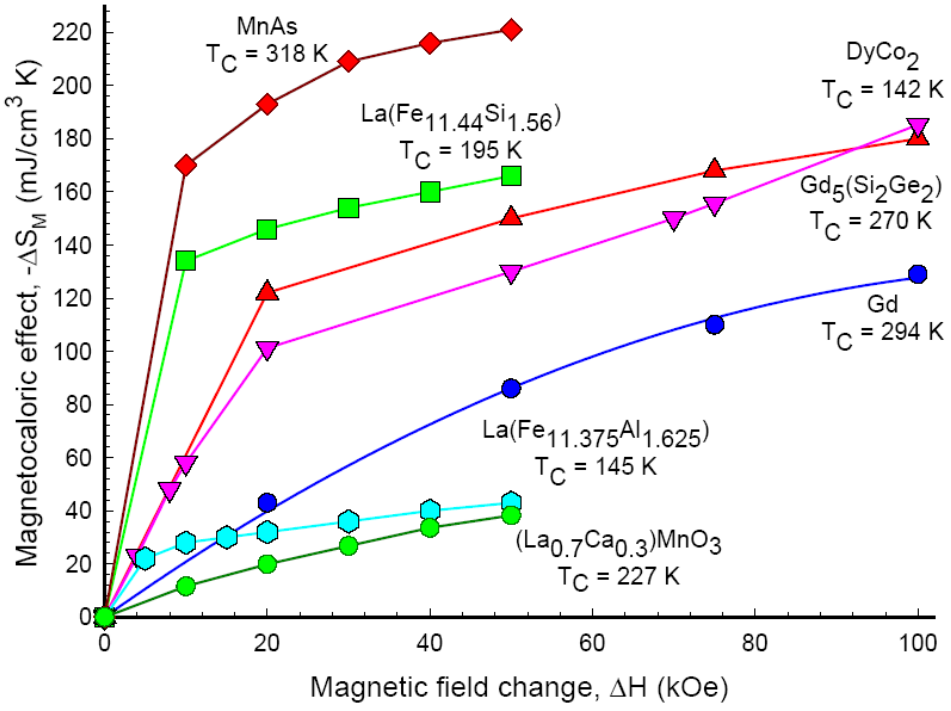
$\Delta T_{max}$

# New MCE materials

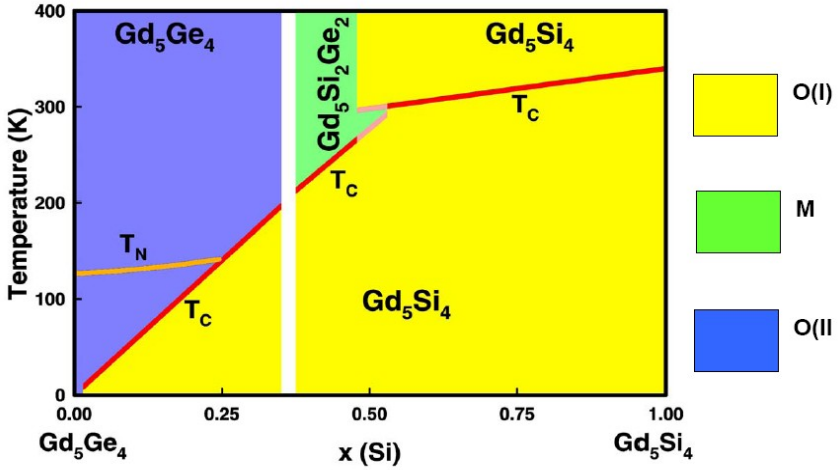



Temperature jump

From K Gschneider

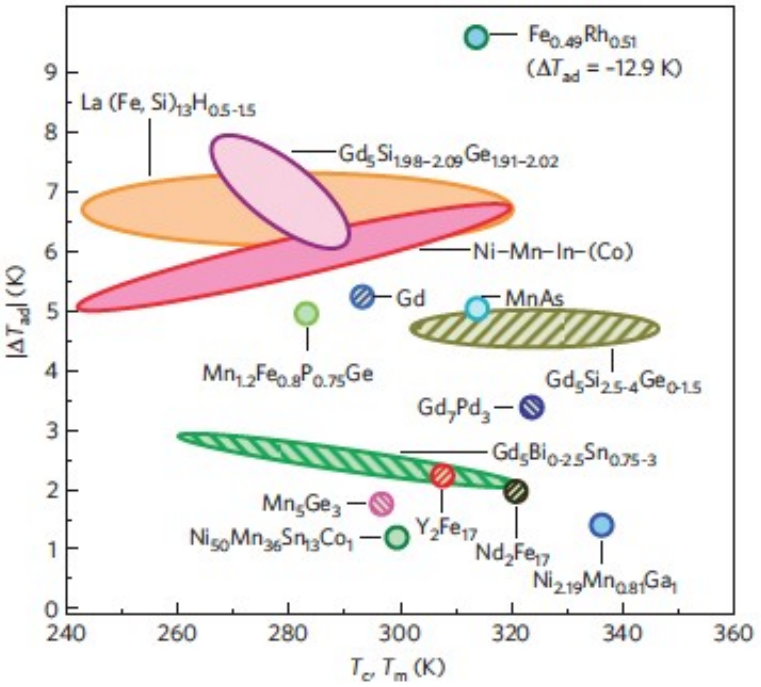


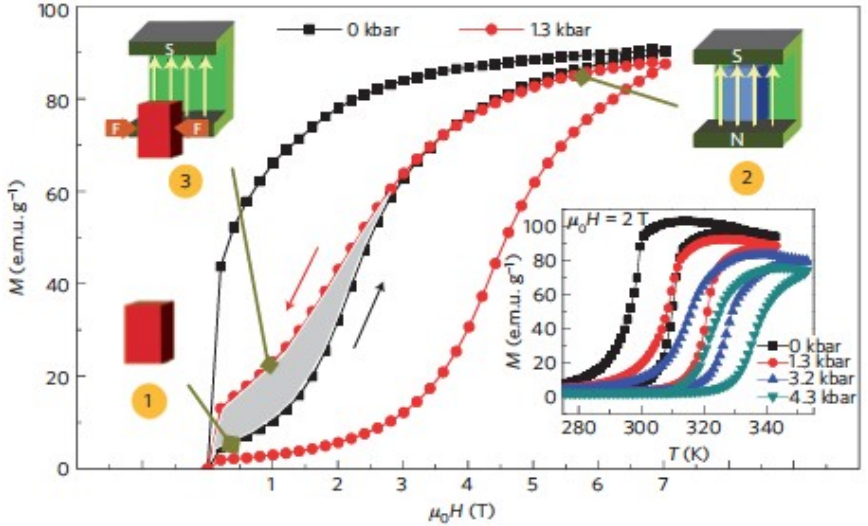

Entropy jump

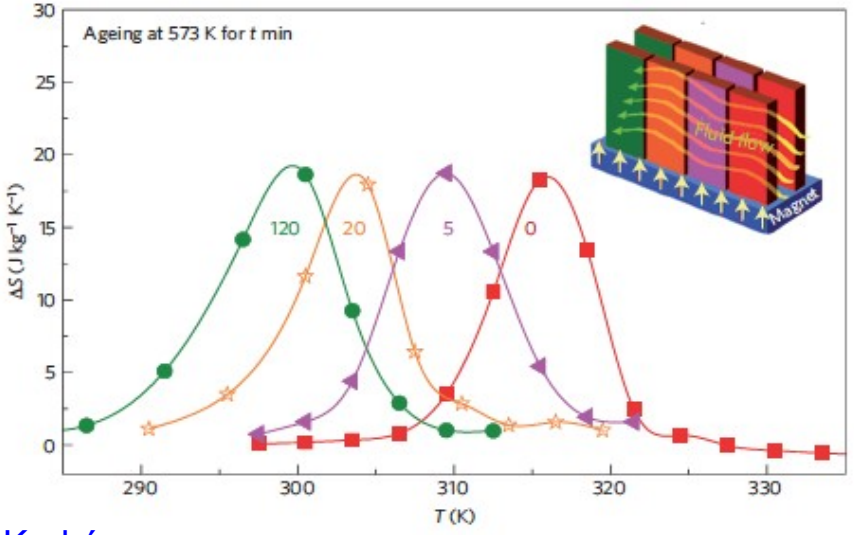


# Heusler systems as magneticaloric materials

## $Ni_2MnIn$ + Co magnetic shape memory alloys



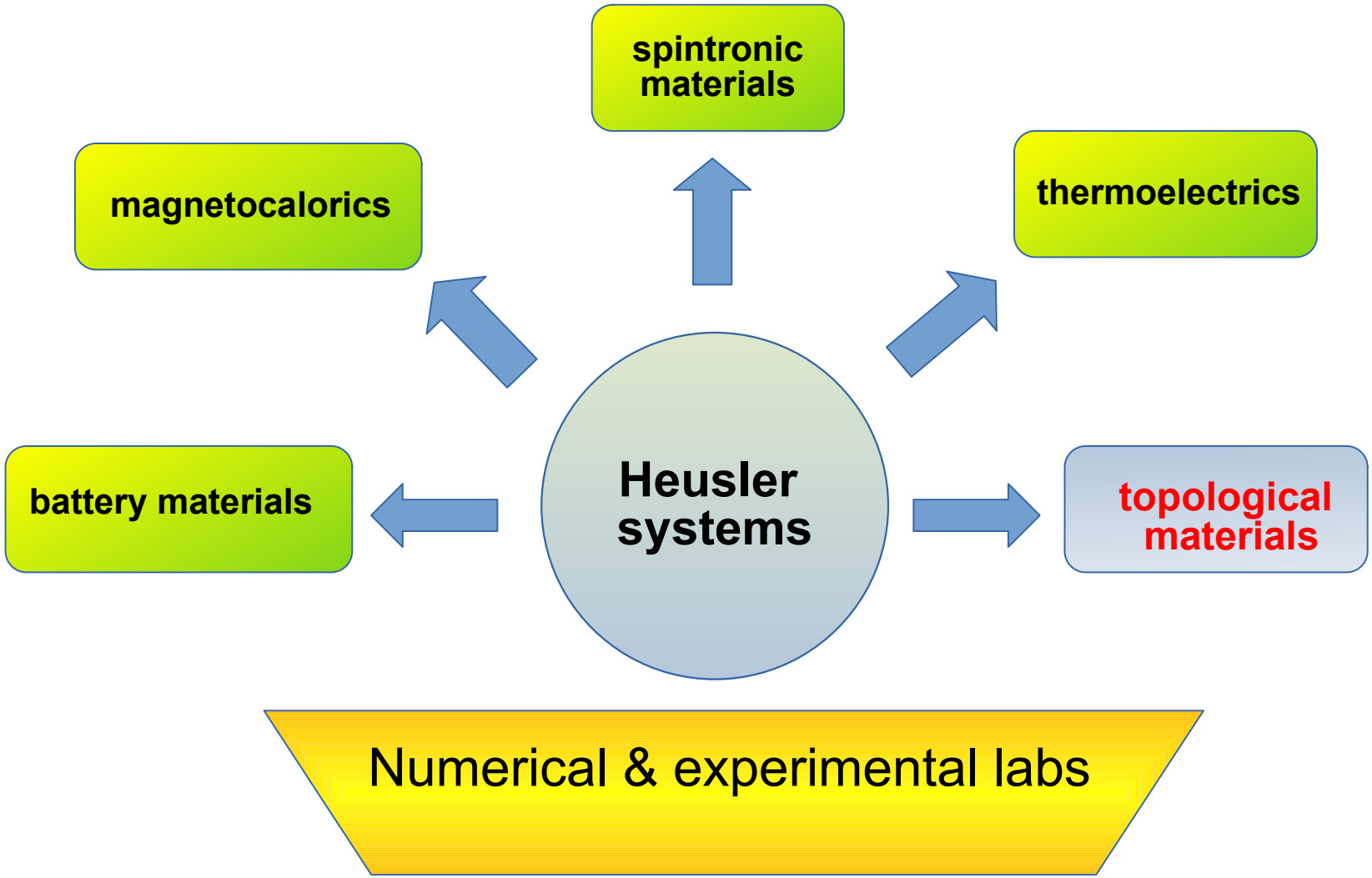



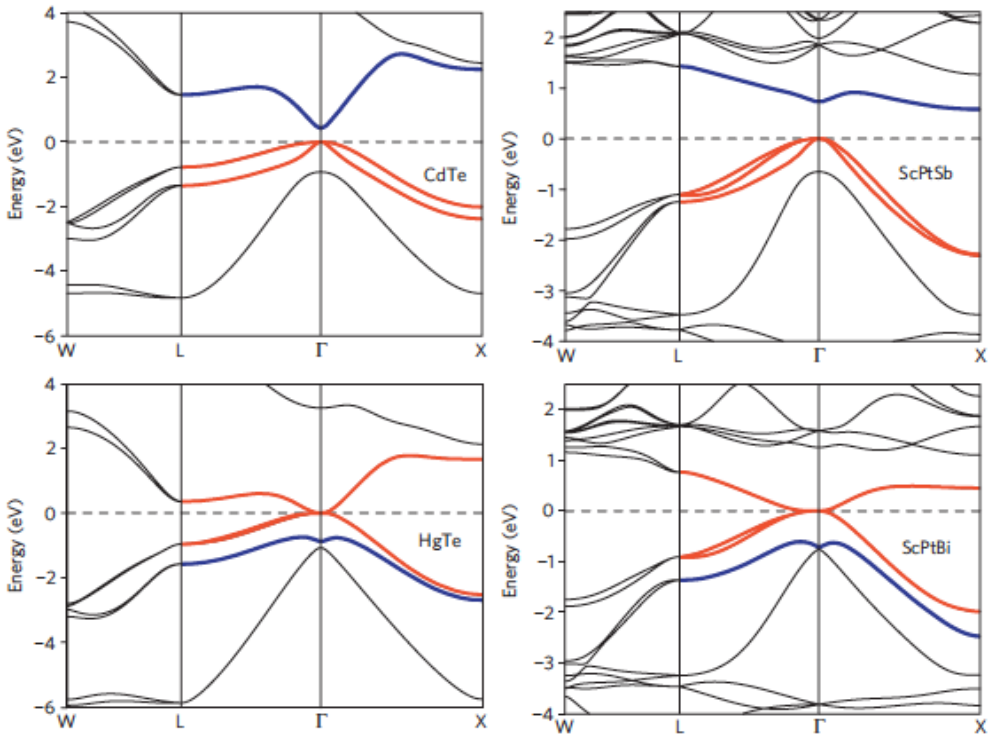



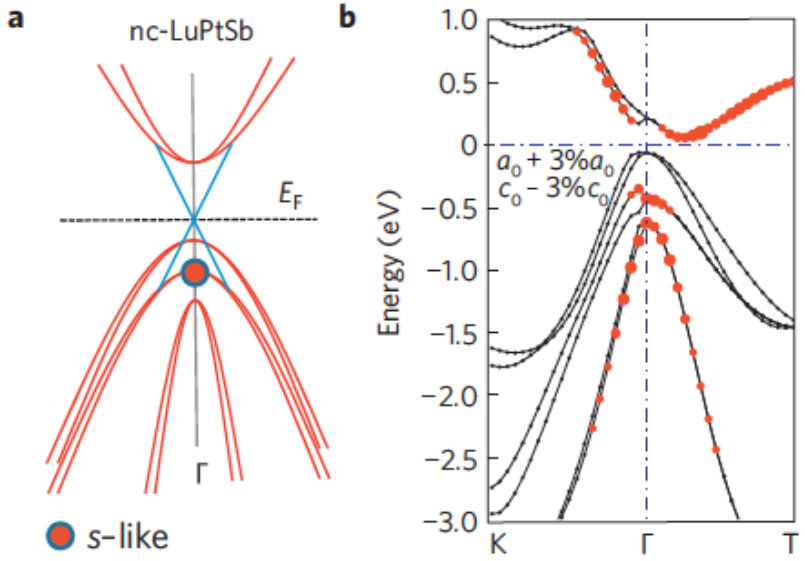

ARTICLES
PUBLISHED ONLINE: 27 MAY 2012 | DOI: 10.1038/NMAT3334
nature materials

**Giant magnetocaloric effect driven by structural transitions**

Jian Liu[1]*, Tino Gottschall[1]*, Konstantin P. Skokov[1], James D. Moore[1] and Oliver Gutfleisch[1,2]


spintronic materials
magnetocalorics
thermoelectrics
Heusler systems
battery materials
topological materials
Numerical & experimental labs

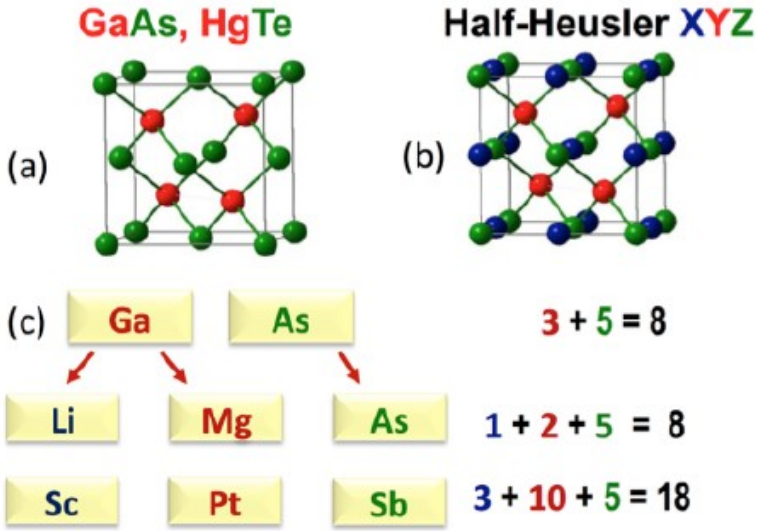



nature materials
LETTERS
PUBLISHED ONLINE: 30 MAY 2010 | DOI: 10.1038/NMAT2770

# Tunable multifunctional topological insulators in ternary Heusler compounds

Stanislav Chadov[1], Xiaoliang Qi[2,3], Jürgen Kübler[4], Gerhard H. Fecher[1], Claudia Felser[1]* and Shou Cheng Zhang[3]*

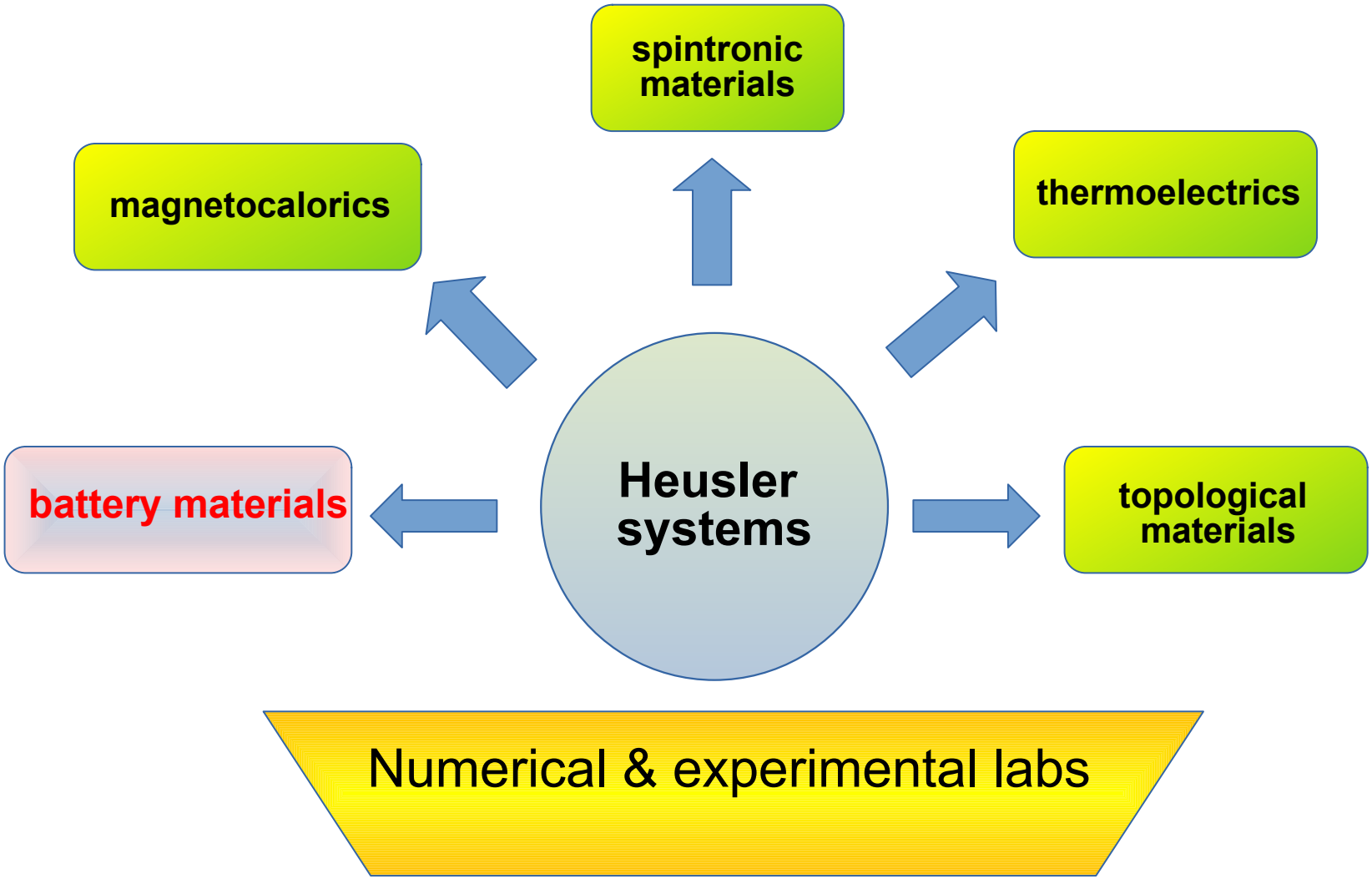



from: B. Yan & A. de Visse

LETTERS
PUBLISHED ONLINE: 30 MAY 2010 | DOI: 10.1038/NMAT2771
nature materials

# Half-Heusler ternary compounds as new multifunctional experimental platforms for topological quantum phenomena

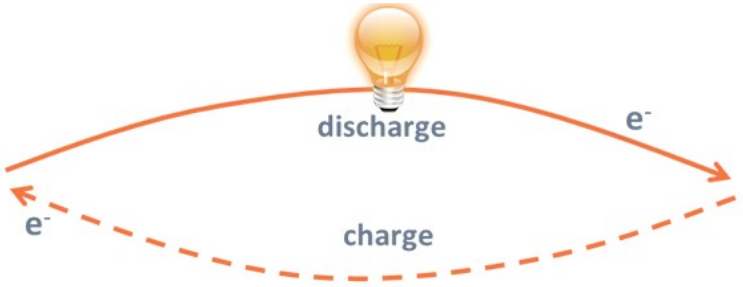
Hsin Lin[1], L. Andrew Wray[2], Yuqi Xia[2], Suyang Xu[2], Shuang Jia[3], Robert J. Cava[3], Arun Bansil[1] and M. Zahid Hasan[2,4,5]*

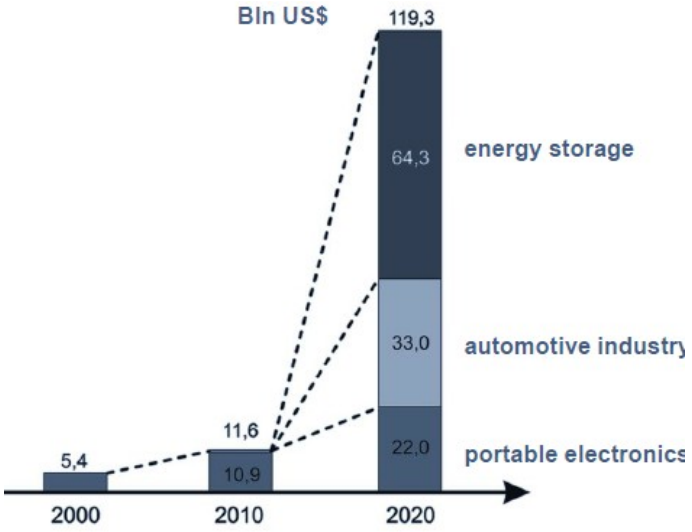

spintronic materials
magnetocalorics
thermoelectrics
battery materials
Heusler systems
topological materials
Numerical & experimental labs

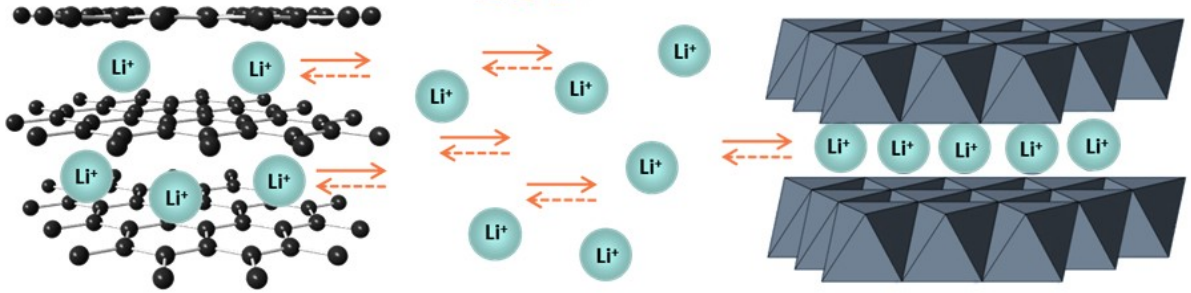
# Li-ion battery cathode materials

Must be gradually replaced by Na-ion battery?

***world's resources of Li likely insufficient...***



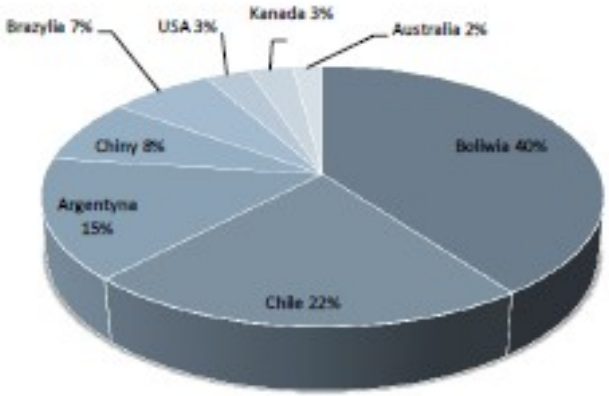

graphite anode
$Li_xC_6$

elektrolyte
$Li^+$

cathode
$Li_{1-x}CoO_2$

$C_6 + xLi^+ + xe^- \leftrightarrow Li_xC_6$

$Li_1CoO_2 - xLi^+ - xe^- \leftrightarrow Li_{1-x}CoO_2$



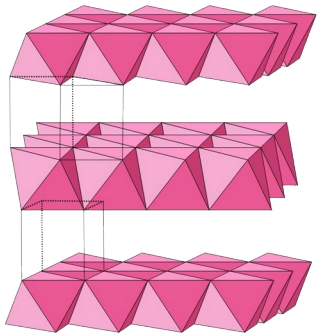

Global lithium reserves

Kim et al. Adv. Energy Mater. 2 (2012) 860.

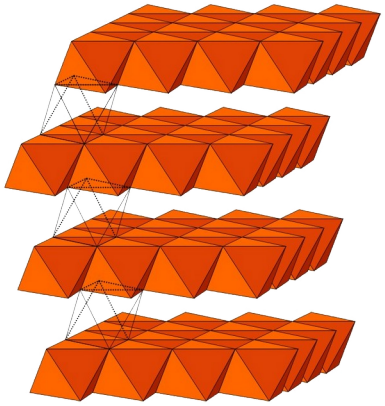
from J. Molenda

# Types of crystal structure capable for alkaline-ion intercalation

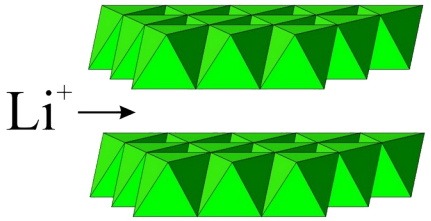
$Na_xCoO_2$



$LiCoO_2$

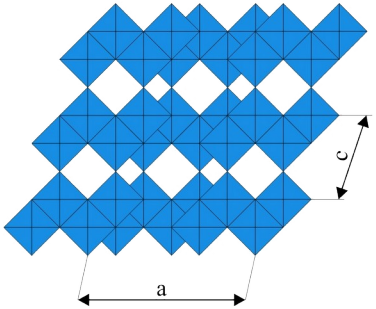


$TiS_2$

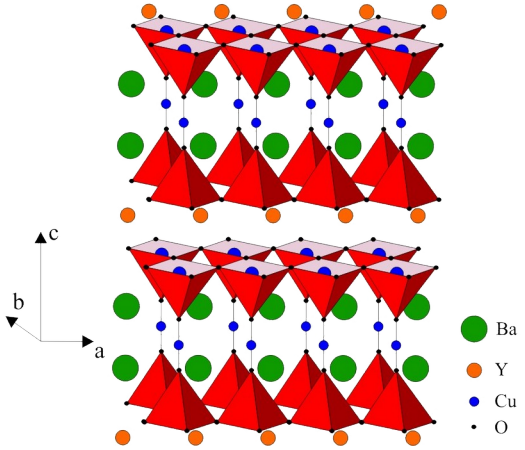



$xLi^+ + xe^- + M_aX_b \Leftrightarrow Li_xM_aX_b$ (M = transition metal, X = O, S)

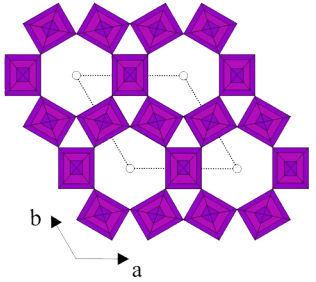
$VO_2$




$YBa_2Cu_3O_7$




$WO_3$




From J. Molenda

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# Heusler alloys as battery materials?

Short communication

## Electrochemical behaviour of Heusler alloy $Co_2MnSi$ for secondary lithium batteries

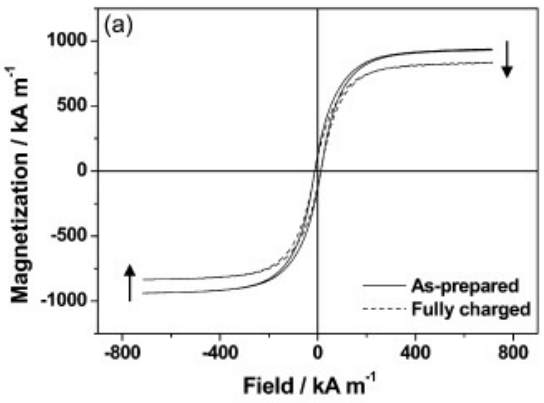
Jun H. Park[a], Dae H. Jeong[a], Sang M. Cha[a], Yang-Kook Sun[b], Chong S. Yoon

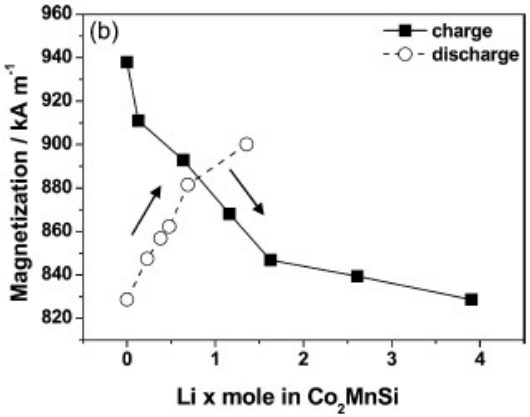
[a] Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea
[b] Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

$$2Li + Co_2MnSi \rightarrow Li_2MnSi + 2Co$$

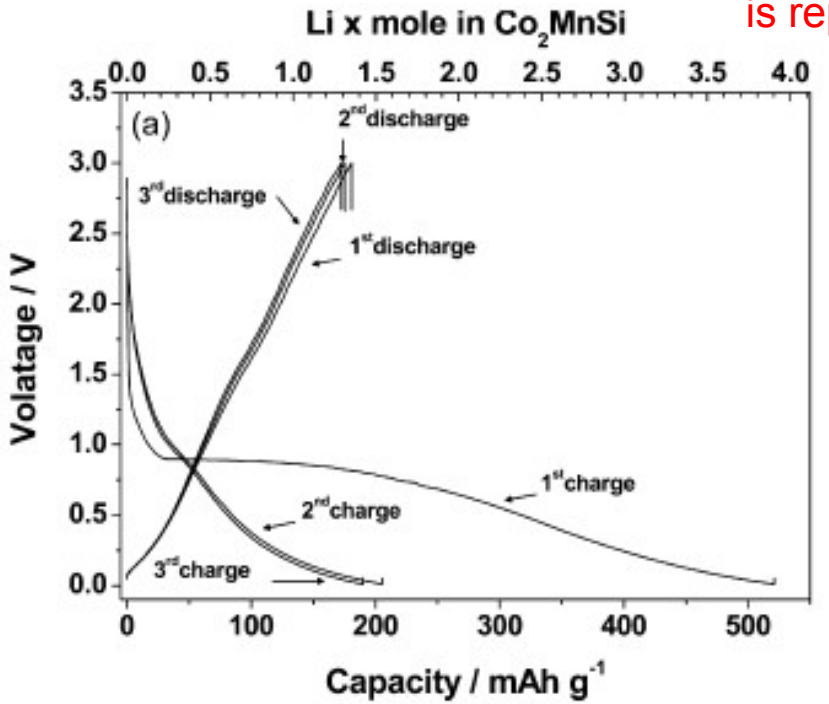
$$Li_2MnSi \rightarrow xLi + Li_{2-x}MnSi \quad (1st discharge)$$

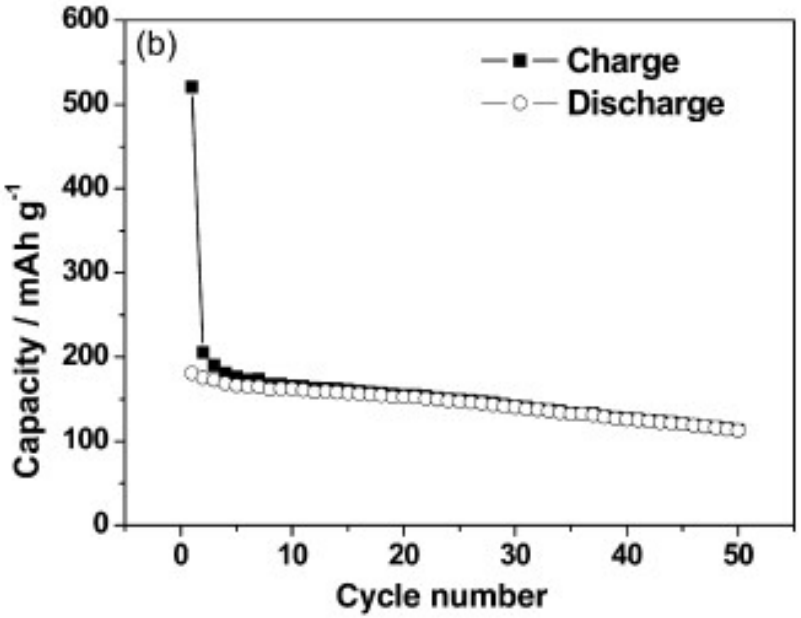
$$Li_{2-x}MnSi + xLi \rightarrow Li_2MnSi \quad (2nd charge)$$




Li may substitue Co or Mn, depending on relative chemical potentials
BUT magnetisation measurements confirm that Co is replaced



# Summary

Heusler alloys exhibit outstanding variety of physical properties, which are related to particular interplay of electronic structure features and crystal structure.

The fact that 3, 4 (or more) different atoms occupy 4 equivalent *fcc* sublattices seems to be responsible for exceptional richness of observed physical behaviors, but also result in a presence of different forms of disorder (chemical, topological).

The properties “on request” of Heusler alloys can be easily tunable, controllable by using external fields (temperature, magnetic field, electric field, stress), doping, substitution, which already opened many opportunities for their applications.

AGH

# Collaboration

**S. Kaprzyk, K. Kutorasiński**
*AGH University of Science and Technology, Kraków, Poland*

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*Universite H. Poincare & CNRS, Nancy, France*

**L. Jodin, P. Pecheur, H. Scherrer**
*Ecole des Mines & CNRS, Nancy, France*

**J. Pierre, D. Fruchart, M. Kouacou**
*Polygone Scientifique CNRS, Grenoble, France*

**R. Skolozdra**
*I. Franko University, Lviv, Ukraine*

**K. Kaczmarska**
*Institute of Physics, Silesian University, Katowice, Poland*

Dziękuję za uwagę