JOHANNES GUTENBERG UNIVERSITÄT MAINZ

moment
Materials for Optical, Magnetic and Energy Technologies

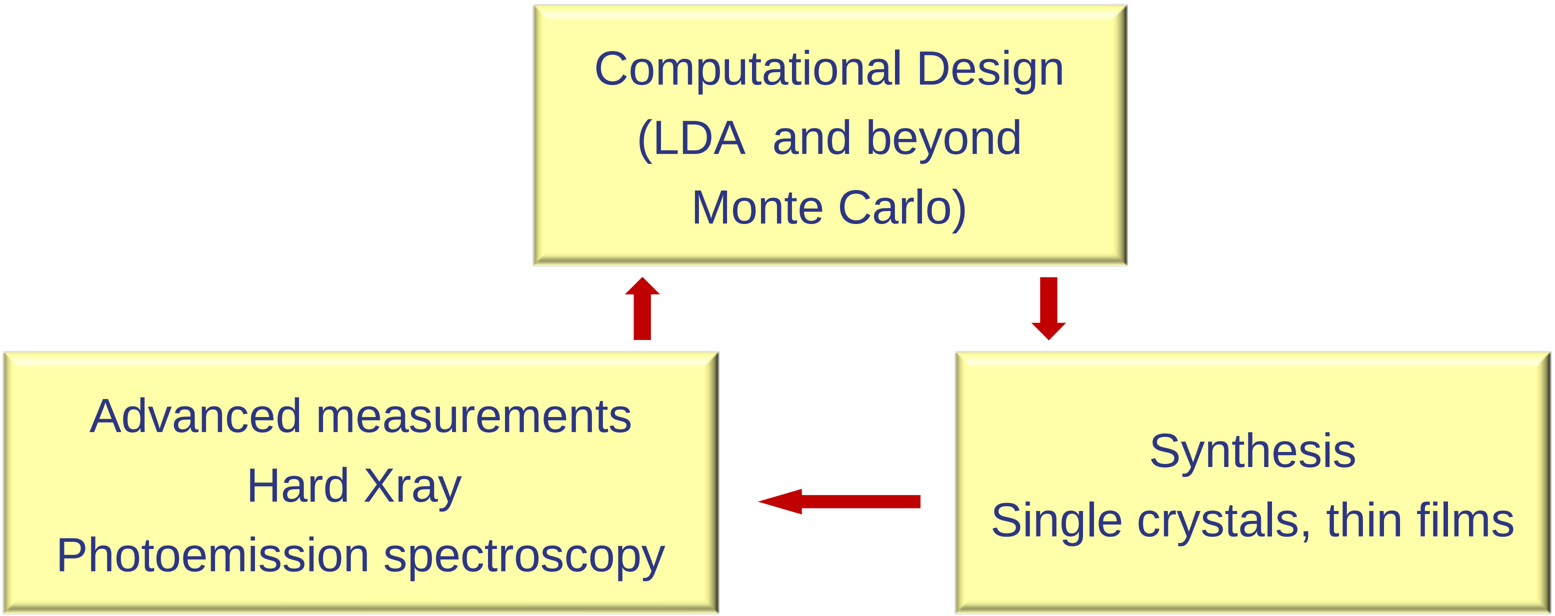
Heusler Compounds for Thermoelectric and Spincaloric Applications

Claudia Felser

www.superconductivity.de

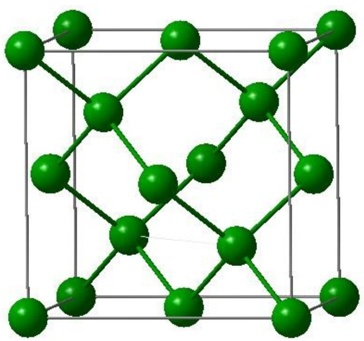
Concept

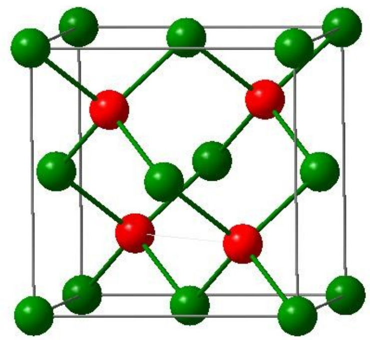
Goal: Directed Design of new functional Materials

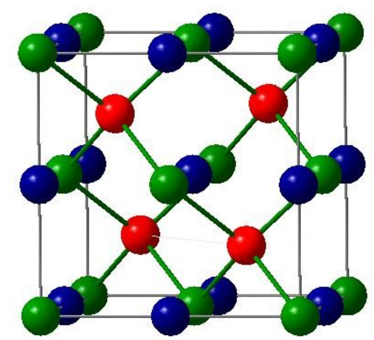


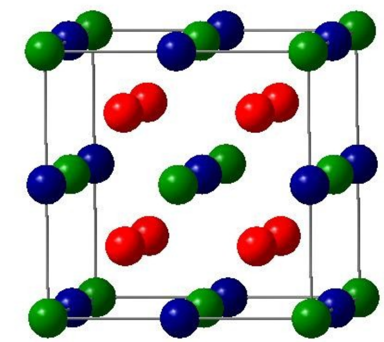
Heusler compounds

Diamond | **ZnS** | **Heusler XYZ $C1_b$** | **X_2YZ $L2_1$**









C 2.55	N 3.04
Si 1.90	P 2.19
Ge 2.01	As 2.18
Sn 1.96	Sb 2.05

H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89		Hf 1.30	Ta 1.50	W 1.70	Re 1.90	Os 2.20	Ir 2.20	Pt 2.20	Au 2.40	Hg 1.90	Tl 1.80	Pb 1.80	Bi 1.90	Po 2.00	At 2.20	Rn
Fr 0.70	Ra 0.90																
			La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.20	Gd 1.20	Tb 1.10	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.10	Lu 1.27
			Ac 1.10	Th 1.30	Pa 1.50	U 1.70	Np 1.30	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.30	Cf 1.30	Es 1.30	Fm 1.30	Md 1.30	No 1.30	Lr 1.30

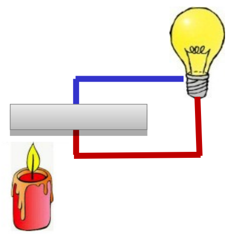
Graf T, Felser C, Parkin SSP, IEEE TRANSACTIONS ON MAGNETICS 47 (2011) 367

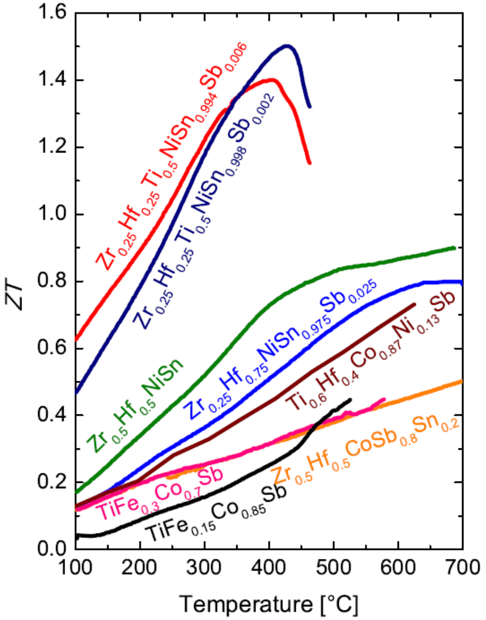
Graf T, Felser C, Parkin SSP, Progress in Solid State Chemistry (2011), doi:10.1016/j.progsolidstchem.2011.02.001

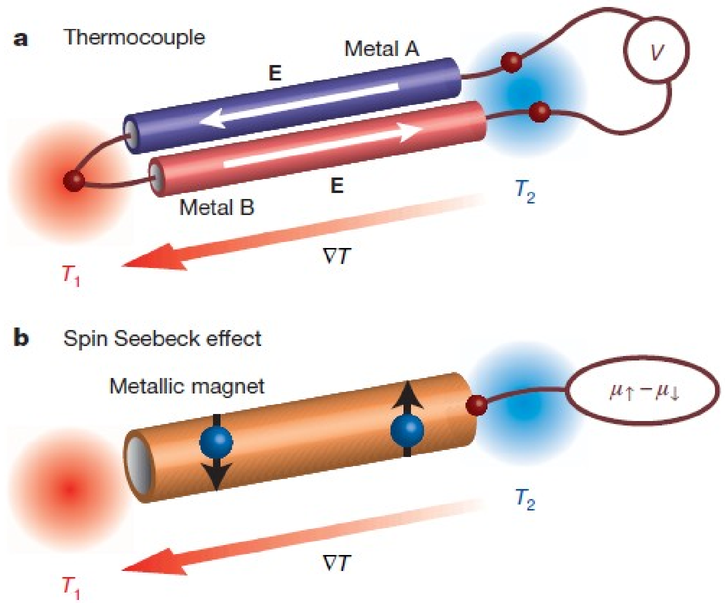
Thermoelectric and Spintronics

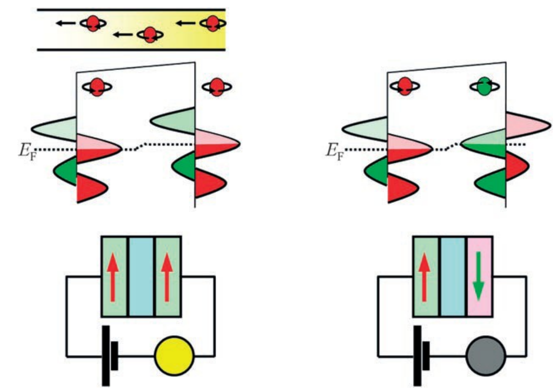
Observation of the spin Seebeck effect

K. Uchida[1], S. Takahashi[2,3], K. Harii[1], J. Ieda[2,3], W. Koshibae[4], K. Ando[1], S. Maekawa[2,3] & E. Saitoh[1,5]







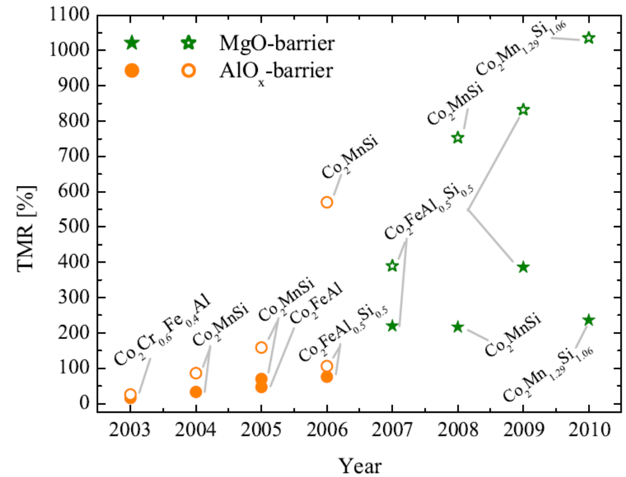


What do we need

High Seebeck coefficient

High Spinpolarization

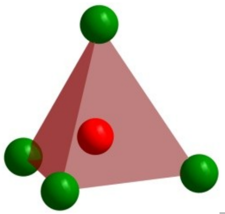
Tunable Spin Orbit coupling



K. Uchida, et al. Nature 455 (2008) 788

Counting electrons

From wide to low band gap semiconductor



Ga As

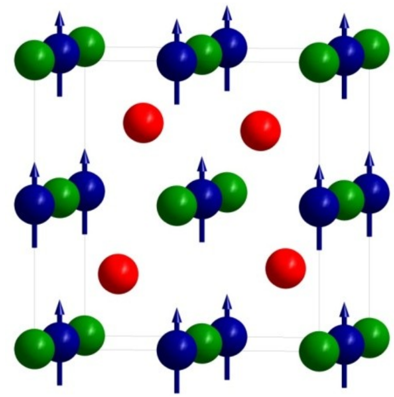
$13 + 5 = 18$

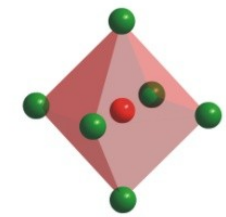
Li Mg As

$1 + 2 + 5 = 8$

Zr Ni Sn

$4 + 10 + 4 = 18$





Pt RE Bi

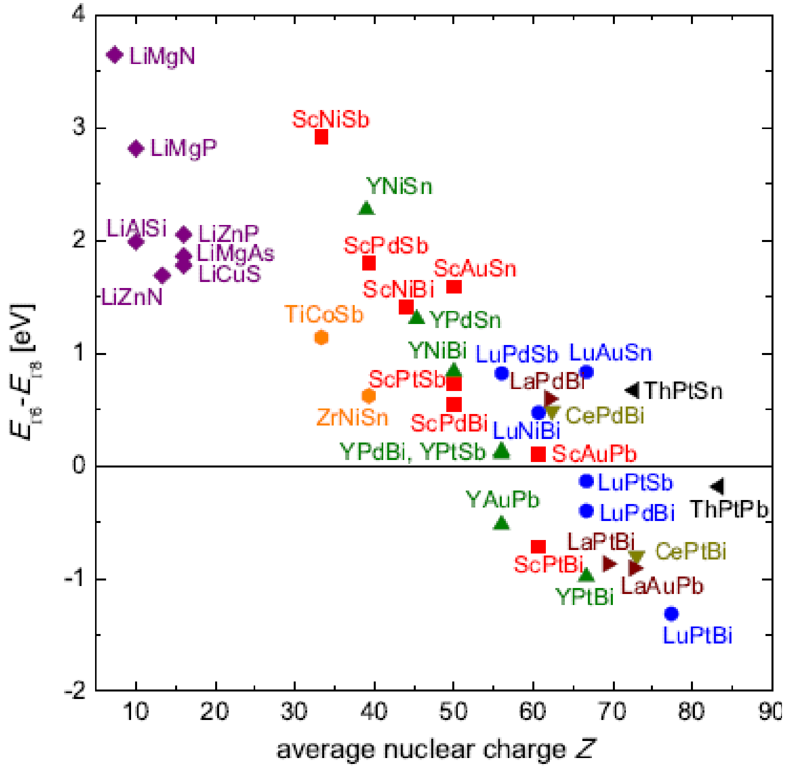
$10 + 3\ (+f^{n}) + 5 = 18 + n$

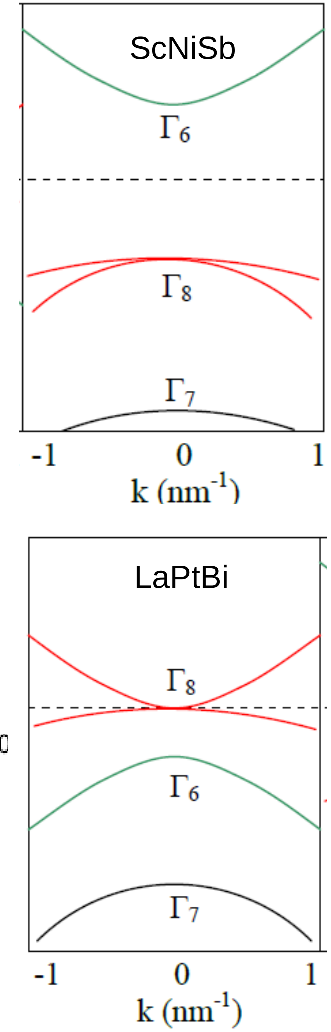
Pt Mn Bi

$10 + 3\ (+d^{4}) + 5 = 18 + 4$

Kandpal *et al.*, CF J. Phys. D **39** (2006) 776

Band gapsfrom 4 eV to zero



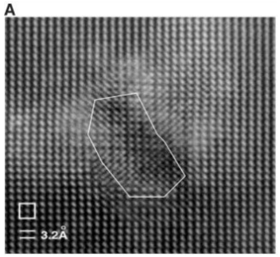


Both need

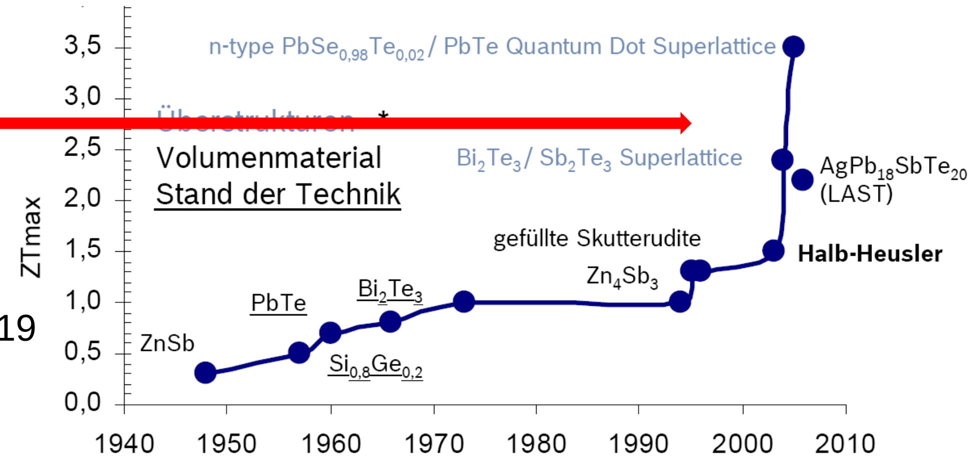
Low band gaps

High spin orbit coupling

Why Heuslers …



KF Hsu et al. Science 303 (2004) 819

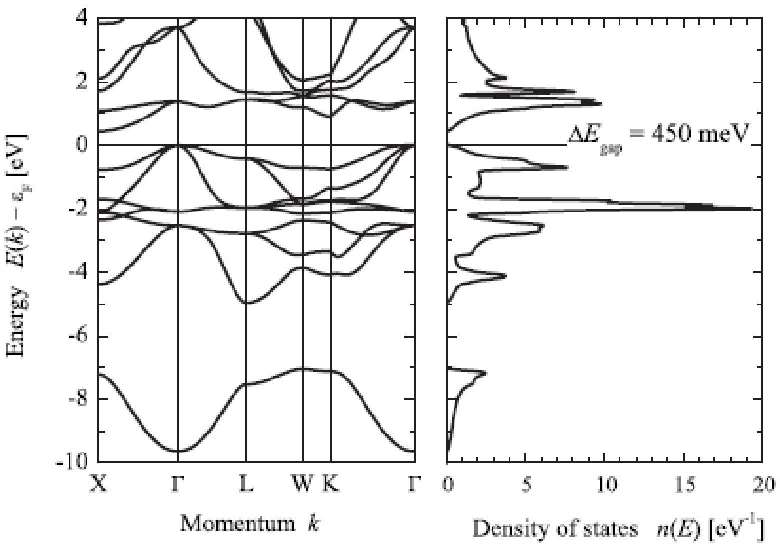


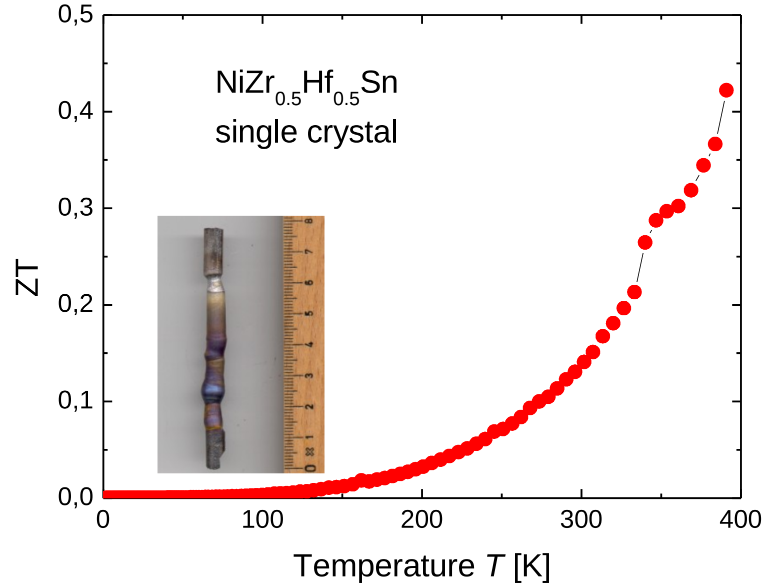
Typ	Material	Price in $/kg (metals)
V-VI	Bi_2Te_3	140
IV-VI	PbTe	99
Zn_4Sb_3	Zn_4Sb_3	4
Silicides	p-MnSi1.73	24
	n-$Mg_2Si_{0.4}Sn_{0.6}$	18
	$Si_{0.80}Ge_{0.20}$	660
	$Si_{0.94}Ge_{0.06}$	270
Skutterutides	$CoSb_3$	11
Half-Heusler	TiNiSn	55
n/p-Clathrate	$Ba_8Ga_{16}Ge_{30}$	1000 without Ba
Oxides	p-$NaCo_2O_4$,	17 without Na, O
Zintl Phasen	p-$Yb_{14}MnSb_{11}$	92
Th_3P_4	$La_{3-x}Te_4$	160

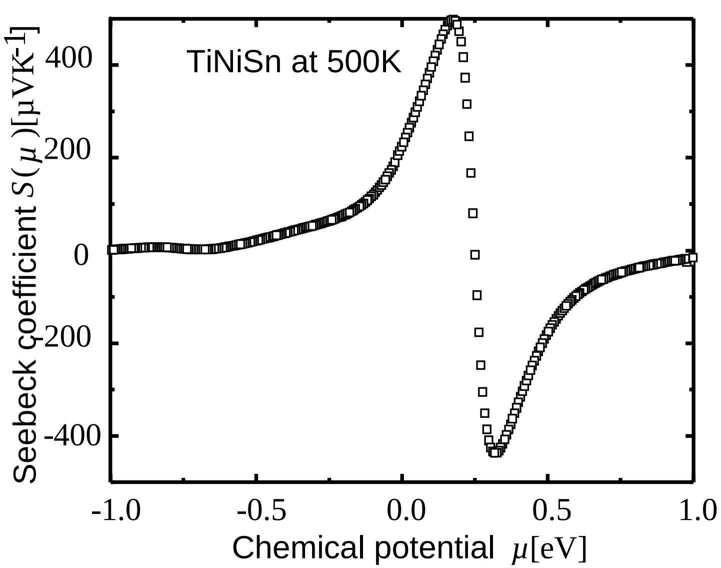
Fraunhofer Institut Physikalische Messtechnik

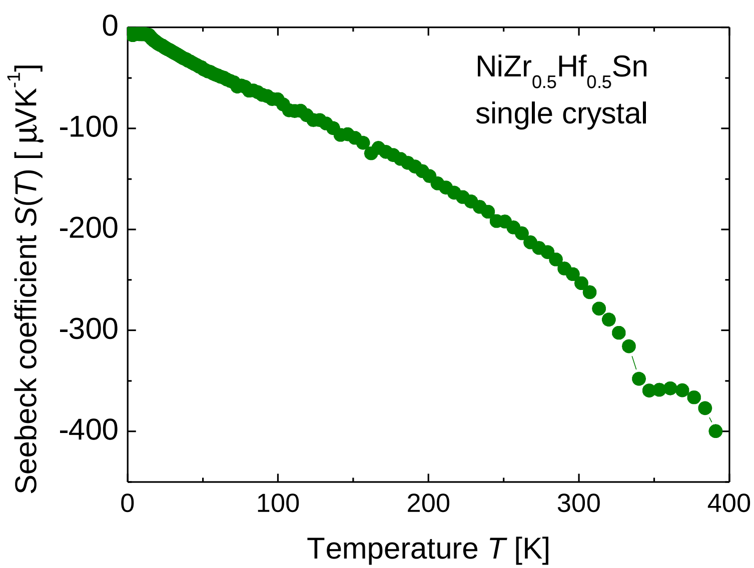
BOSCH

Band engineering



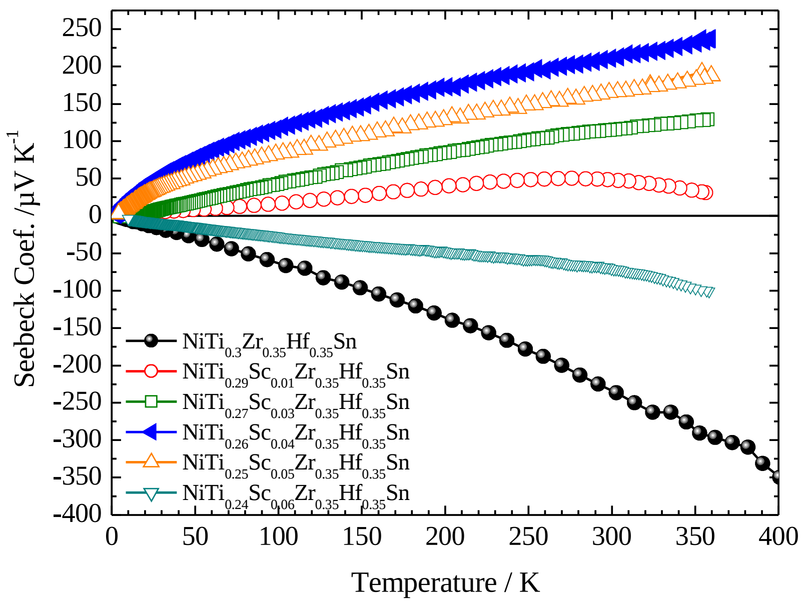






Band structure calculations:TB-LMTO 47 or Wien2k Code (DFT, GGA), Transport with the Boltz trap code

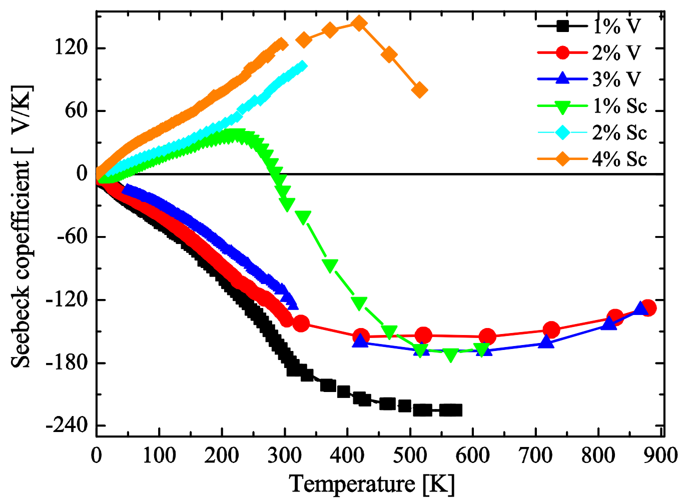
p-type NiTiSn with Hf, Zr doped with Sc

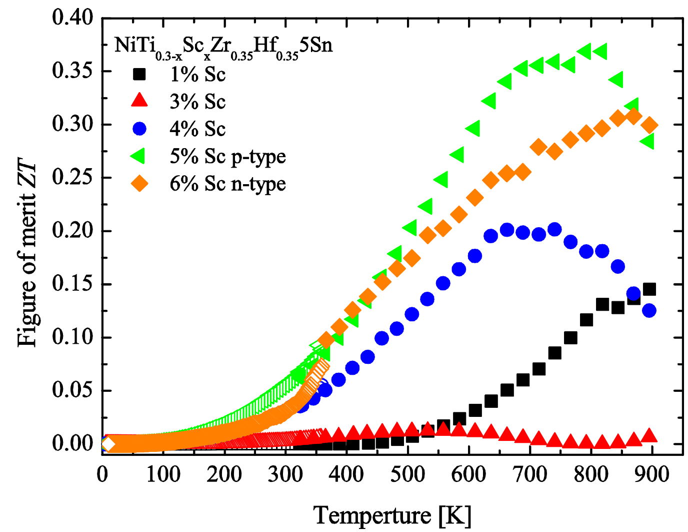


Resonable ZT for the p-type material at high T

Better than CoTiSb based materials

What is the problem? Thermal conductivity



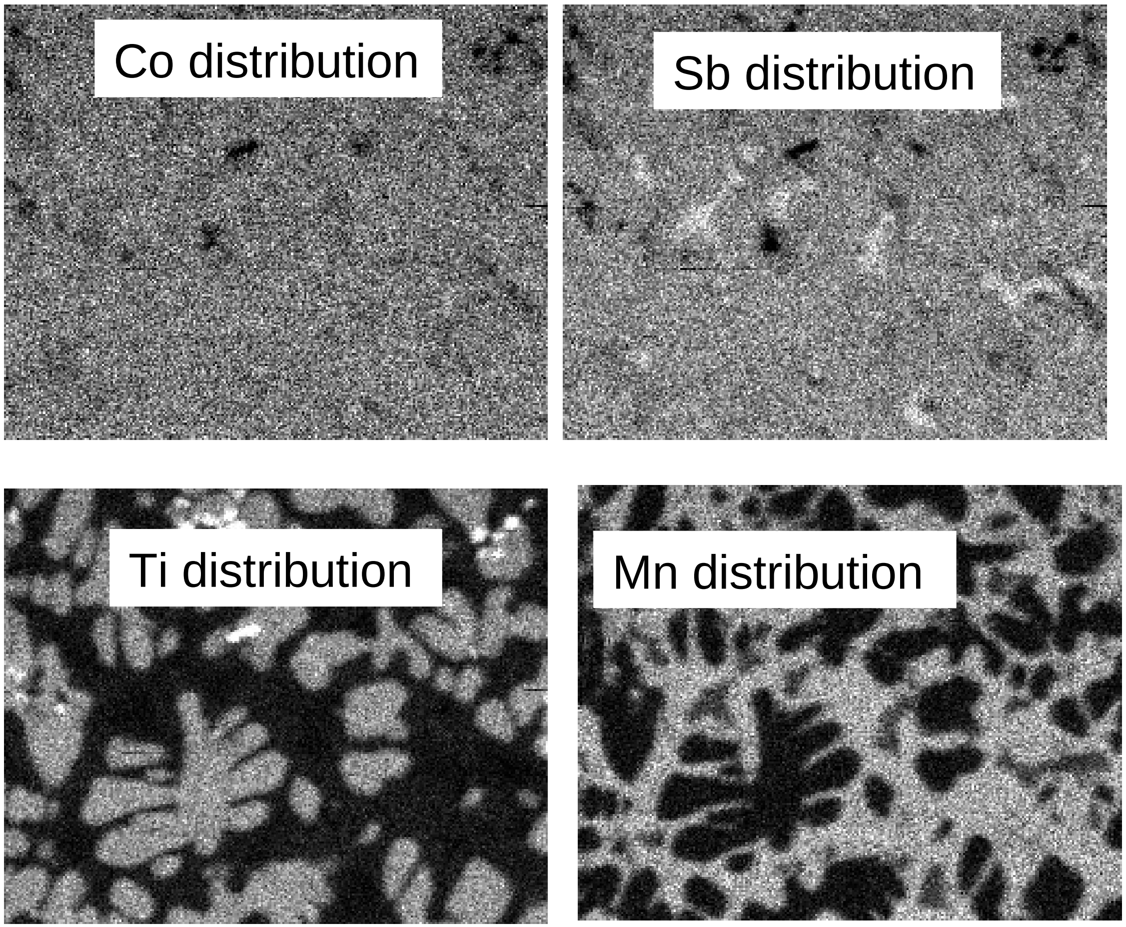


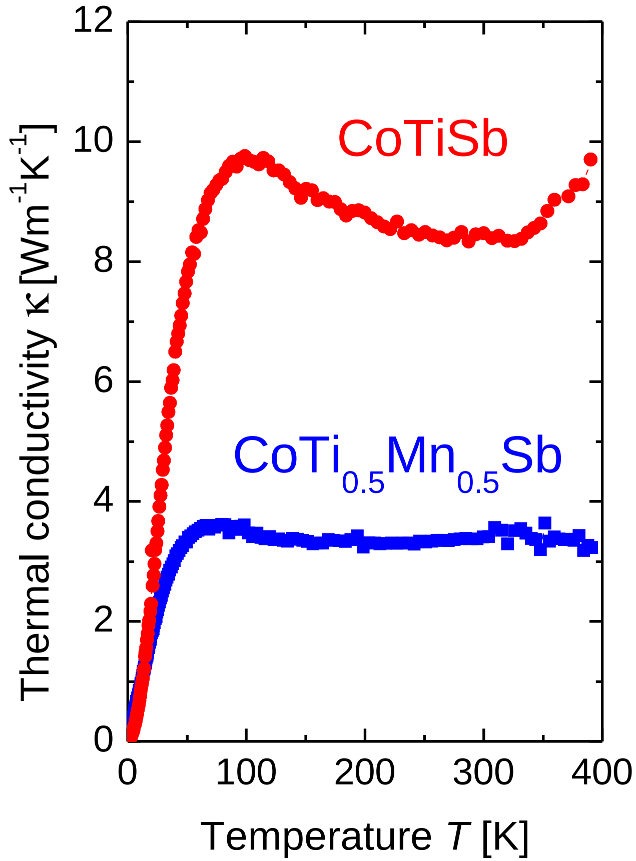
Graf T, Felser C, Parkin SSP, IEEE TRANSACTIONS ON MAGNETICS 47 (2011) 367

Graf T, Felser C, Parkin SSP, Progress in Solid State Chemistry (2011), doi:10.1016/j.progsolidstchem.2011.02.001

Thermal conductivity: nano structuring

$CoTi_{0.5}Mn_{0.5}Sb$

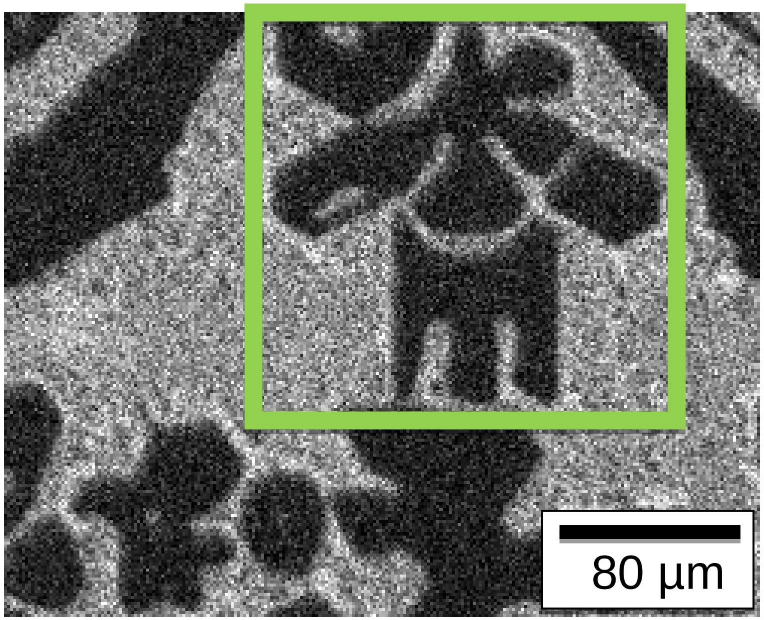


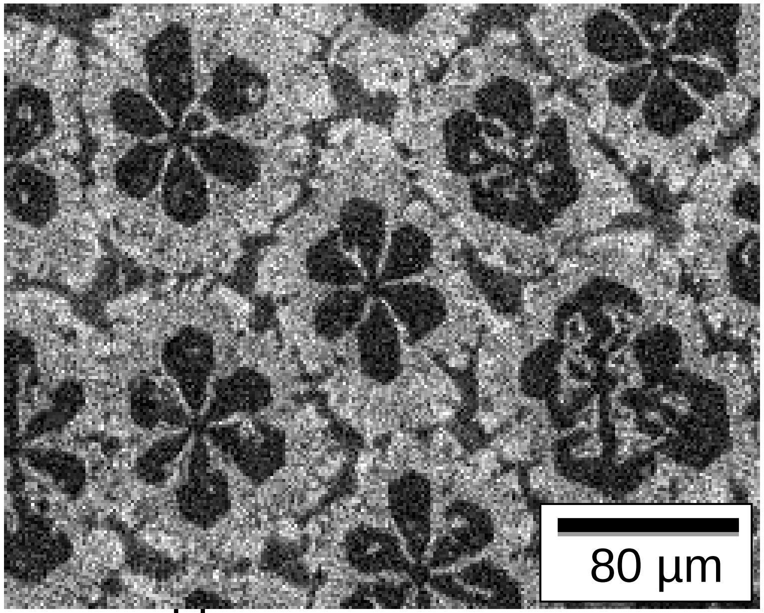


Bosch, Mainz, Patent submitted
T. Graf,et al. Scripta Mater. 63 (2010) 1216

Annealing and long range order

1000°C,
2 weeks





nature materials

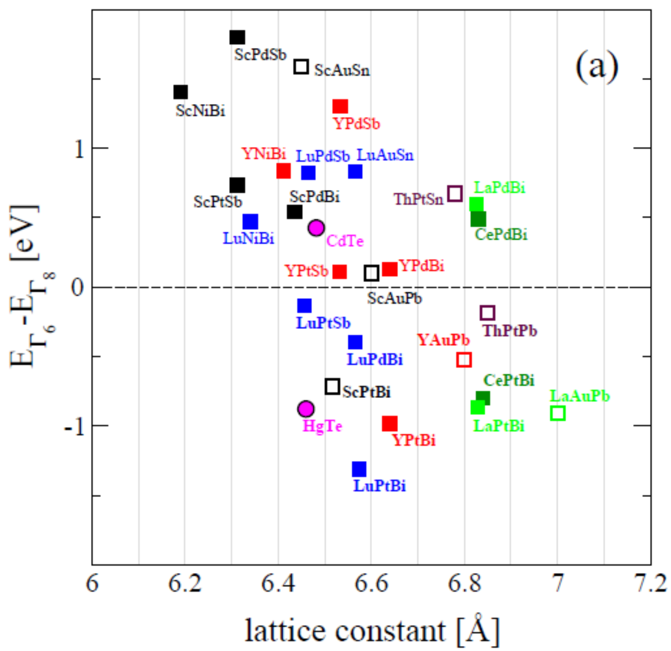
LETTERS

PUBLISHED ONLINE: XX MONTH XXXX | 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]*

Pt RE Bi



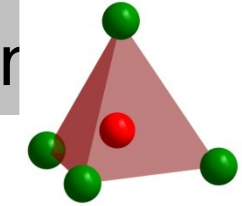
Multifunctional properties

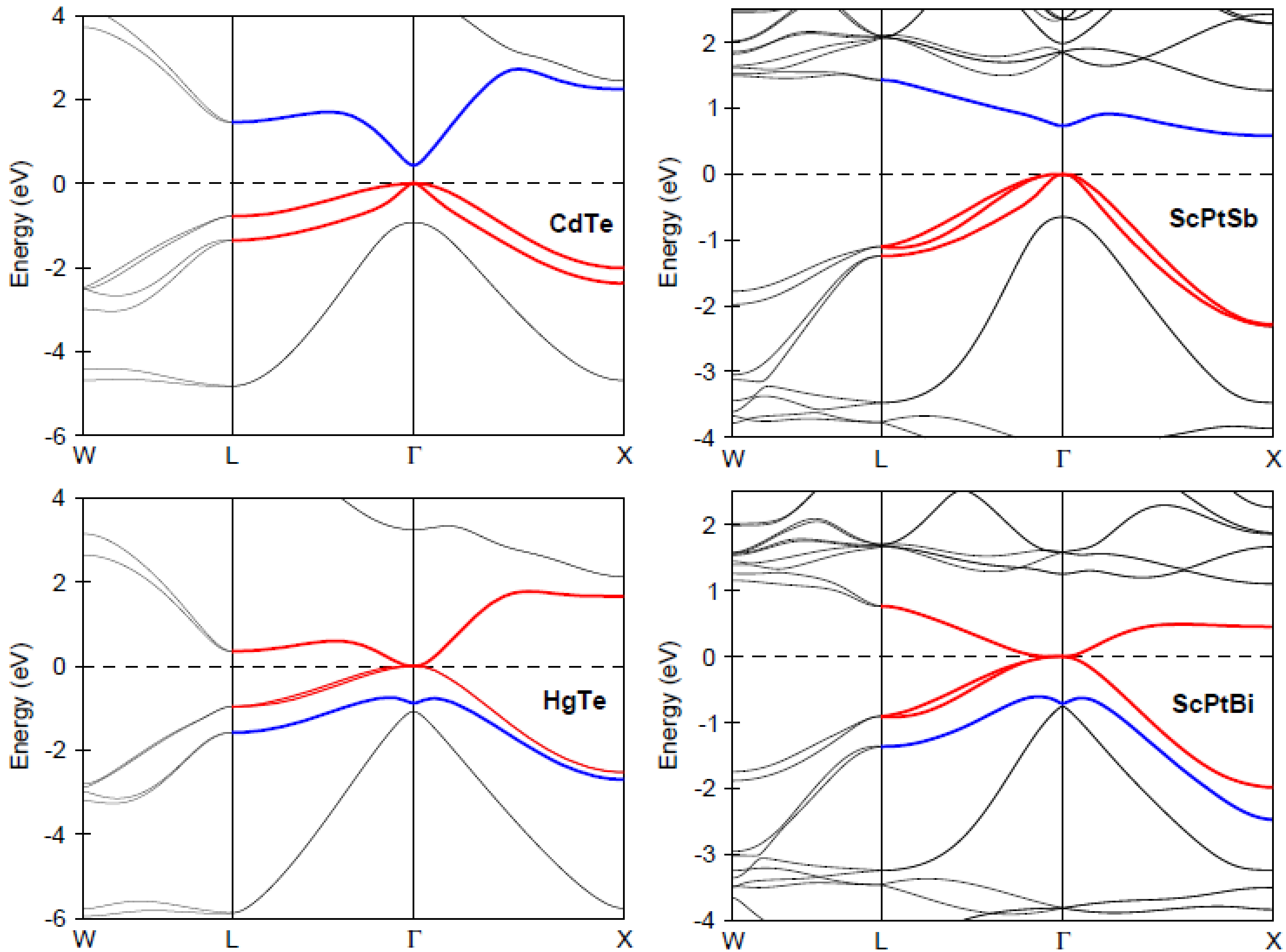
- RE: Gd Magnetism
- RE: La Superconductivity
- RE: Yb Kondo insulator …

and related compounds

Chadov, Qi, Kübler, Zhang, Felser Nature Mat. 9 (2010) 541, arXiv:1003.0193
Zhang, Chadov, Müchler, Yan, Qi, Kübler, Zhang, Felser, Phys. Rev. Lett. (2011) 156402, arXiv:1010.2195

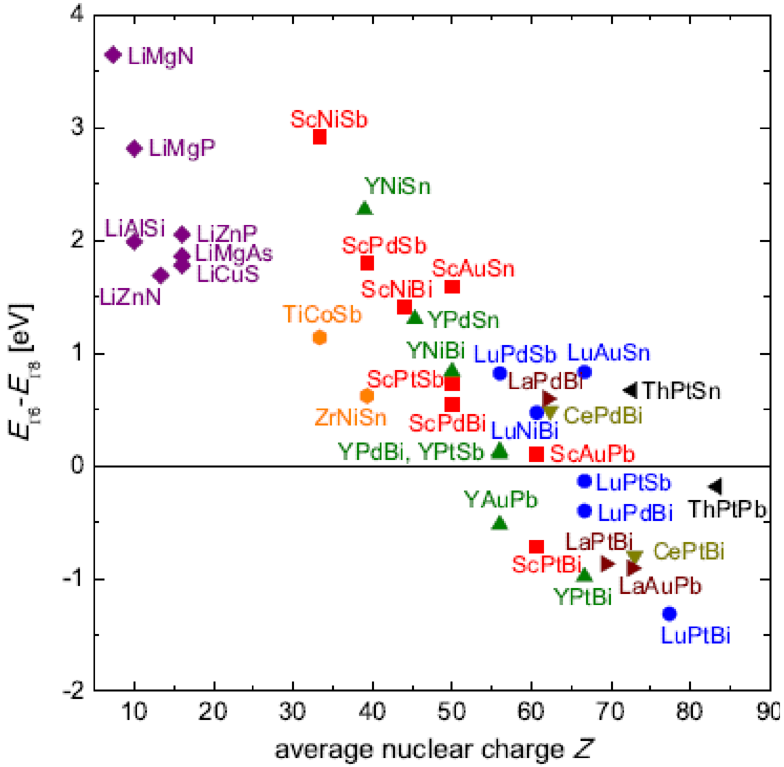
Zero gap: fingerprints, binaries→ternar

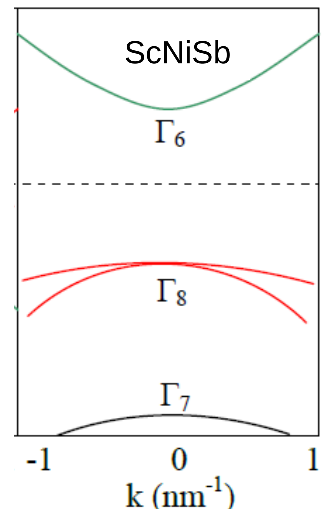


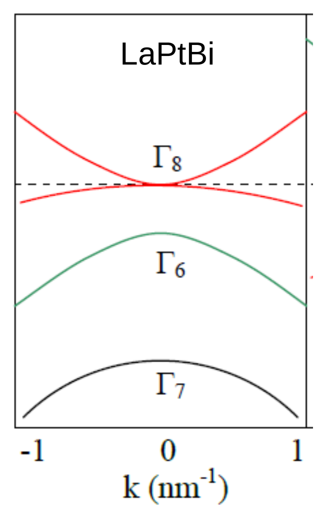


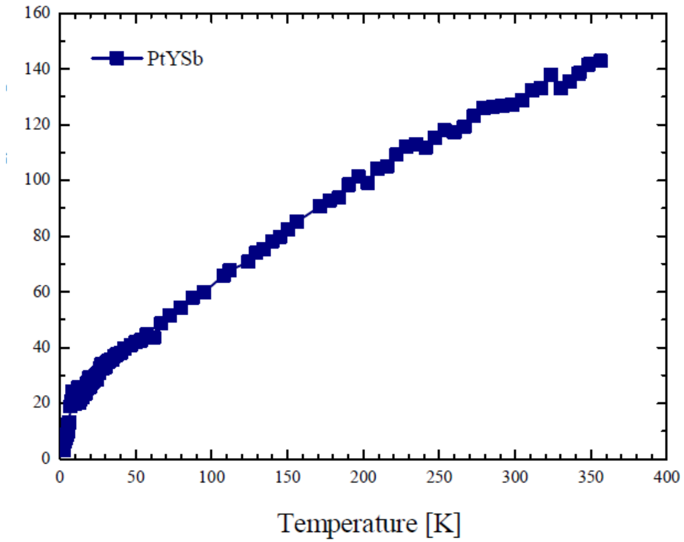
Chadov, Qi, Kübler, Zhang, Felser Nature Mat. 9 (2010) 541, arXiv:1003.0193 .

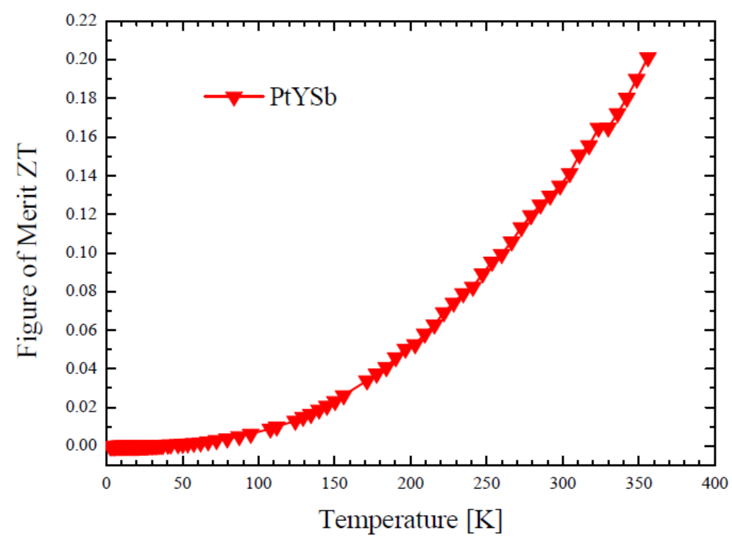
Good TI are good thermoelectrics









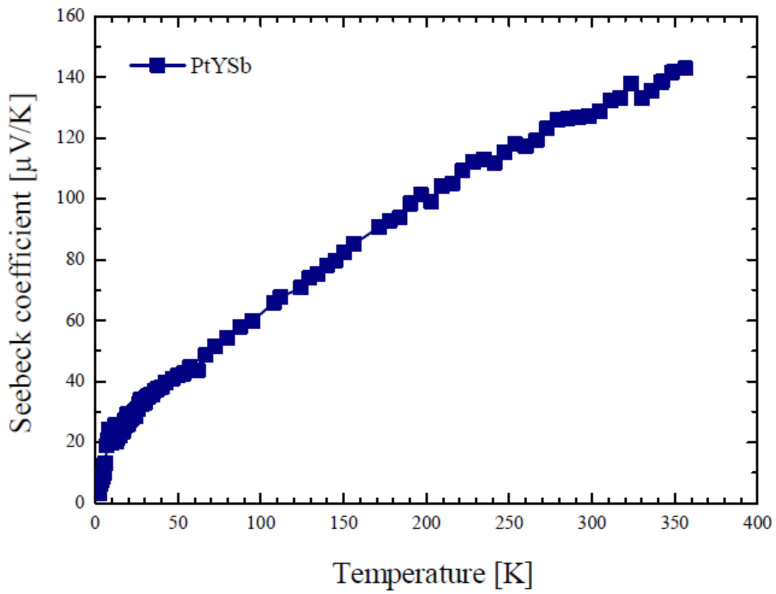


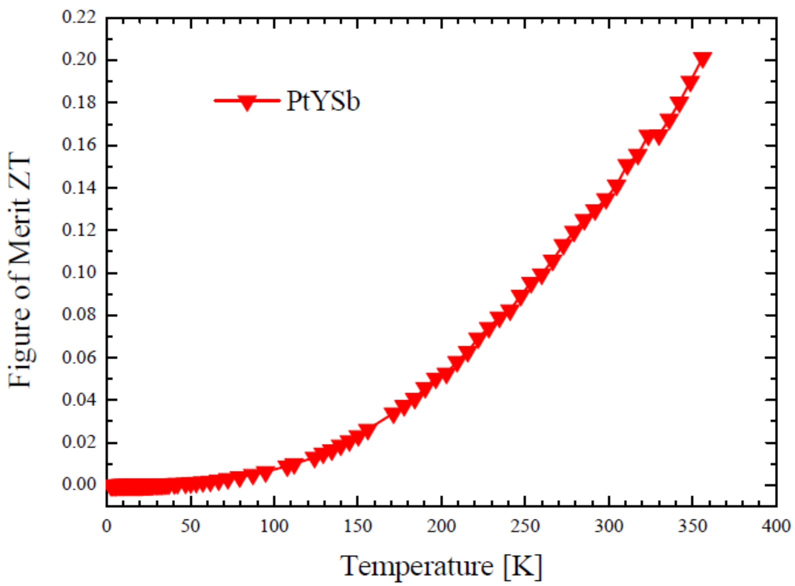
Both need

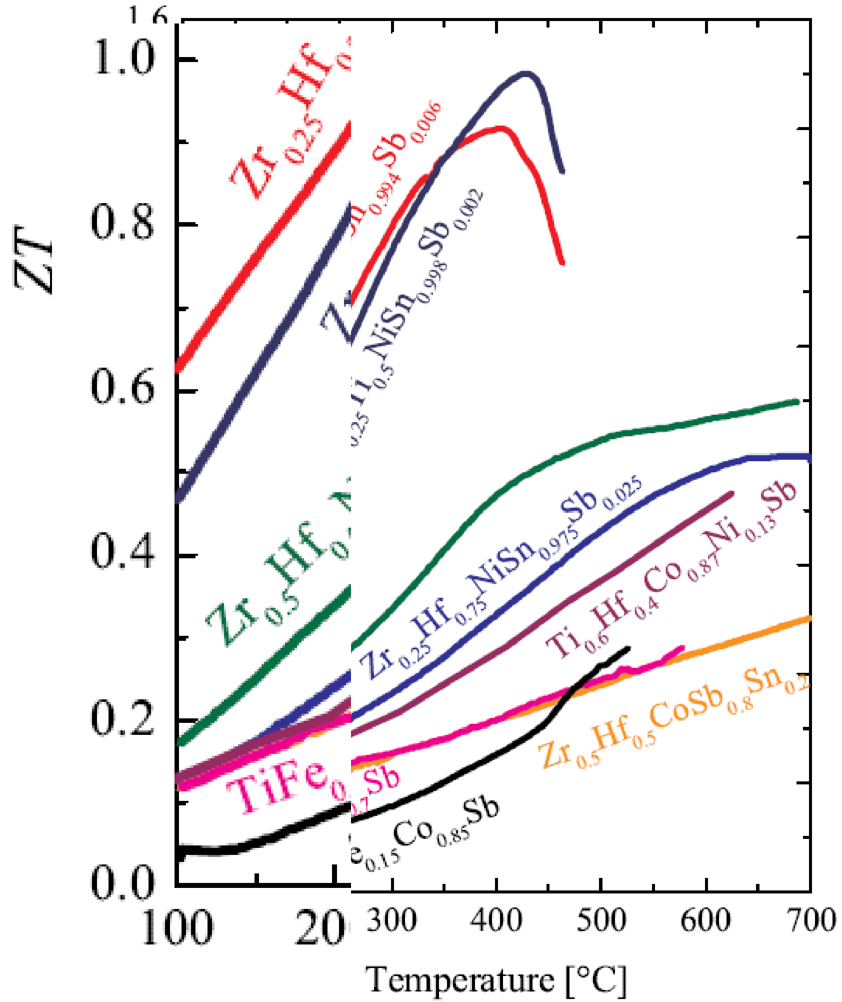
Low band gaps

High spin orbit coupling

Good thermoelectrics are good TI





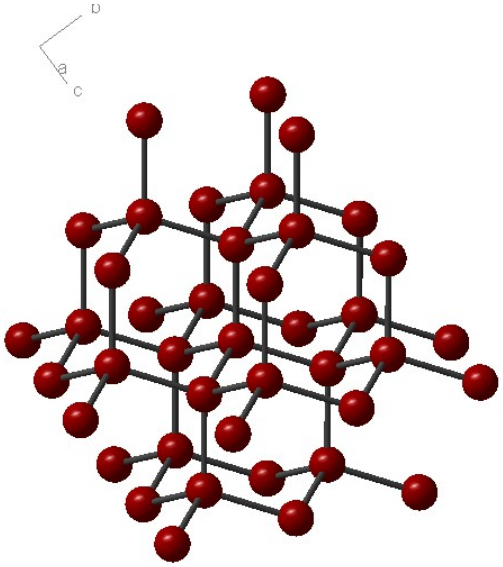


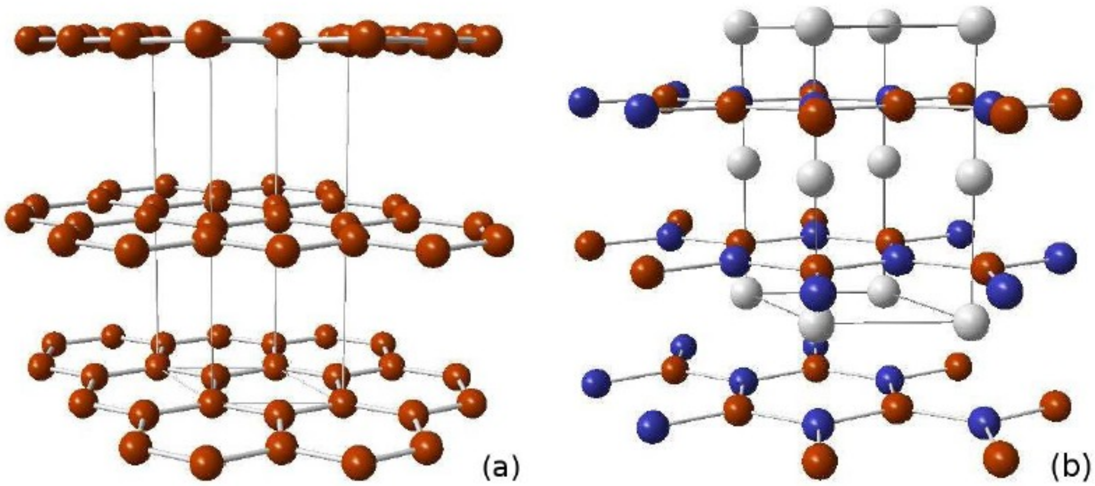
R. Asahi et al. J. Phys.: Cond. Mat. **20** (2008) 64227

K. Miyamoto et al. Appl. Phys. Express **1** (2008) 081901

VK Zaitsev et al. PRB 7**4** (2006) 045207

From diamond to graphite





From cubic to hexagonal

From non centro symmetric to centro symmetric

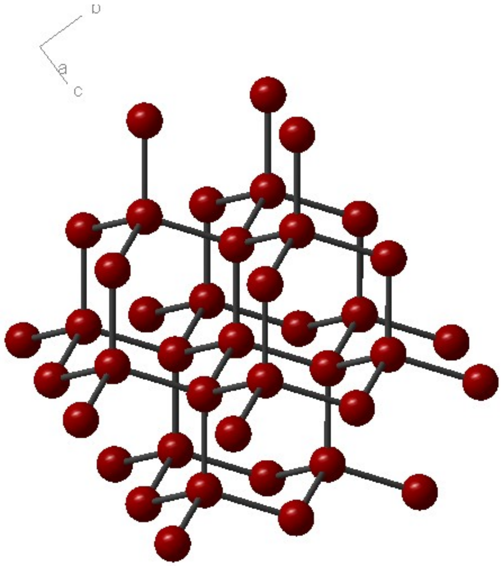
→ allows determination of the parity

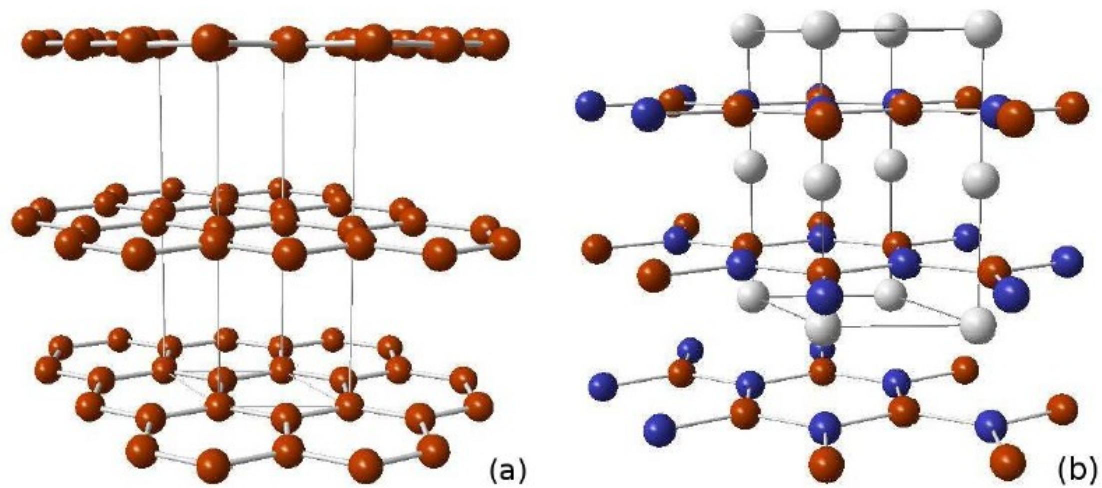
From sp^3 to sp^2 (p)

Breaking the symmetry $a = b \neq c$

→ 3D topological insulator

From diamond to graphite





Pt **RE** **Bi**

$10 + 3\,(+f^{n}) + 5 = 18 + n$

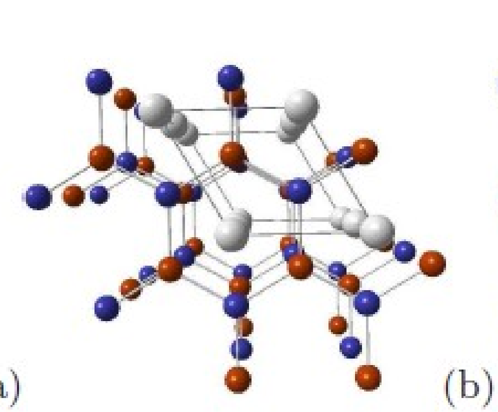
K **Hg** **Sb**

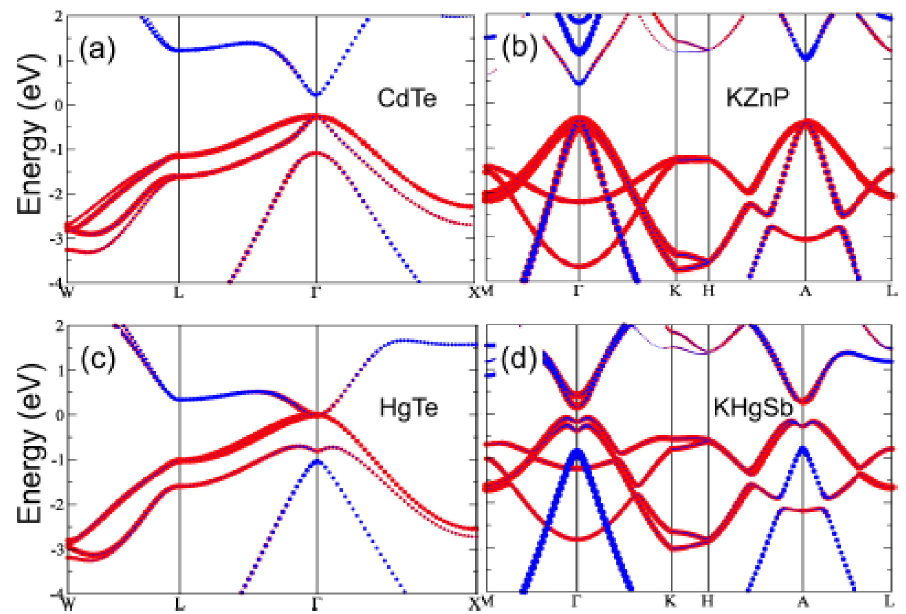
$1 + 12 + 5 = 18$

Li **Au** **Te**

$1 + 11 + 6 = 18$

Honeycomb from sp^3 to sp^2

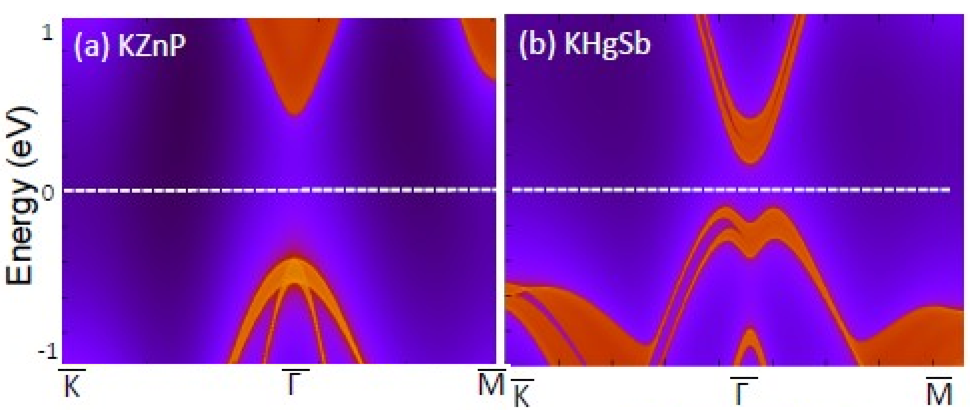




Band inversion is found in the heavier compounds

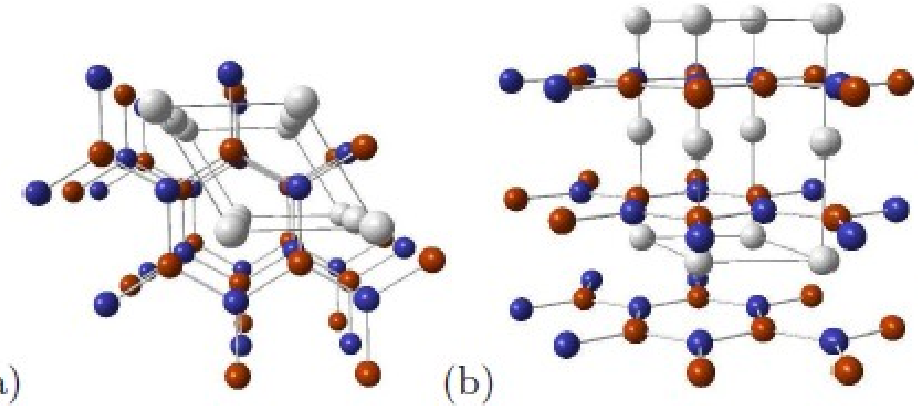
No surface state? Why ?

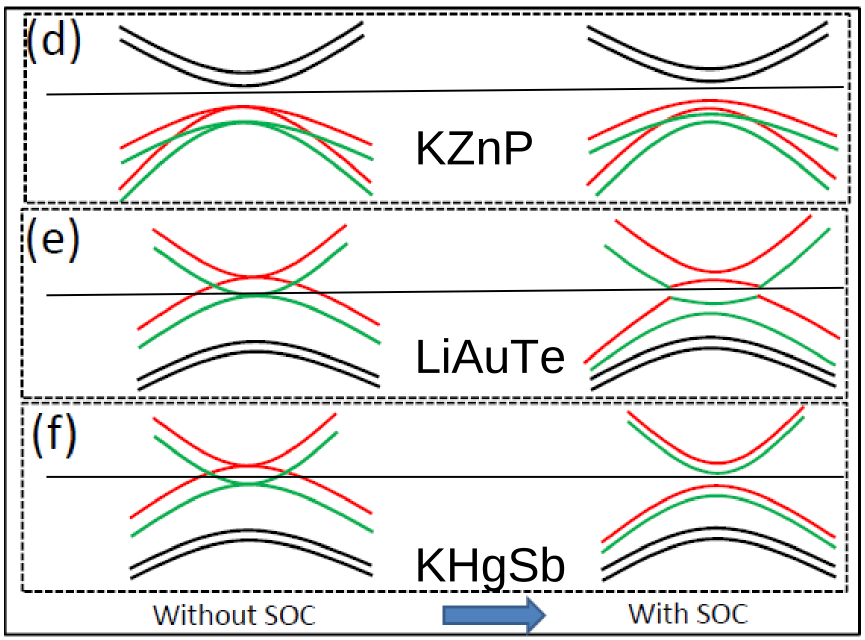
→ Interaction between the two layers in the unit cell

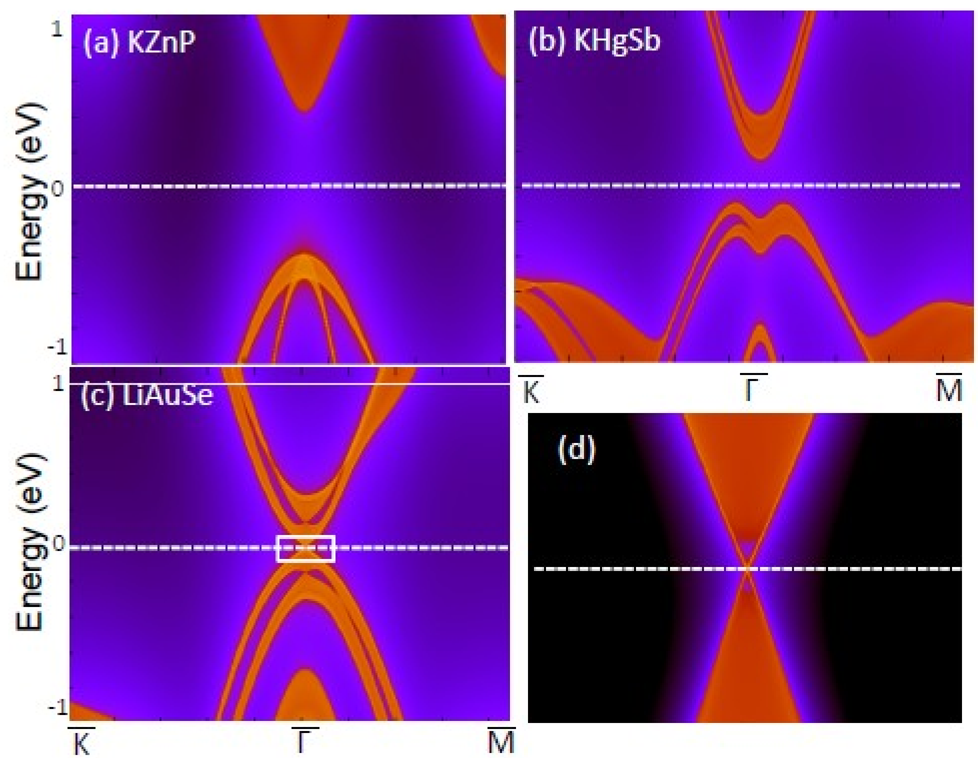


Zhang, Chadov, Müchler, Yan, Qi, Kübler, Zhang, Felser, Phys. Rev. Lett. 106 (2011) 156402 arXiv:1010.2195v

Honeycomb from sp^3 to sp^2

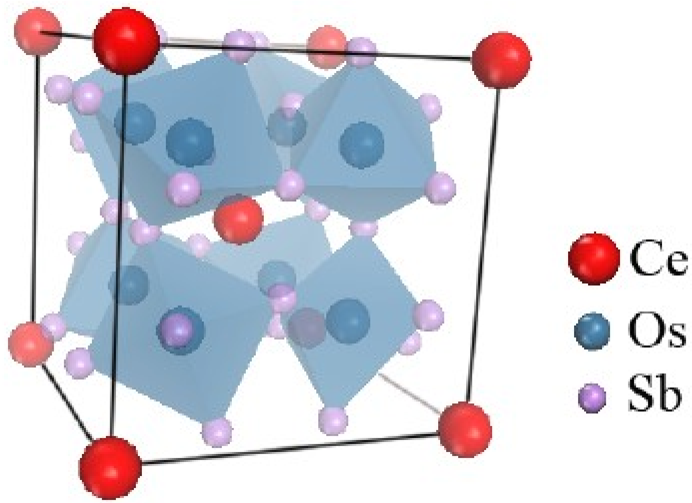




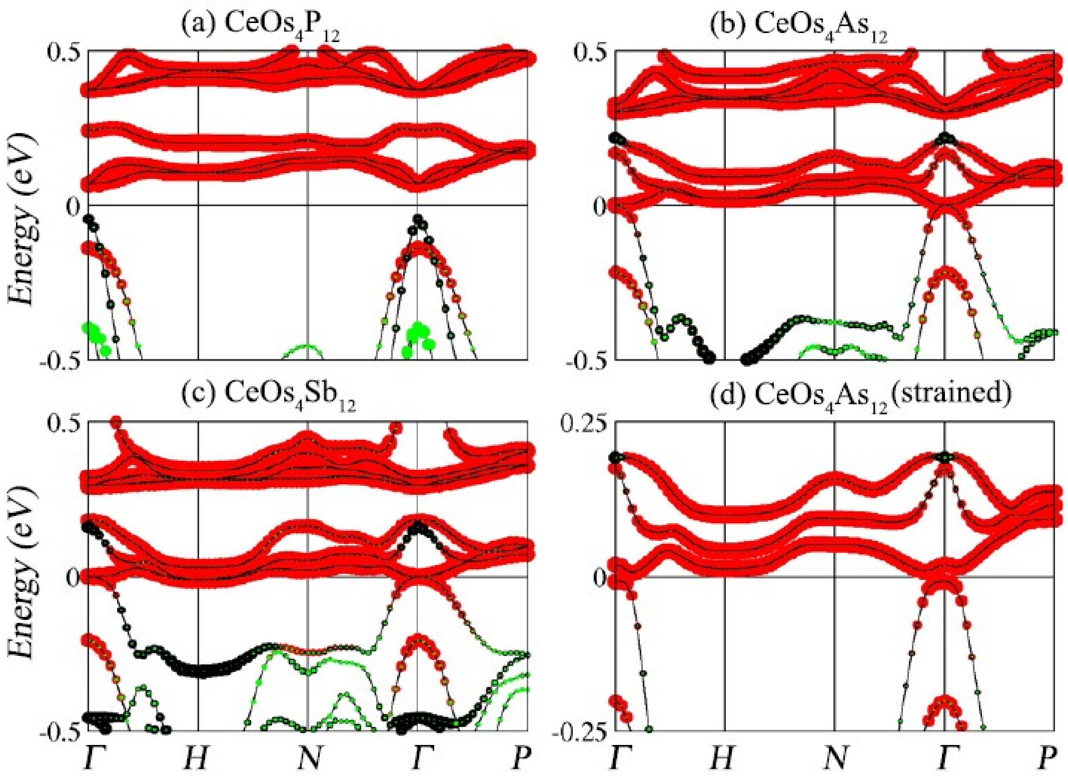


Zhang, Chadov, Müchler, Yan, Qi, Kübler, Zhang, Felser, Phys. Rev. Lett. 106 (2011) 156402
arXiv:1010.2195v1

Skutterudites



Band inversion between d and f bands of different parity



B. Yan, L Müchler, HJ Zhang, XL Qi,, SC Zhang, C. Felser, PRL under review, arXiv:1104.0641

Design scheme

Good thermoelectric materials are candidates for topological insulators

Tunable semiconductors | **Chemical solutions**

Semiconductor with tunable Gaps | Ternary compounds

Low band gap | 18 valence electrons

Odd number of Dirac cones | Direct gap at the Γ point

2dim. - even number of Dirac

Large spin orbit coupling | Heavy elements

2 D TI …. Cubic, we need quantum well structures

Sufficient condition:

Band inversion | small ΔEN

Parity change (structures with inversion symmetry) Eigenvalues

s – p … d - f different degeneration -------- t2g – eg doesn't work

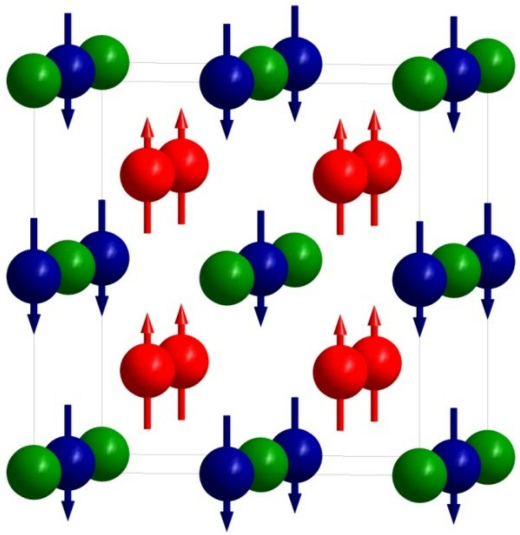
Add new properties multifunctionality | **Rare earth elements …**

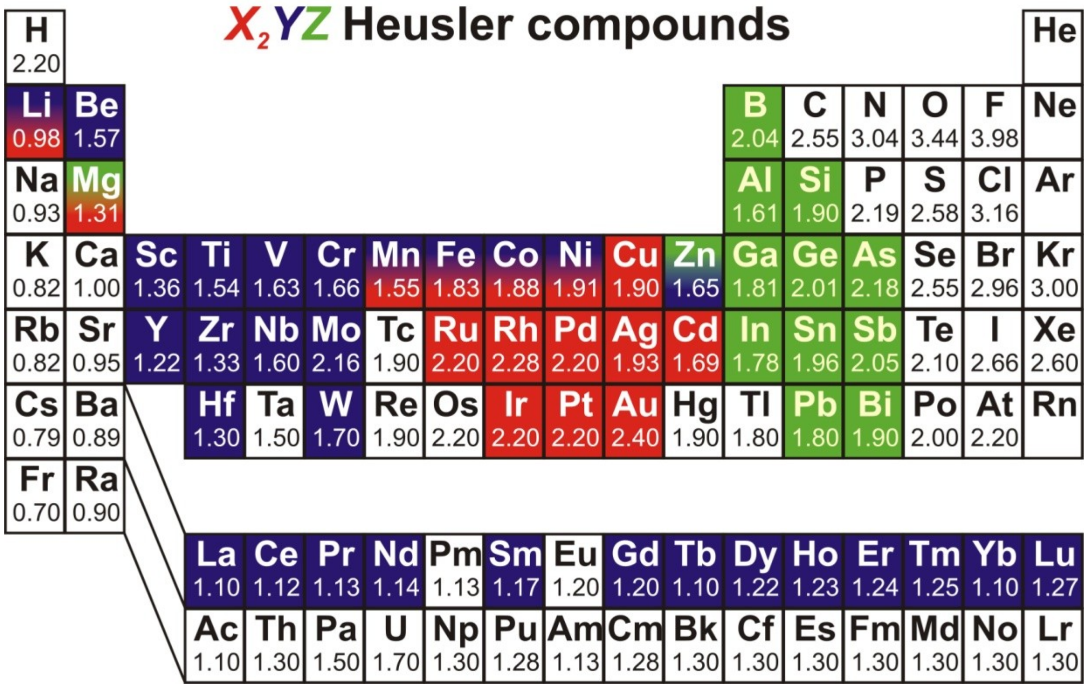
Challenges

Still a need for new compounds with large gaps (300meV) for room temperature effects

Control over charge carriers in low band gap semiconductors …

Magnetic Heusler compounds





CCFA - $Co_2Cr_{0.6}Fe_{0.4}Al$

1903: First „Heusler“ compound Cu_2MnAl by Friedrich Heusler

1983: De Groot and Kübler: Prediction of half metallicity

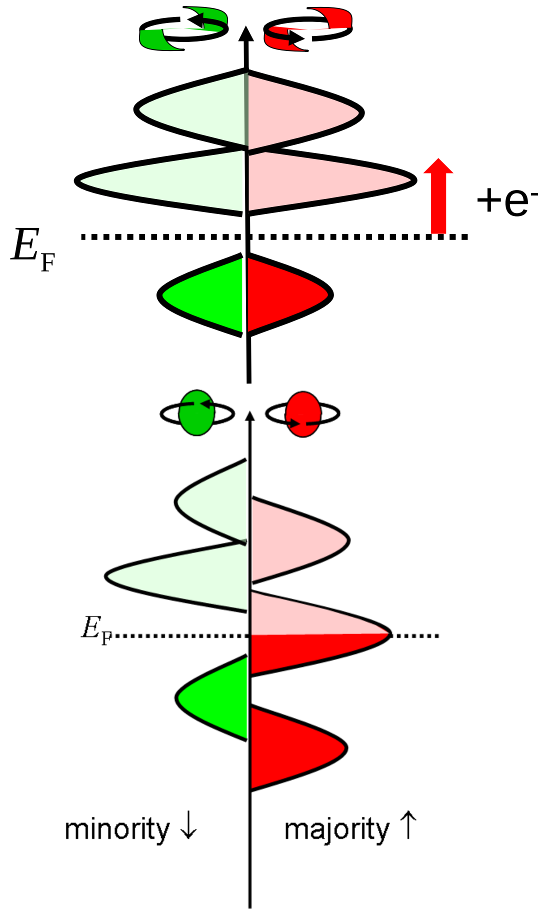
1999: Discovery of high MR in CCFA by us (Patent IBM, CF)

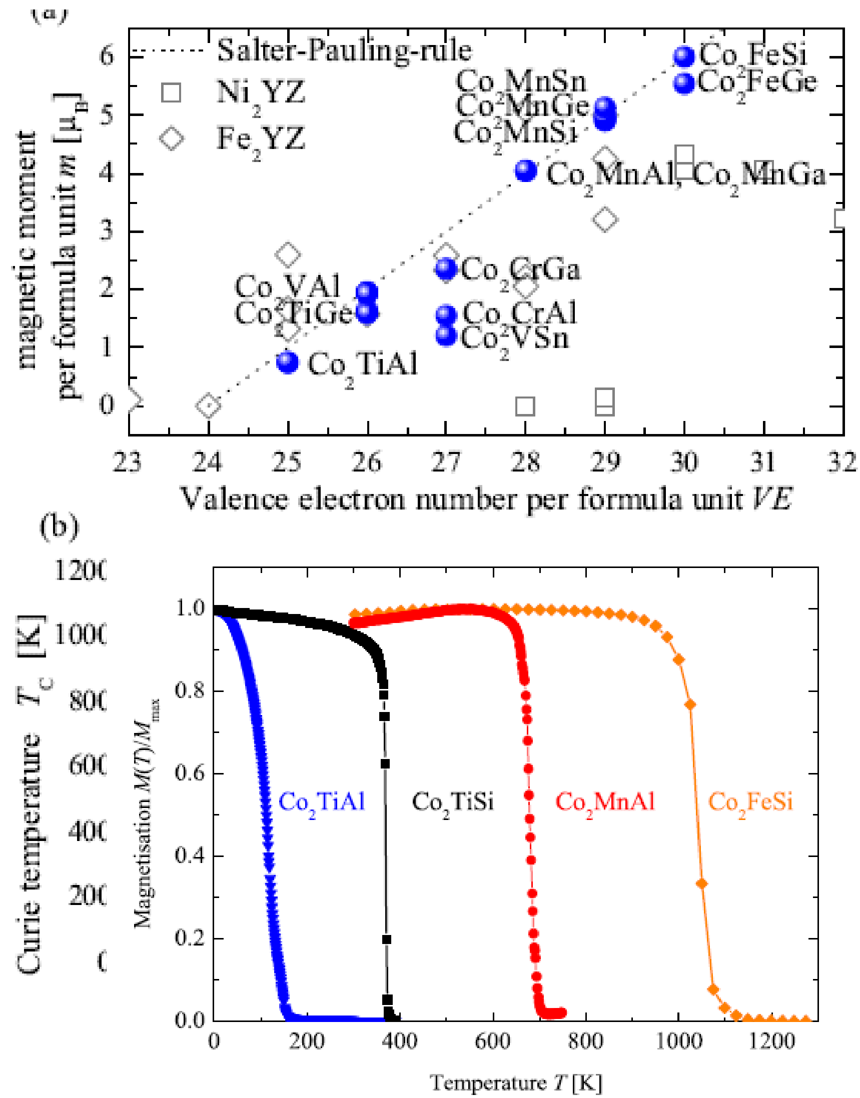
2003: First TMR device with 19% room temperature effect by K. Inomata

From semiconductors to half metallic ferromagnets

X_2YZ

Example: Co_2MnSi Co_2MnSi: $2\times 9 + 7 + 4 = 29$ $Ms = 5\mu_B$



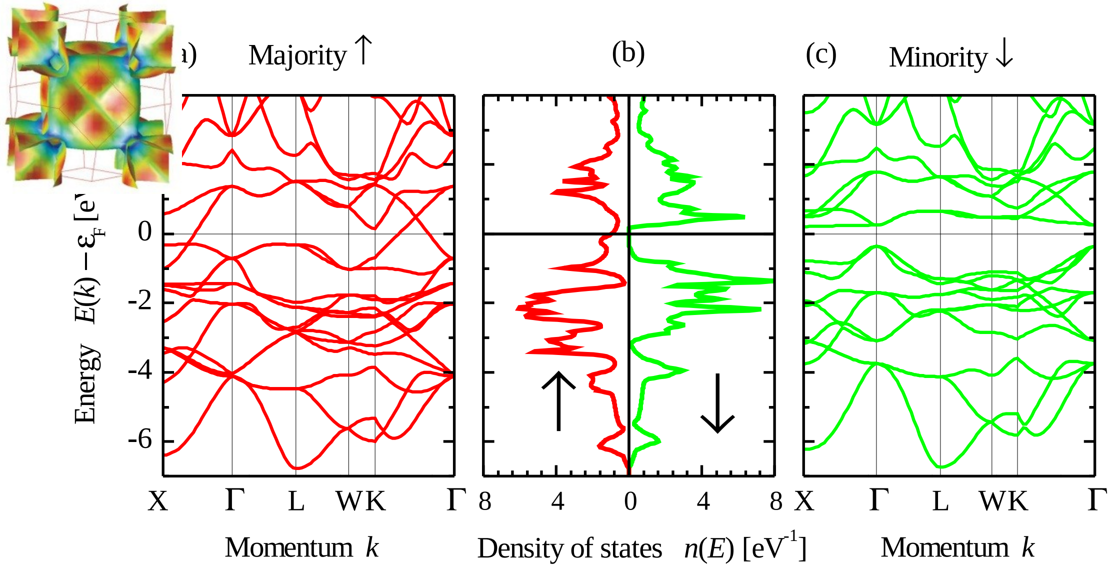


Galanakis *et al.*, PRB **66**, 012406 (2002)

Felser *et al.*, Angewandte Chemie, **I46** 668 (2007)

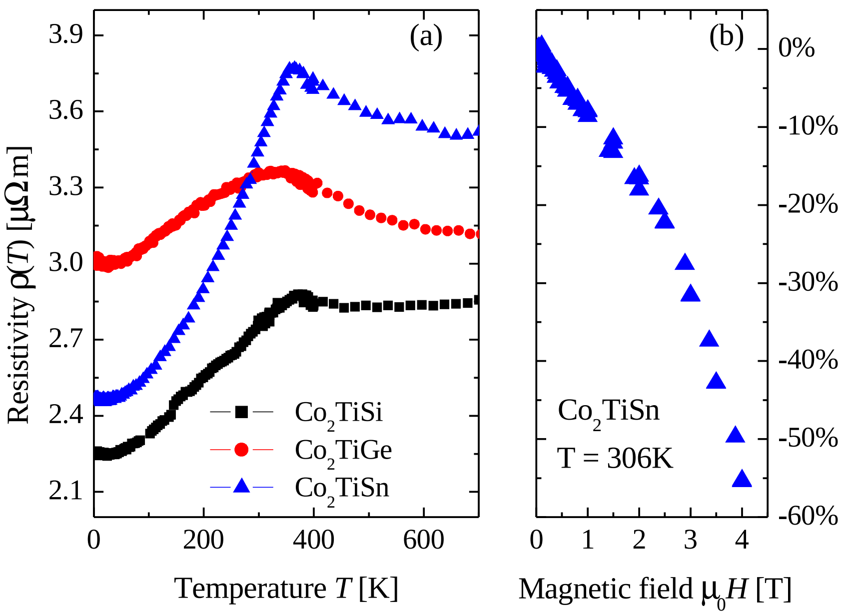
Graf T, Felser C, Parkin SSP, IEEE TRANSACTIONS ON MAGNETICS 47 (2011) 367)

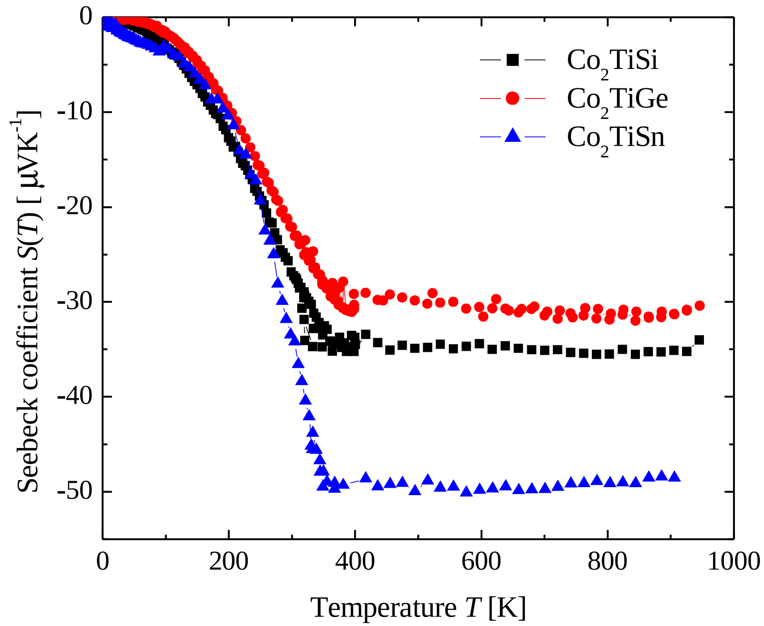
High Seebeck coefficient in Co_2TiZ



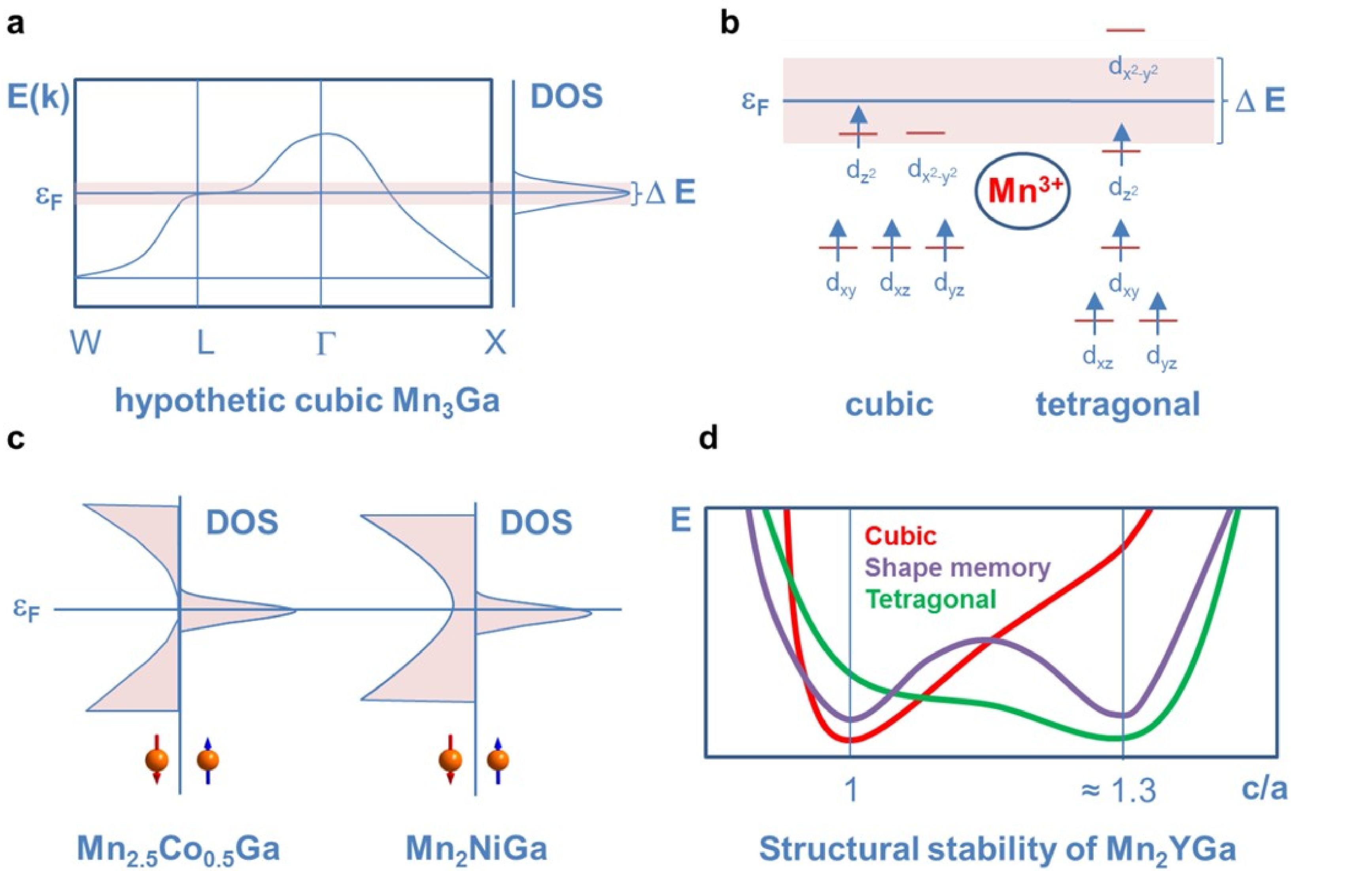
Half metallic ferromagnets

- High Seebeck coefficient
- Van Hove → MIT
- Pinning of the EF



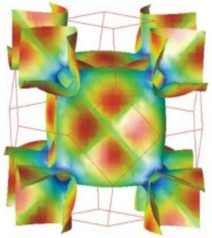


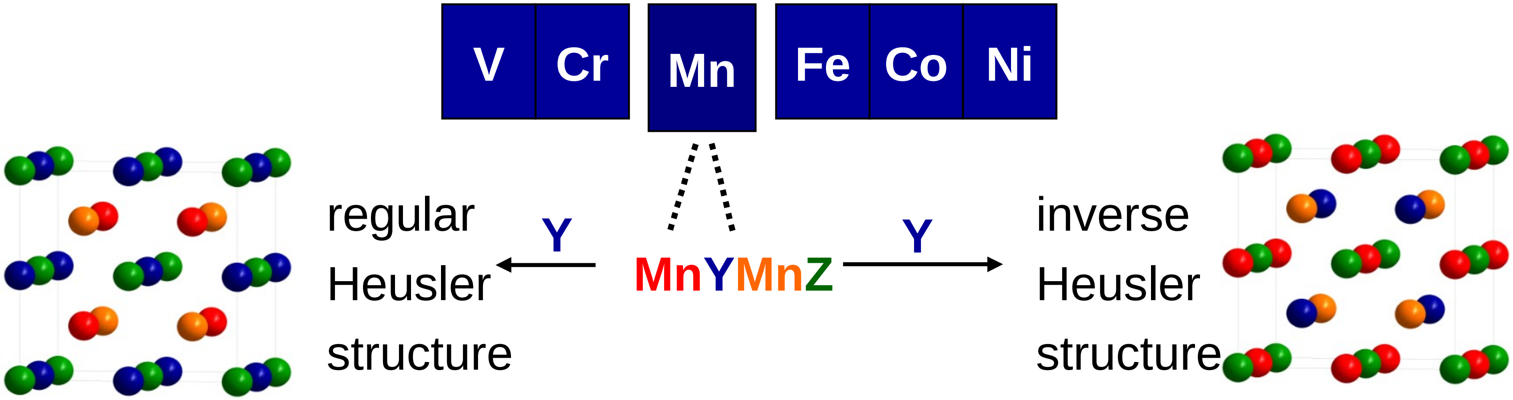
Barth et al. Proc. Phil. Trans A, accepted and Phys. Rev. B 81 (2010) 064404 arXiv:0907.3562v1

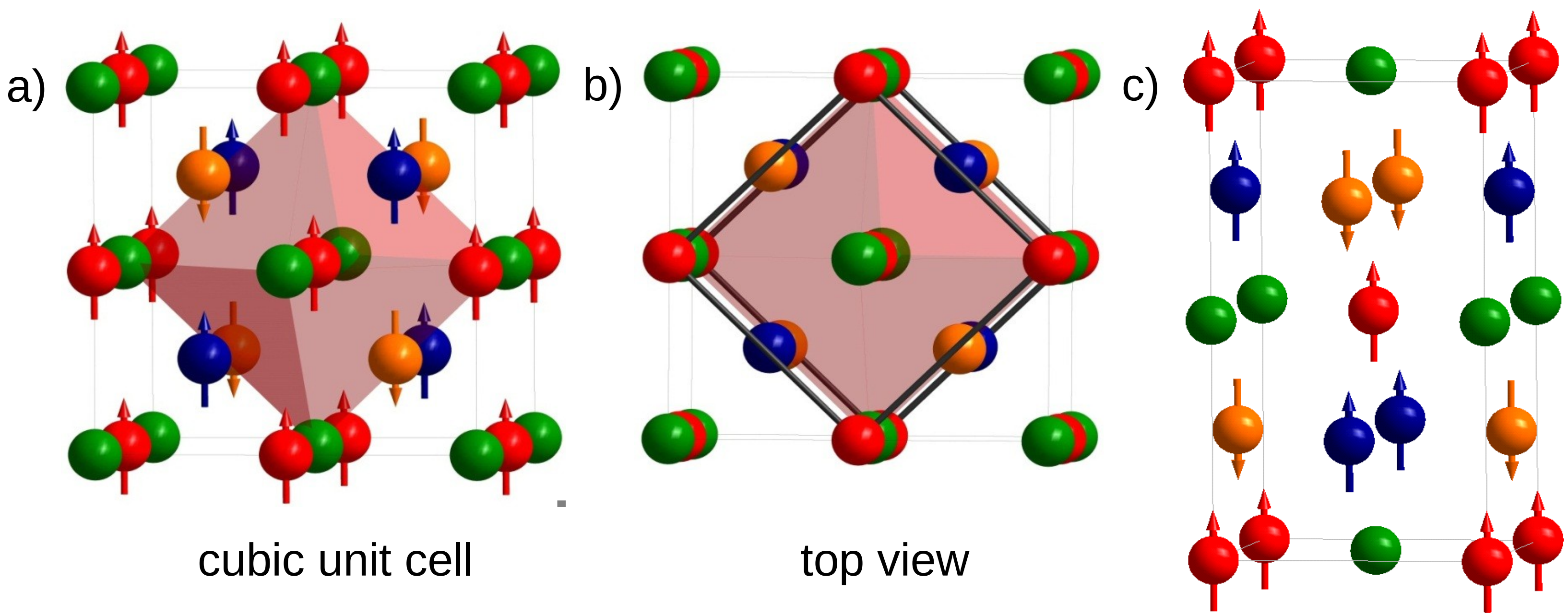


Winterlik et al. submitted

Much more to do ... inverse tetragonal







cubic unit cell

top view

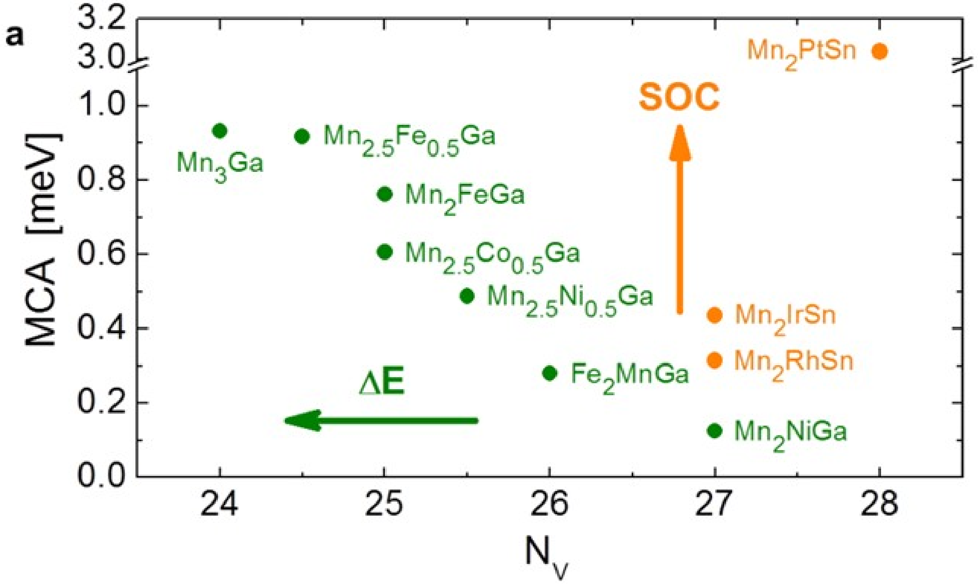
tetragonal unit cell

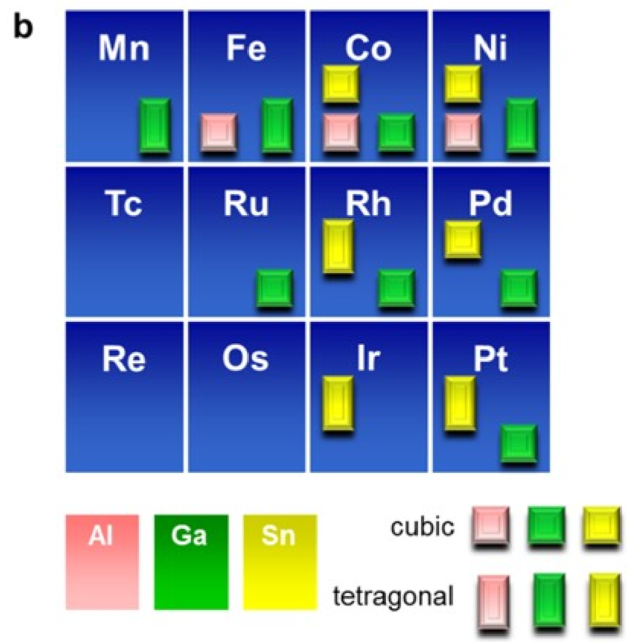
Graf T, Felser C, Parkin SSP, IEEE TRANSACTIONS ON MAGNETICS 47 (2011) 367

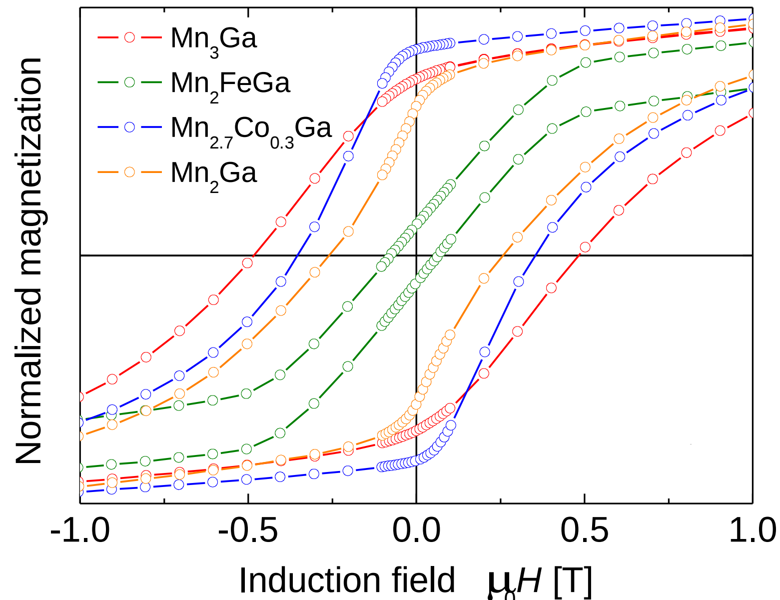
Graf T, Felser C, Parkin SSP, Progress in Solid State Chemistry (2011), doi:10.1016/j.progsolidstchem.2011.02.001

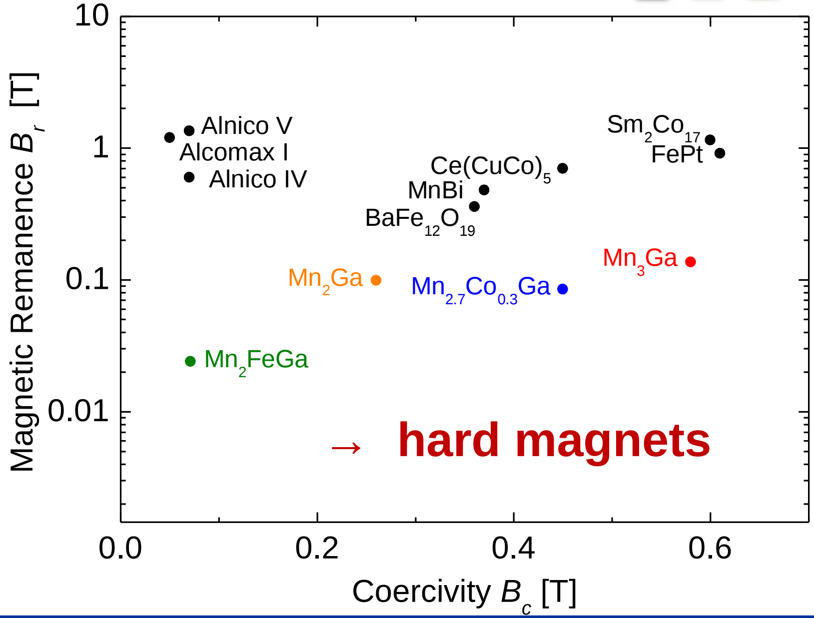
moment

Prediction of a device with switchable Seebeck



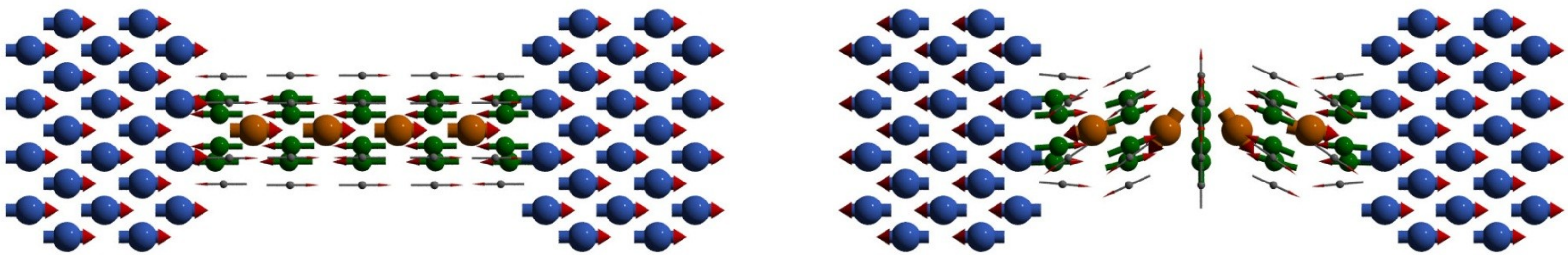


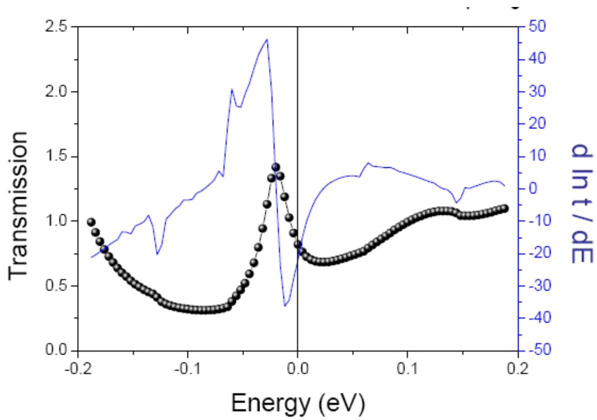


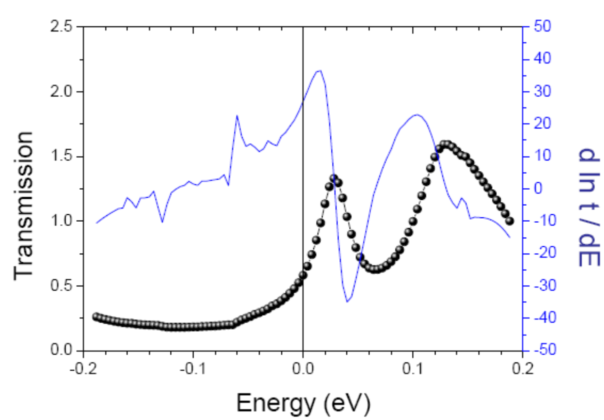


Winterlik et al. submitted

Magneto Seebeck Effect from I Mertig



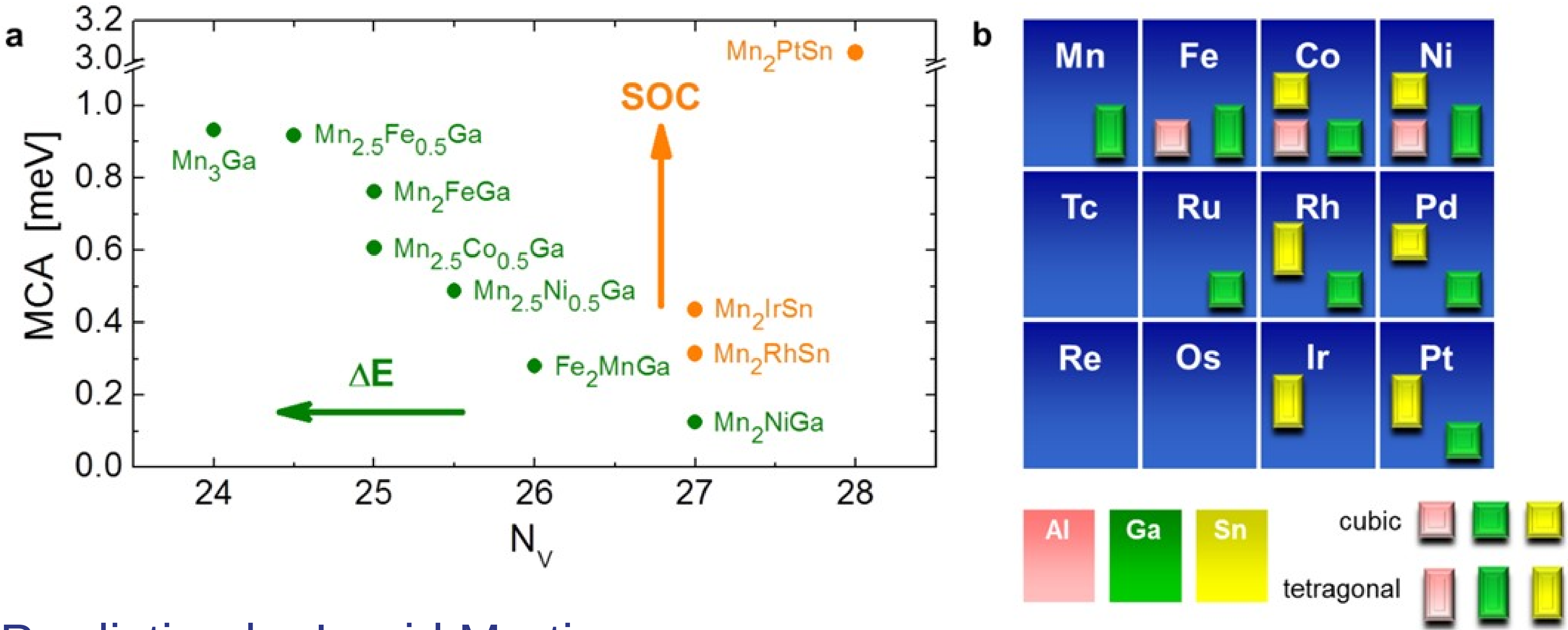




S_P = -161.4 μV/K at 300 K

S_{AP} = 198.4 μV/K at 300 K

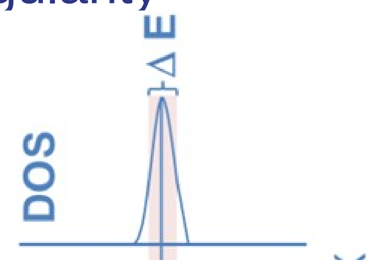
Prediction of a device with switchable Seebeck



Prediction by Ingrid Mertig

Magneto Seebeck effect

- Half metallic ferromagnets
- Van Hove Singularity



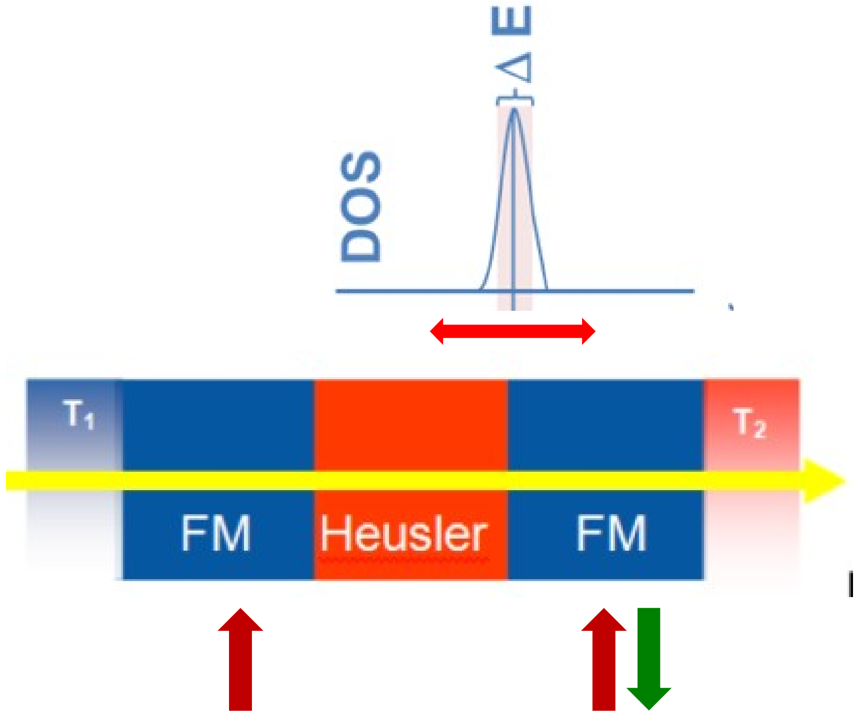
Prediction of a device with switchable Seebeck

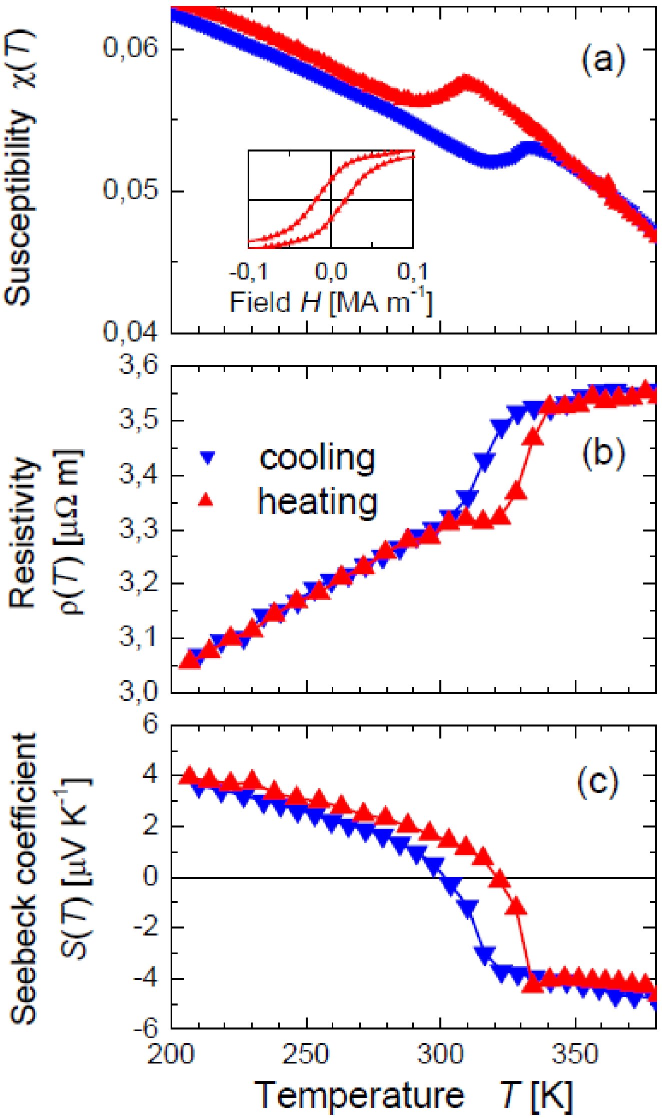
Prediction by Ingrid Mertig

Magneto Seebeck effect

- Half metallic ferromagnets
- Van Hove Singularity

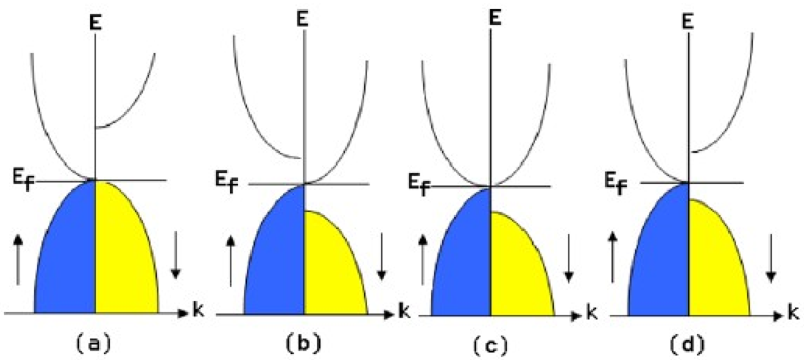
Changing the sign of the Seebeck coefficient by switching the free laye



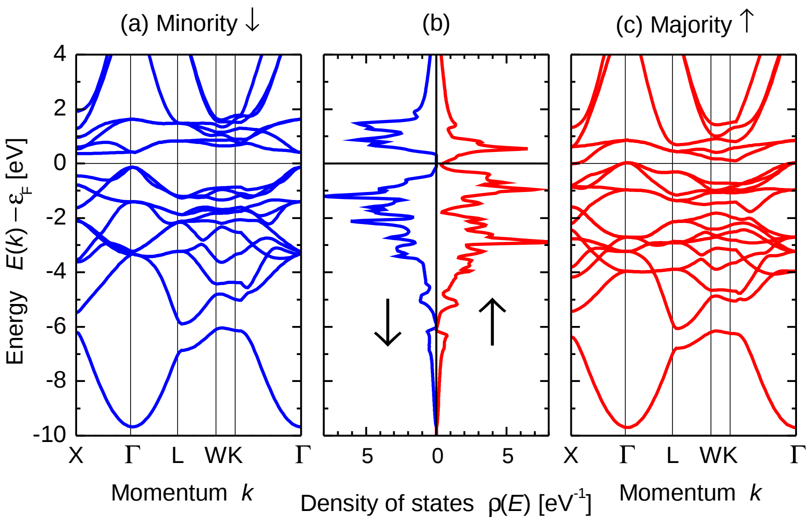


Christian G. F. Blum, et al. APL submitted

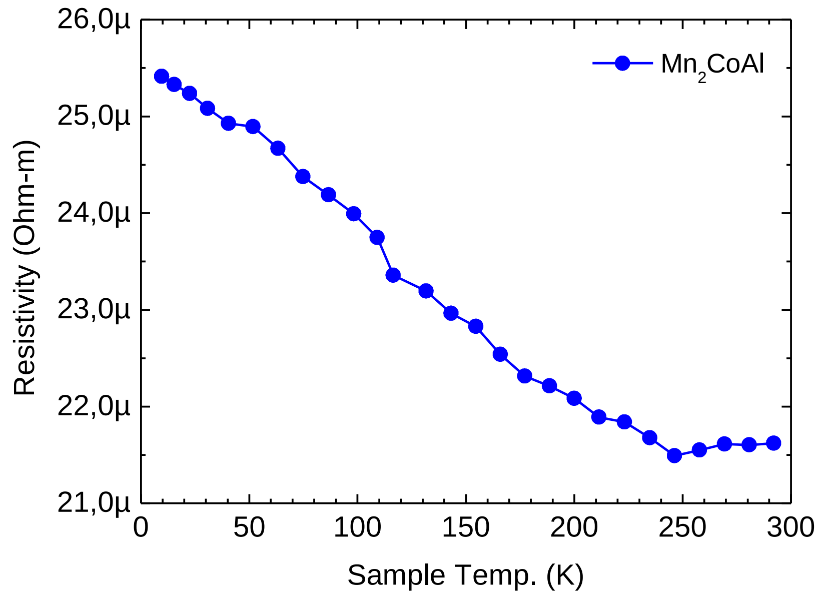
Spin gapless semiconductor Mn_2CoAl

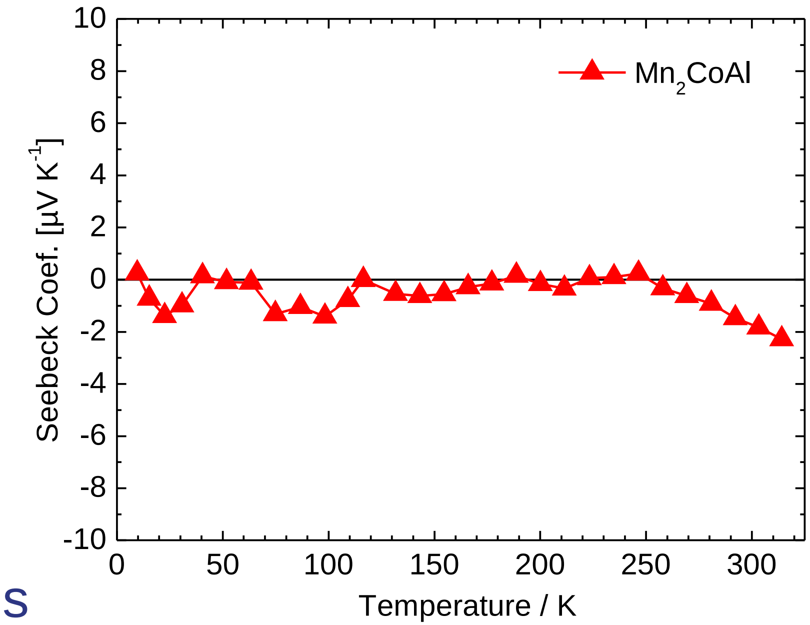


X. L. Wang PRL **100,** 156404 (2008)



- Half metallic ferromagnet 2 μ_B
- Tc > 400 K
- Compensated holes and electrons





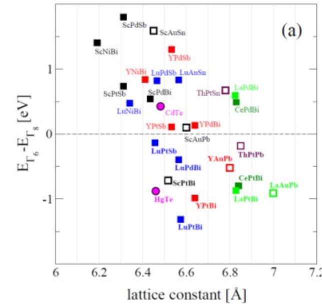
Summary

Virtual Lab: Computational design of new materials

- Properties can be described with DFT

More than 200 semiconducting Heusler compounds

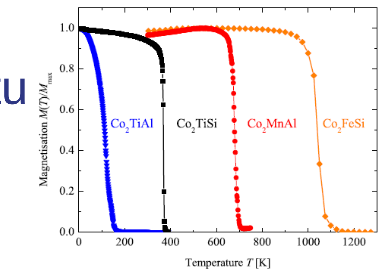
- Thermoelectric devices with high ZT and nano structuring
- Multifunctional topological insulators



Spintronics

- Materials with high spin polarization at high Curie temperatu

➔ TMR devices



Combination of both

- Spin Seebeck effect
- Magneto Seebeck effect
- Spin gapless semiconductors

- Tunable Multifunctional materials ➔ new effects and devices