High Energy Photoemission of Heusler compounds

Claudia Felser

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BESSY: M. Mertin, F. Schäfers, M. Gorgoi

Hokkaido: T. Ishikawa, T. Uemura, M. Yamamoto,

Munich: J. Minar, J. Braun, H. Ebert

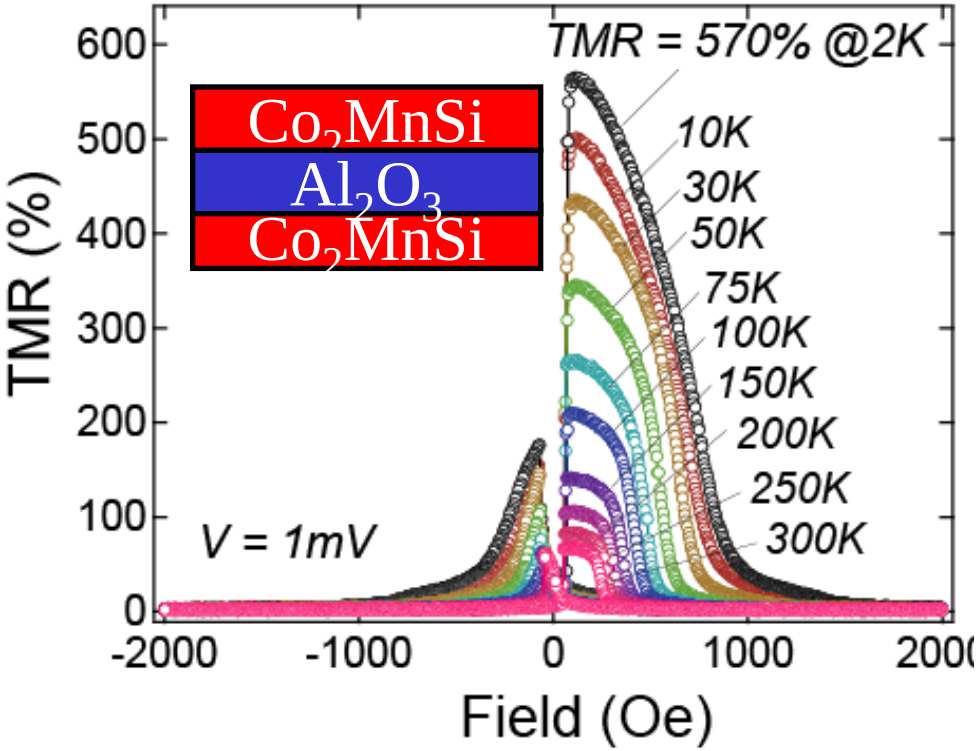
- Concept
- Design scheme for Heusler compounds
- High energy photoemission of bulk materials
- High energy photoemission of burried interfaces
- High resolution and correlations
- Summary

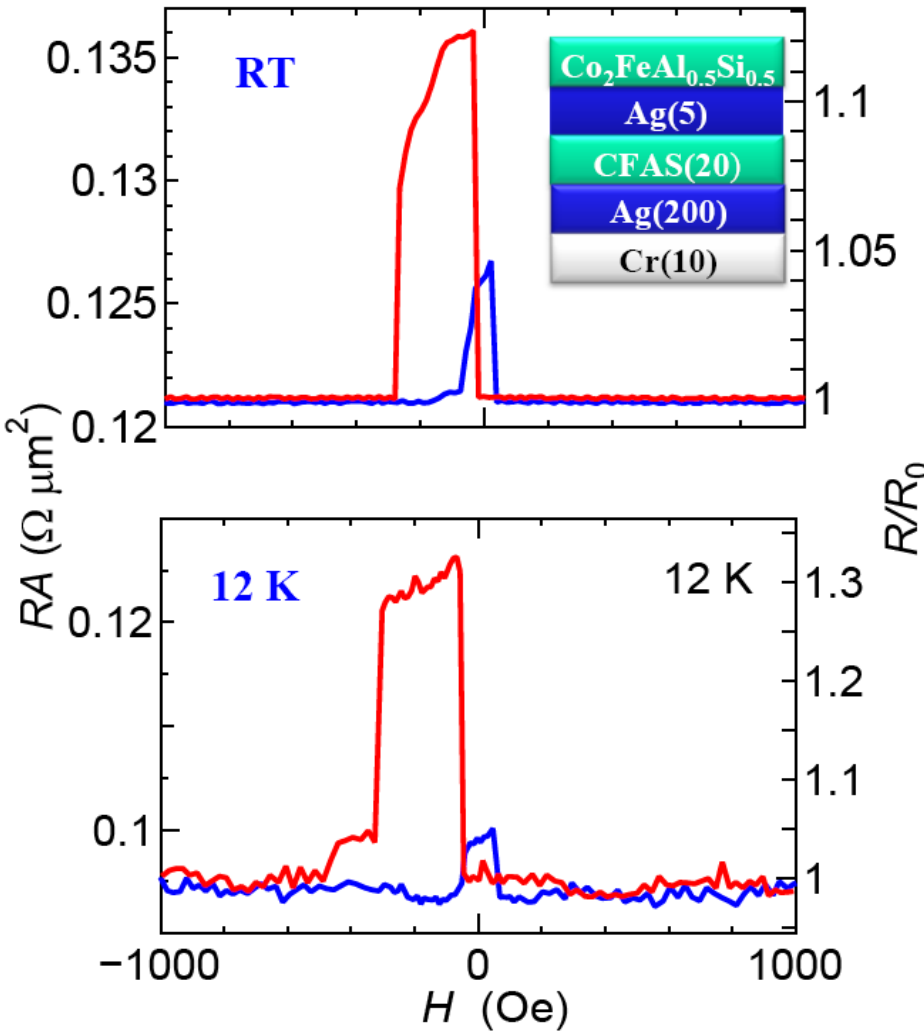
Heusler Compounds as Multifunctional Materials

1905	• Magnetic material:	Cu_2MnAl
1983	• Halfmetallic ferromagnet:	NiMnSb
	• Magneto-optical:	PtMnSb
	• Magneto-mechanic:	Ni_2MnGa
	• Superconductor:	Pd_2YSn
	• Semiconductors:	CoTiSb
	• Heavy fermion:	Fe_2VAl
	• Li-conductor:	LiMnSb
	• Magneto-electronic:	Co_2FeSi
	• Thermo-electric:	TiNiSn
2001	• Diluted Semiconductors	CoTiSb:Fe
	• Magneto-caloric:	CoMnSb:Nb

C. Felser, G. Fecher, B. Balke, Invited Review for Angewandte Chemie, Int. Ed. **46** 668 (2007).

TMR and GMR for applications





TMR ratio = 67% at RT, 580% at 2

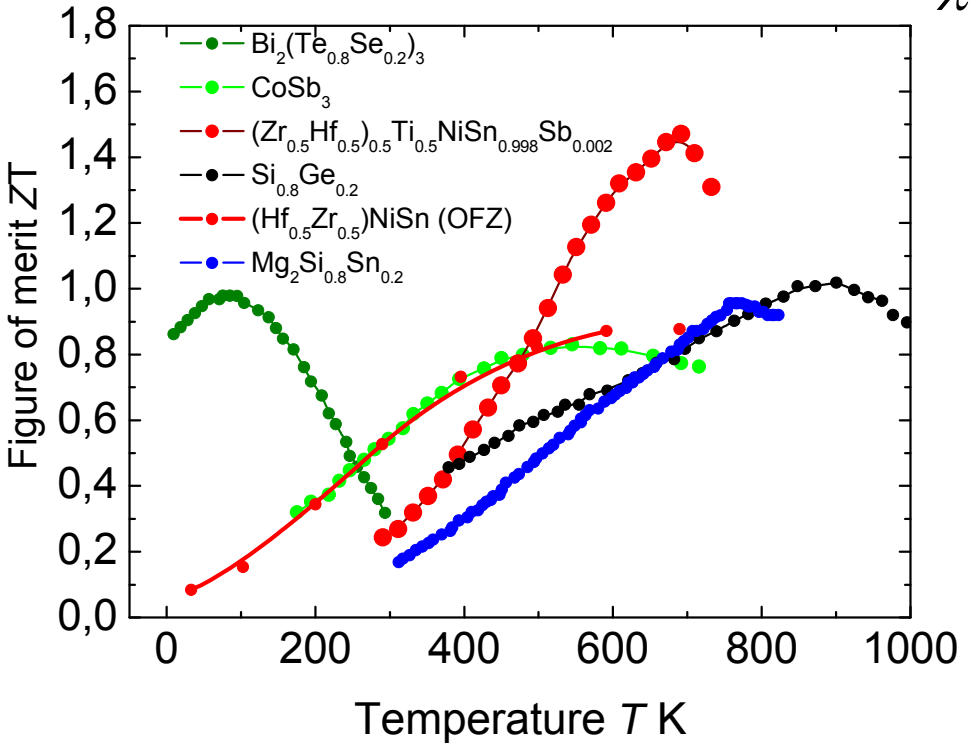
Sakuraba et al. APL **89** (2006) 052508

Sakuraba et al. APL **88** (2006) 192508

Inomata et al. to be published

$C1_b$ Heusler for Thermoelectrics

$$ZT = \frac{\alpha^2 \sigma}{\lambda} T$$



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

BOSCH

R. Asahi et al. J. Phys.: Cond. Mat. **20** (2008) 64227
K. Miyamoto et al. Appl. Phys. Express **1** (2008) 081901
E. Toberer, Nature Mat. **7** (2008) 105
VK Zaitsev et al. PRB **74** (2006) 045207

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

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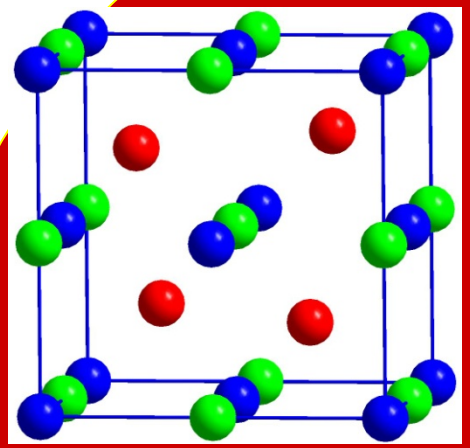
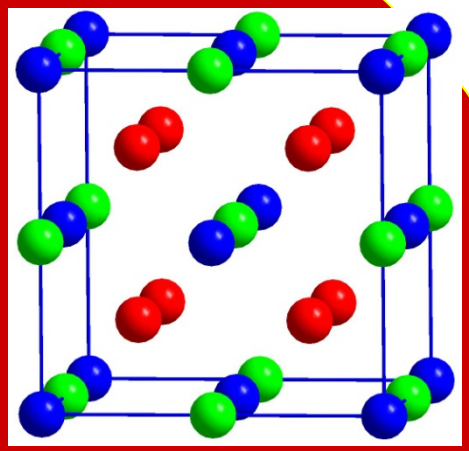
Rational Design

Structure

XYZ



Half-Heusler $C1_b$



Heusler $L2_1$
ホイスラー

X_2YZ

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pd	Bi	Po	At	Rn
Fr	Ra																
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

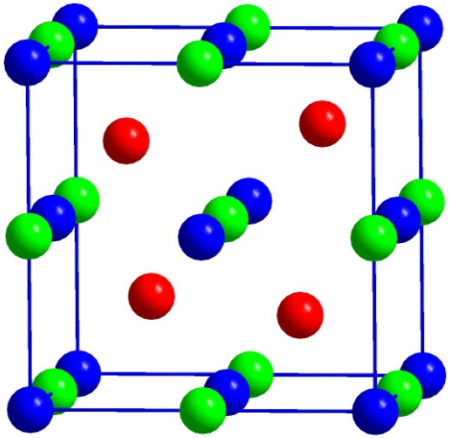
Y

X

Z

Semiconducting Heuslers – Stuffed ZnS

XYZ



Si_2

Ga

As

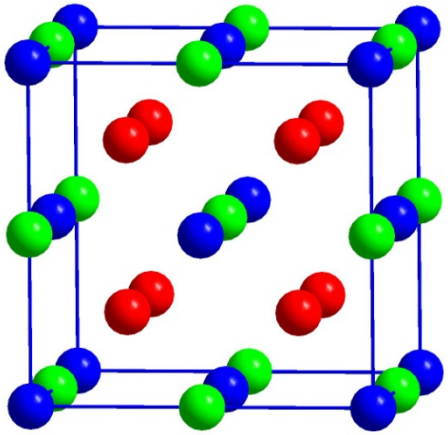
$3 + 5 = 8$

Co

Ti

Sb

$9 + 4 + 5 = 18$



X_2YZ

Li_2

Cu

Sb

$2*1 + 11 + 5 = 18$

Fe_2

V

Al

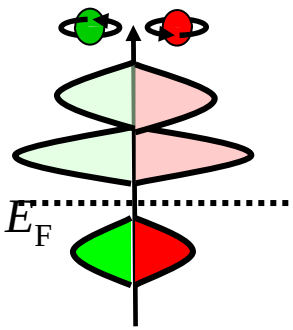
$2*8 + 5 + 3 = 24$

additional t_2-levels

Slater-Pauling Rule

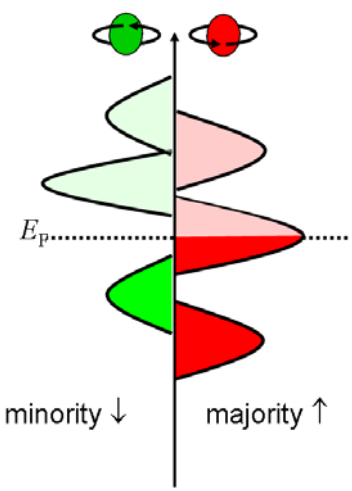
Magic valence electron number X_2YZ 24

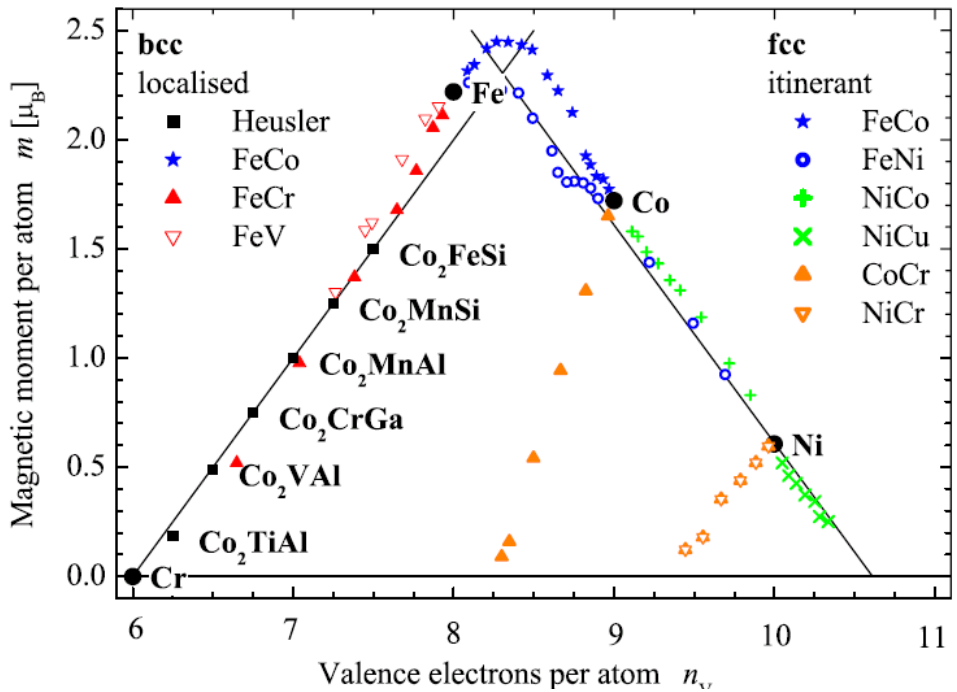
Valence electrons =24 + sat. magnetization



Co_2FeAl

2*9 + 8 + 3 = 29 Ms = $5\mu_B$





Kübler 1983

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

B. Balke et al., Sci. Technol. Adv. Mater. **9** (2008) 014102.

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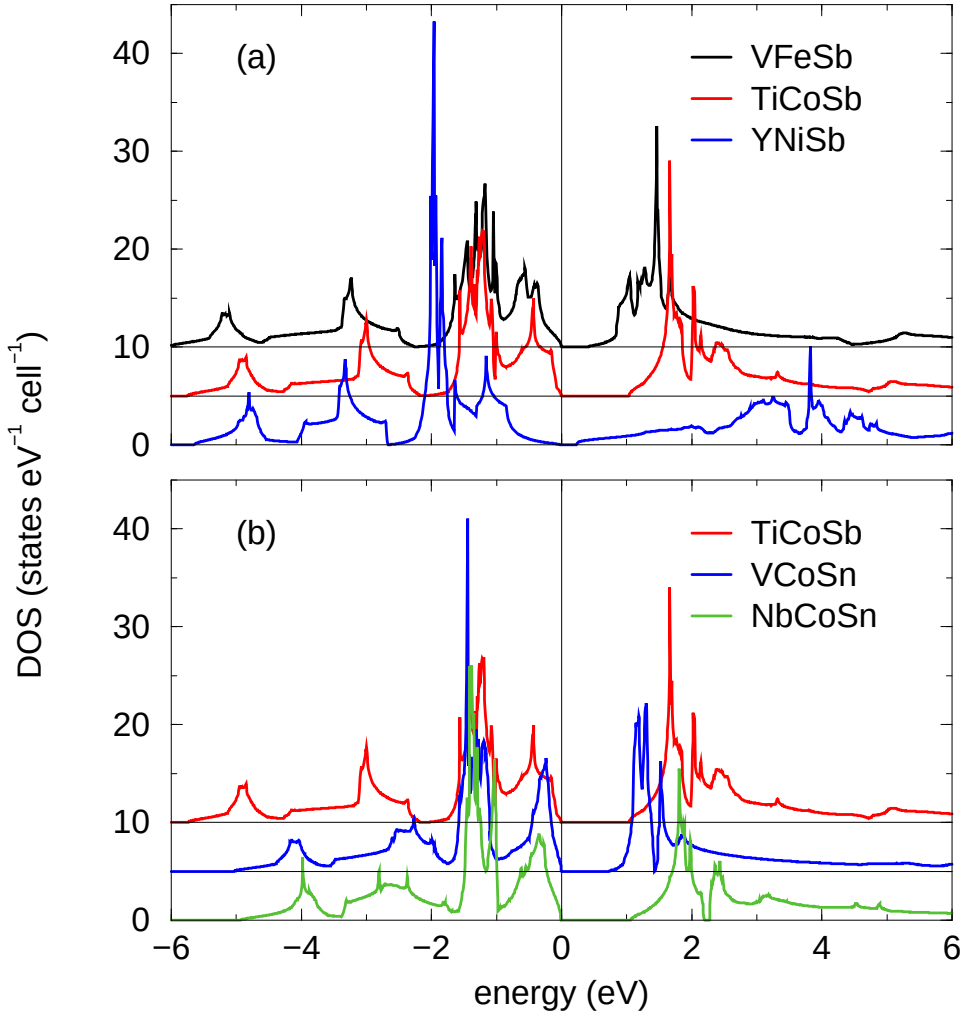
$C1_b$ Heuslers: Tunable Band Structures



CoTiSb

NiTiSn

NiYSb

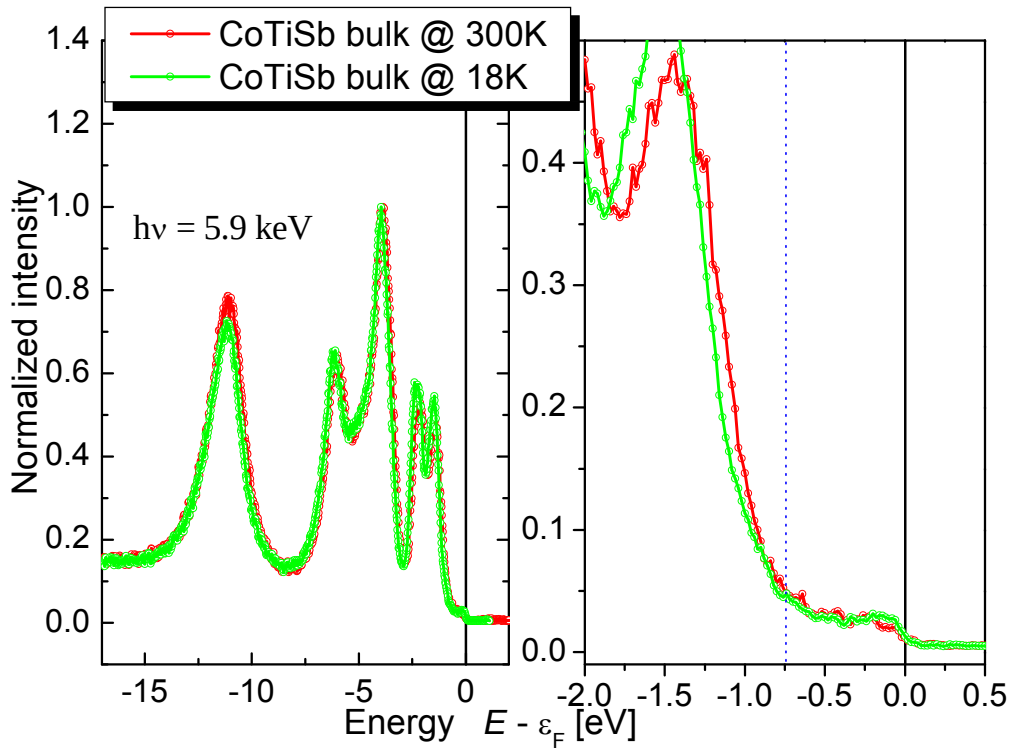
AuYSn

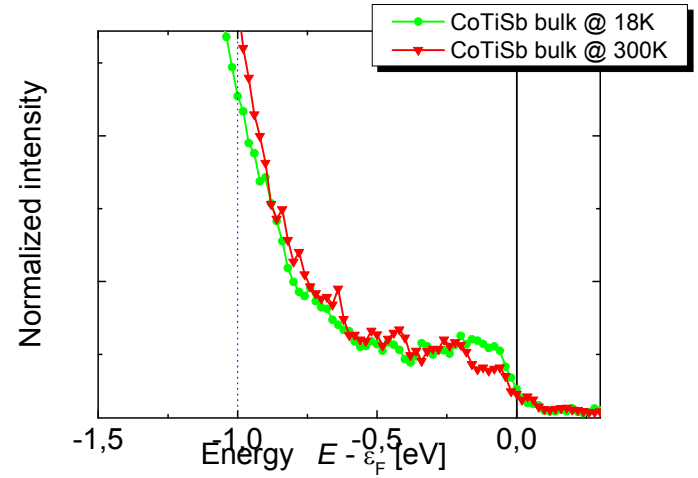
AuYPb

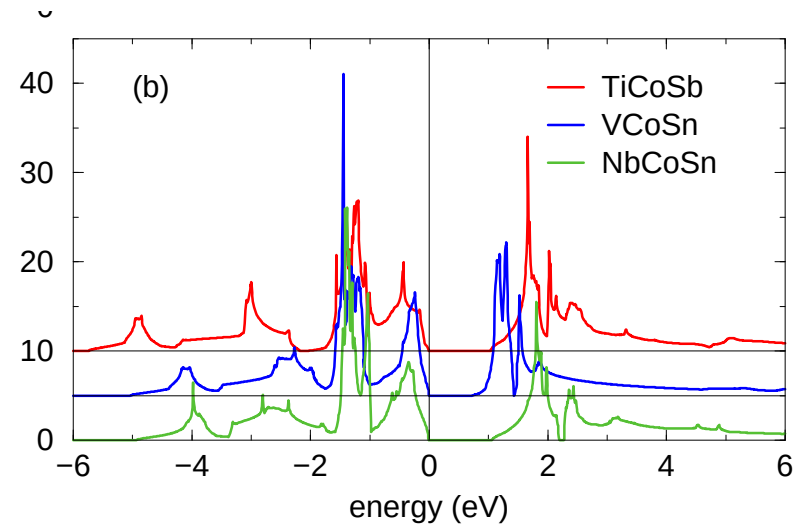
- Tunable gaps
- Easy to substitute
- Cheap

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

Thermoelectrica CoTiSb and Gap







Nice agreement between theoretical and experimental gap: 1 eV gap

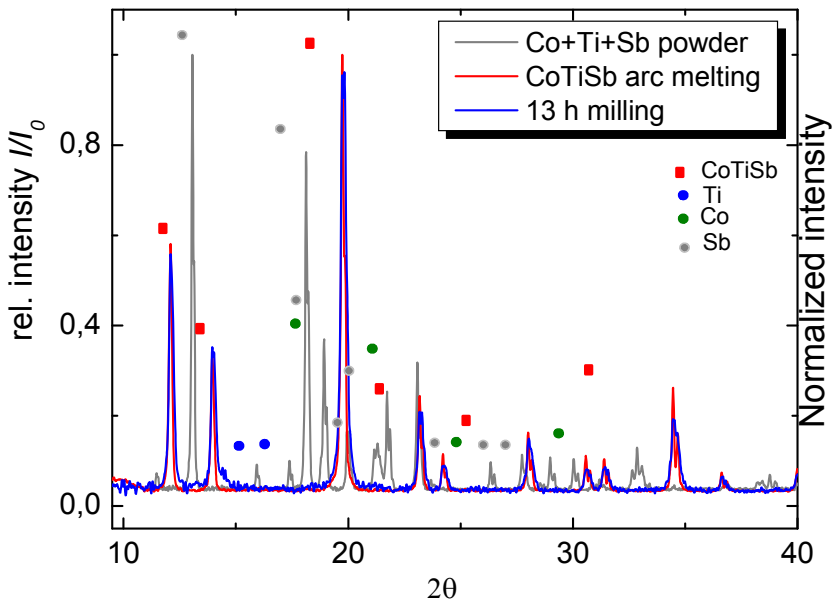
Ball Milling of Thermoelectrica CoTiSb

Starting from elements

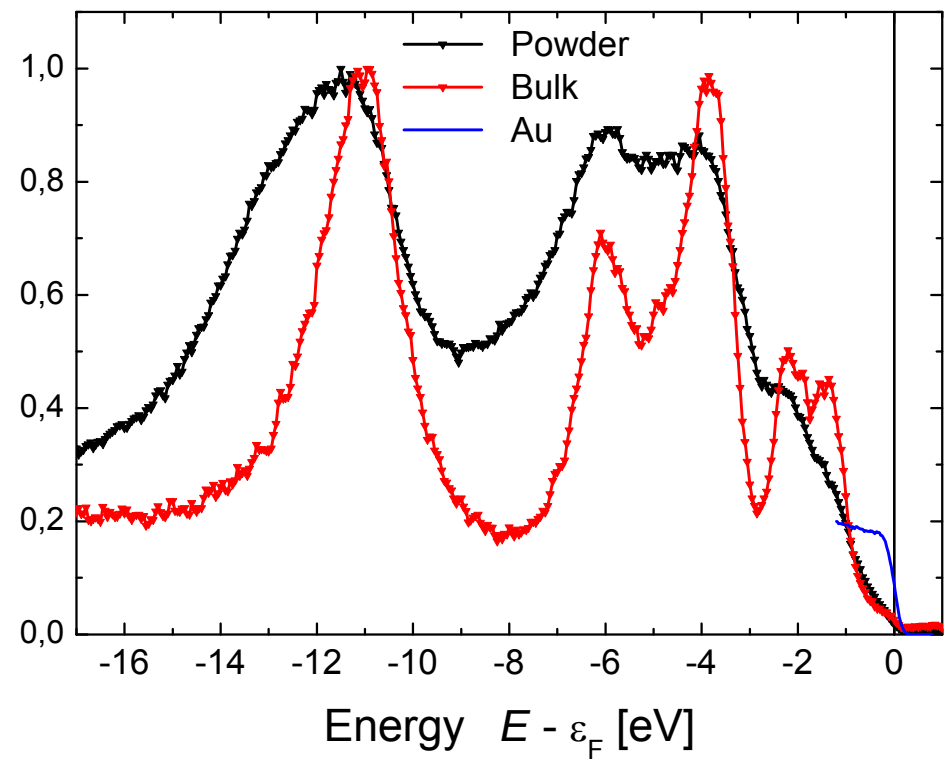
after 13 h nearly the same XRD

difference in the valence band: broadening

XRD

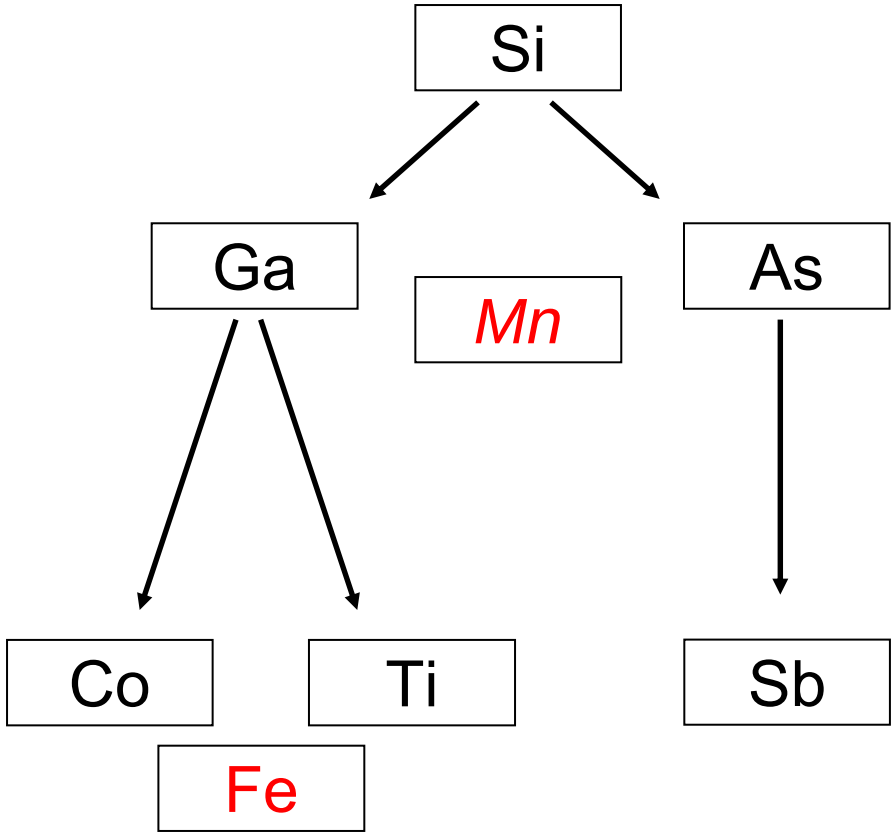


High Energy PES



Ouardi et al. in preparation

Design of a Dilute Magnetic Semiconductor



Valence electrons

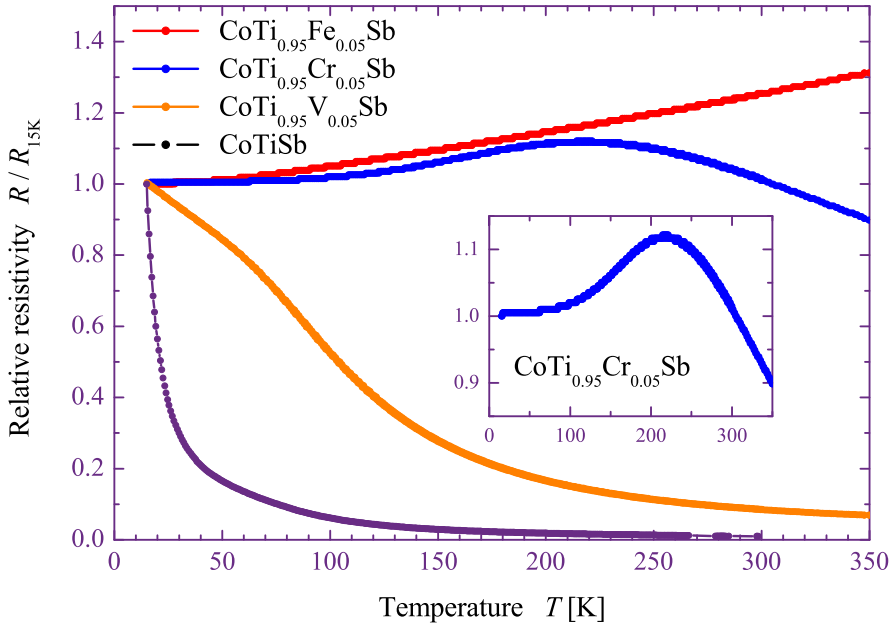
2 x 4 = 8

3 + 5 = 8 + x

Zinc-Blende → C1b

9 + 4 + 5 = 18 ± x

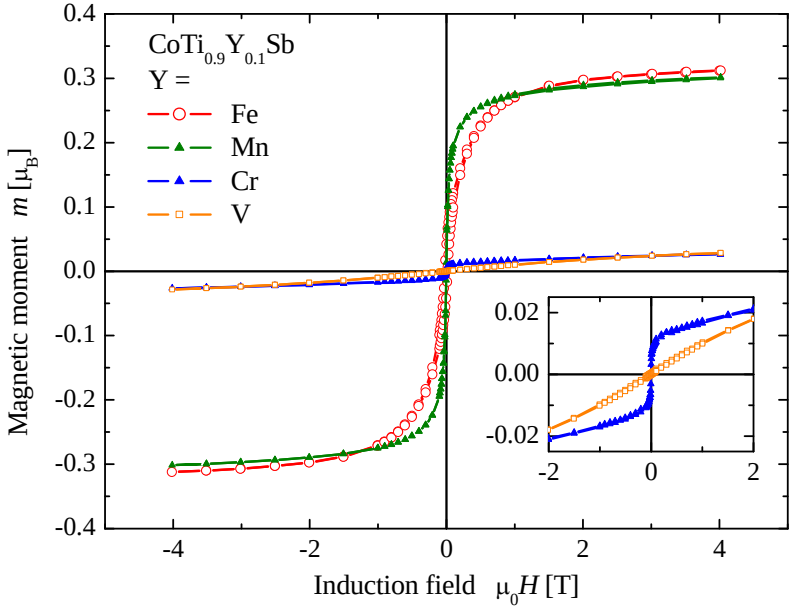
Tunable properties of Half Heuslers



$CoTi_{0.95}M_{0.05}Sb$

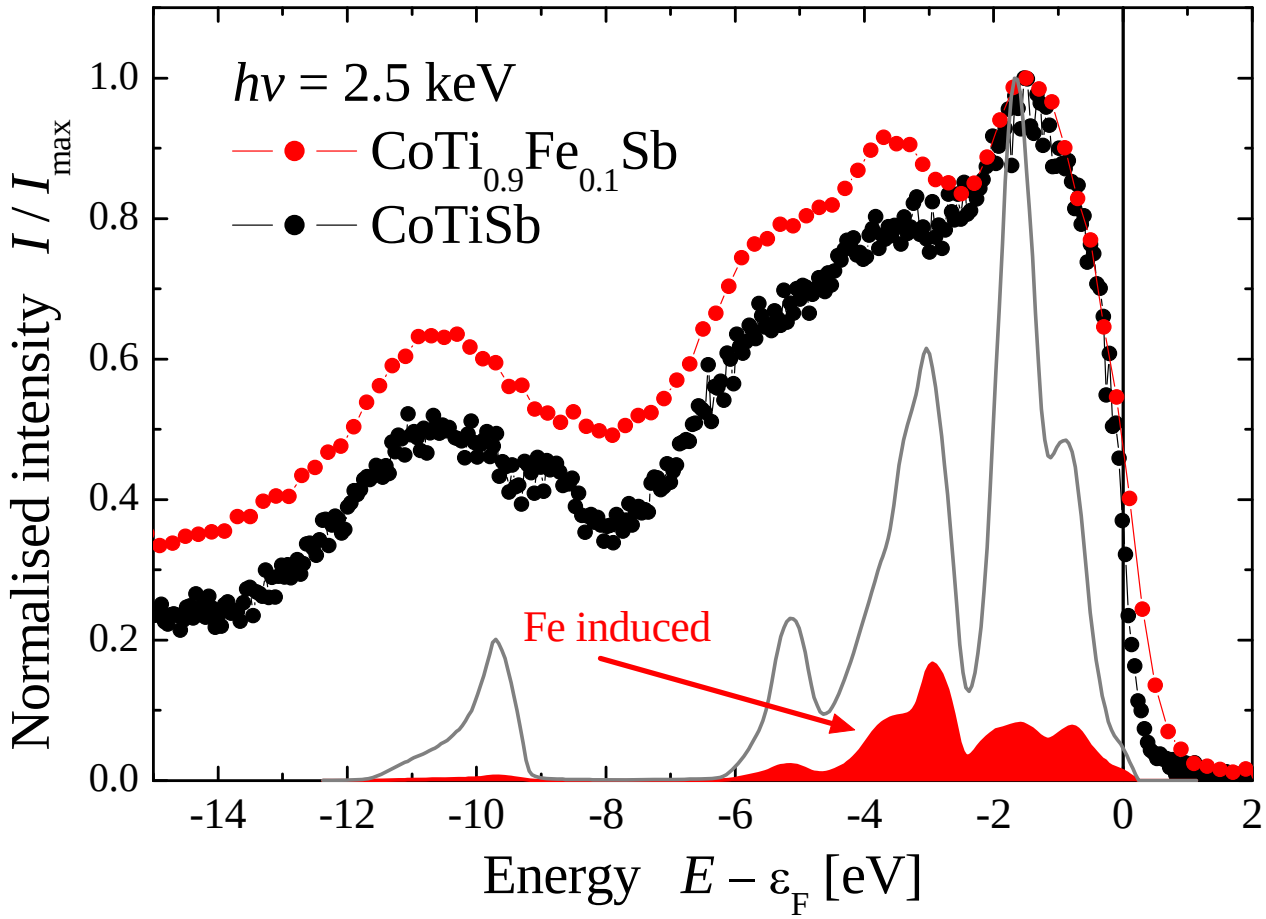
Number of Valence electroncs
Easy to tune

- ferromagnetic M = Fe, Mn, Cr
- paramagnetic M = V
- diamagnetic M = Sc und Ti



Balke et al. Phys. Rev. B **77**, 045209 (2008)

High Energy PES of $CoTi_{1-x}Fe_xSb$



HAXPES reveals the small changes in the density of states that are induced by the substitution by iron.

Balke et al. Phys. Rev. **B 77** (2008) 045209

Fecher et al. JESRP **156-158** (2007) 97

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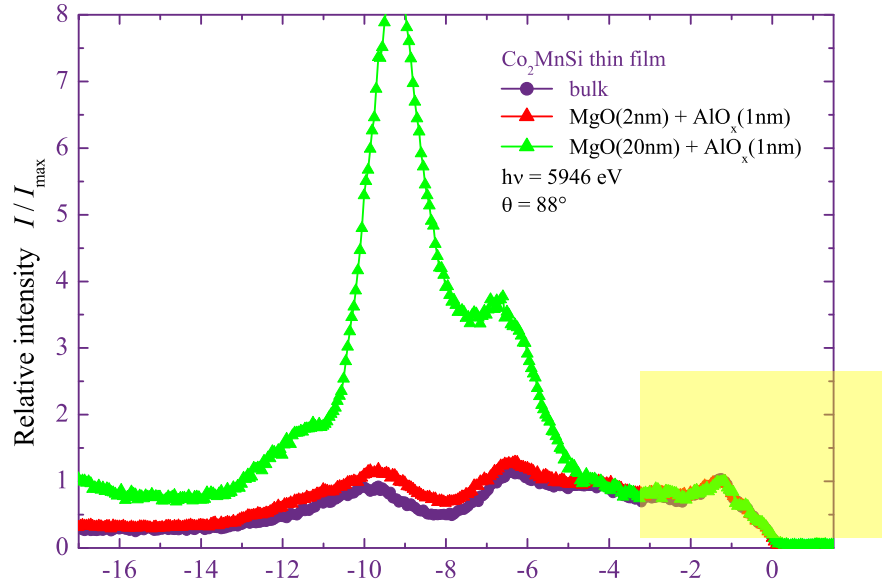
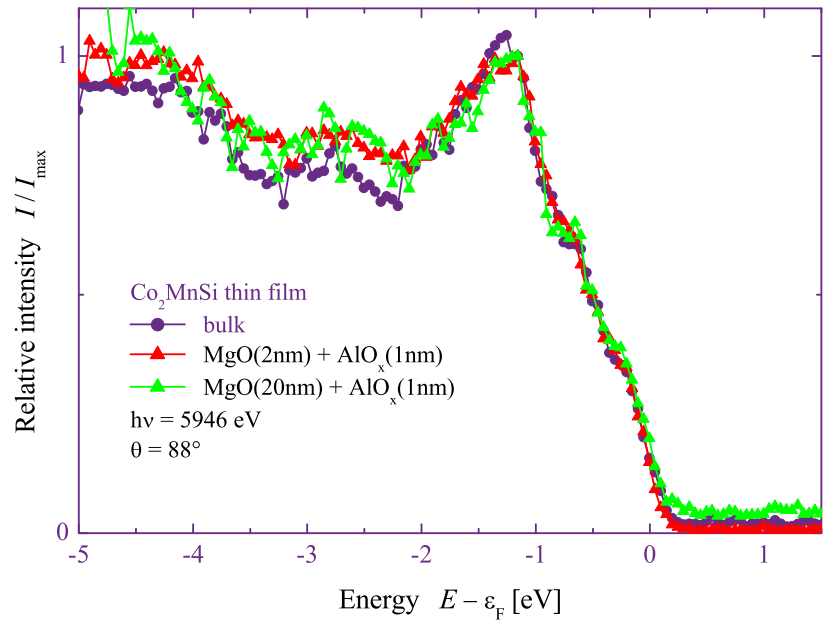
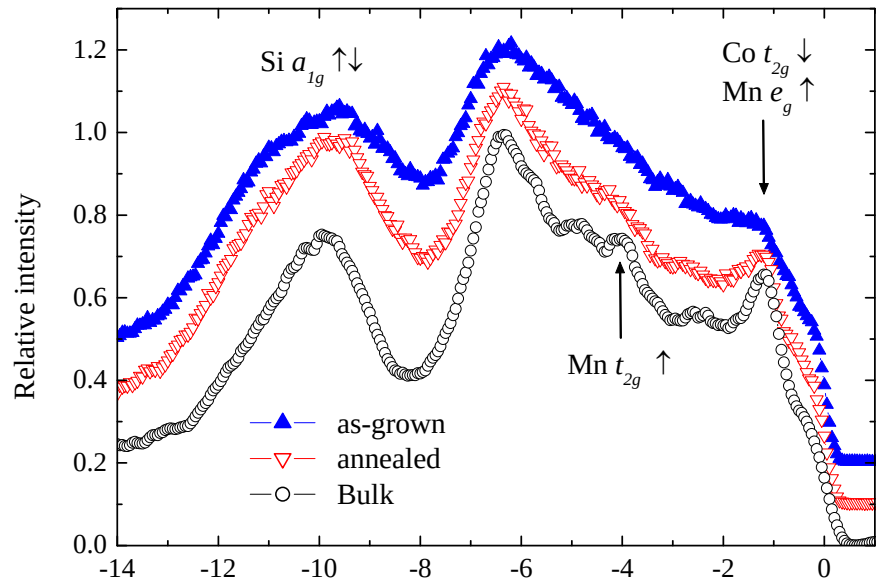
High Energy PES of buried films

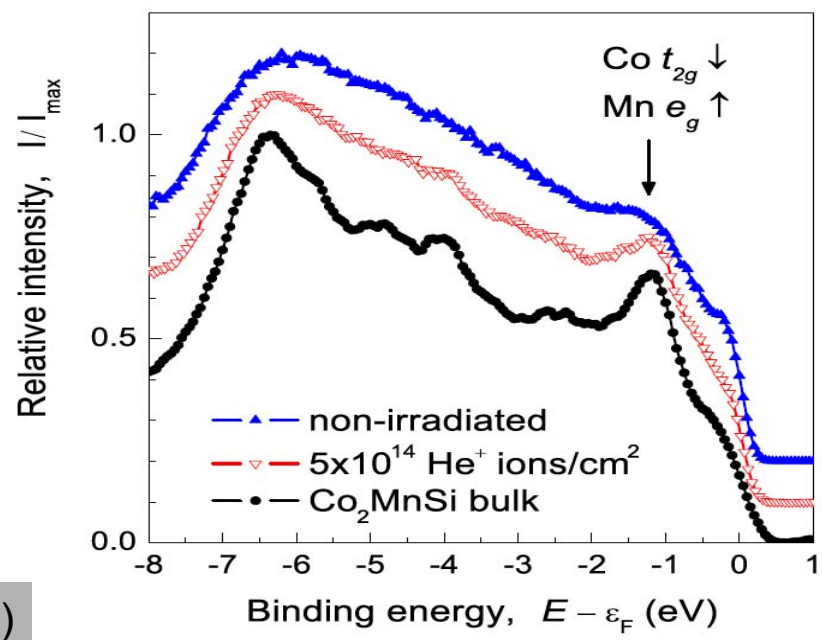




Fecher et al. APL **92** 195313 (2008)
Ouardi et al. J. Phys. **D 42** 084010 (2009)

Film quality studied by High Energy PES





$h\nu$ = 7.94 keV

Irradiation improves the film quality

O. Gaier et al. APL **94** 152508 (2009)

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Problem with Co_2FeSi

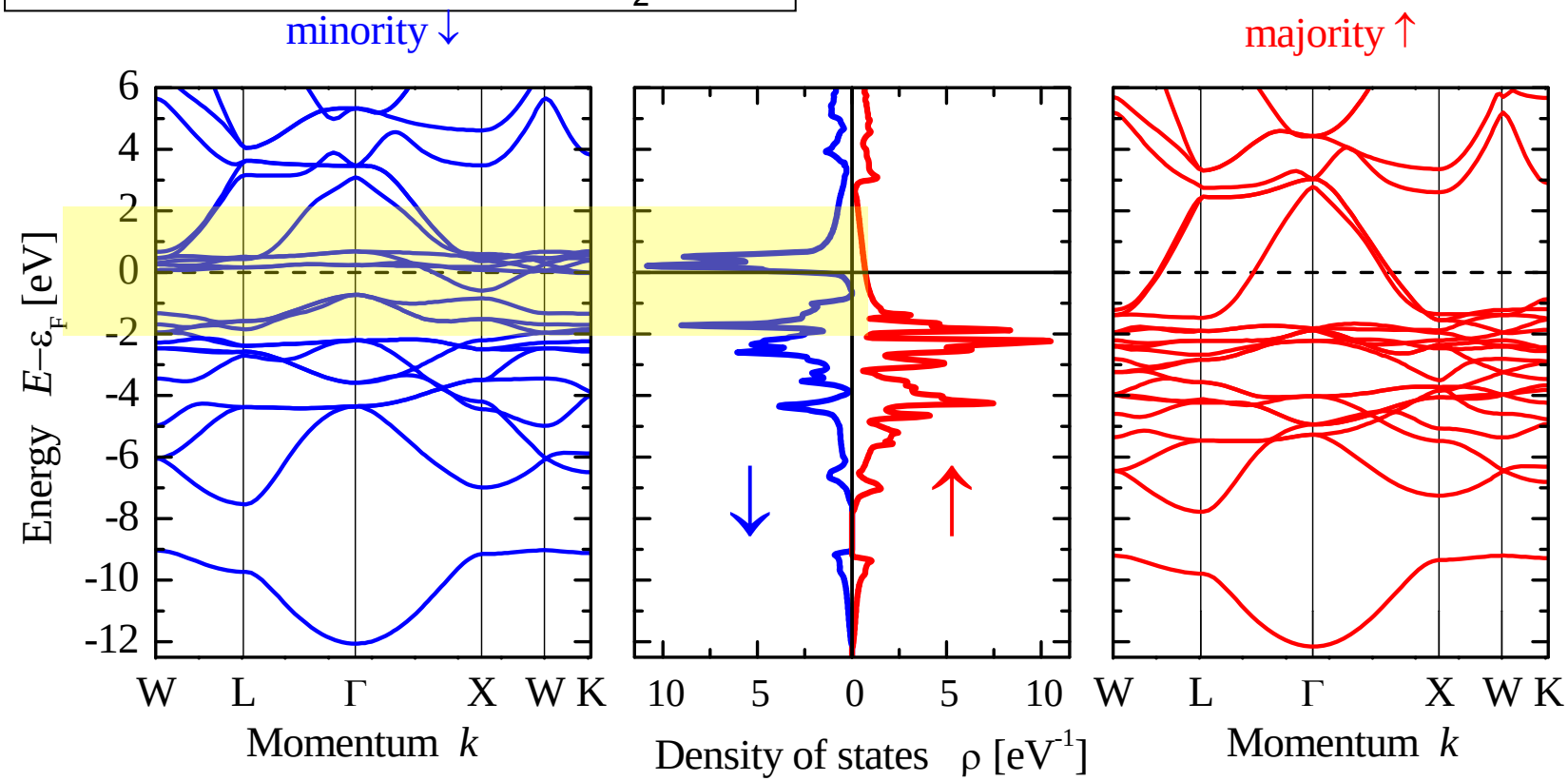
Theory

Full Potential GGA

LSDA does not reflect the correct electronic structure of Co_2FeSi

Experiment: $m_{exp} = 6\ \mu_B$

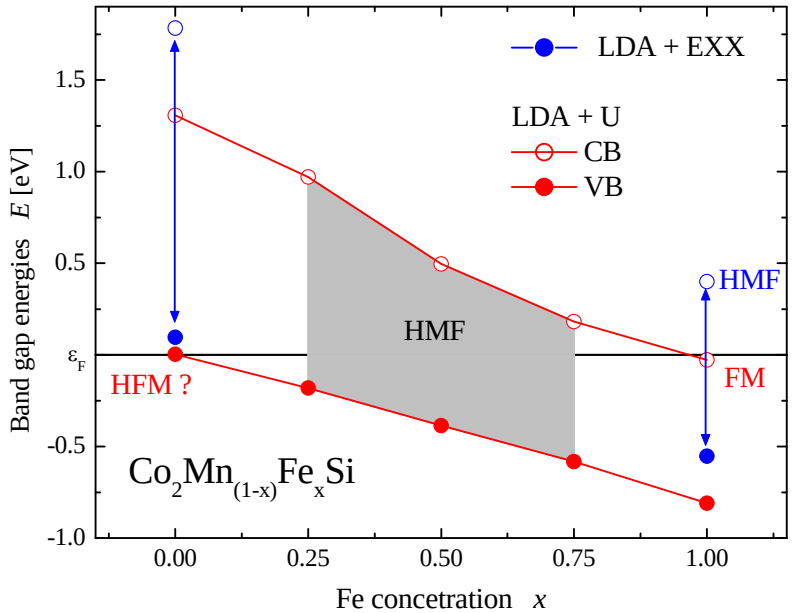
Calculation: $m_{calc} = 5.59\ \mu_B$

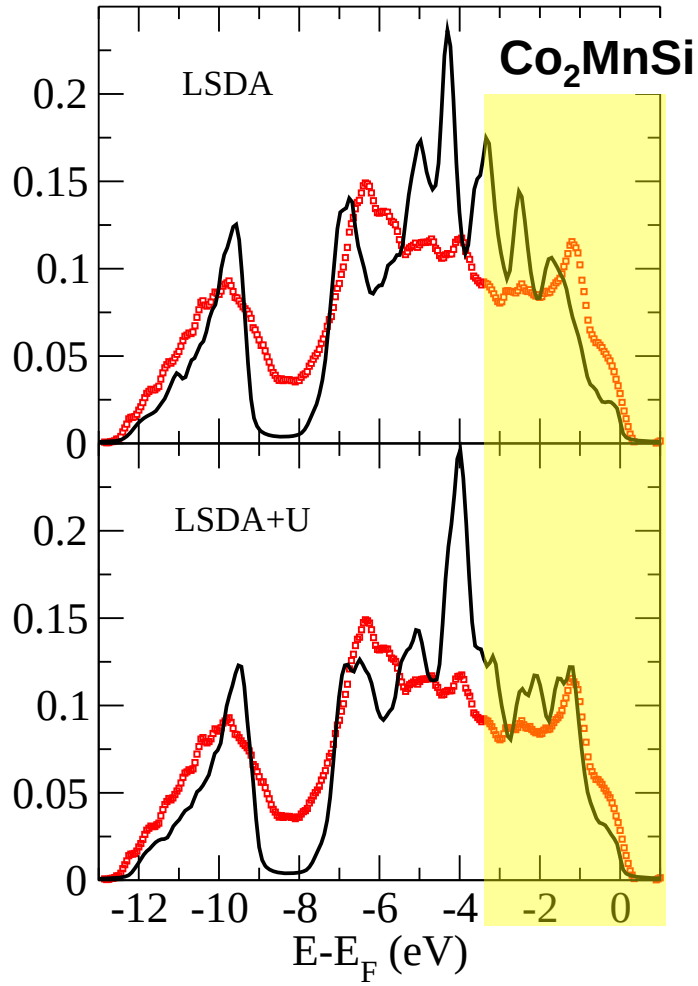


Wurmehl, et al ., APL **88** (2006) 032502.

Wurmehl, et al ., Phys. Rev. **B 72** (2005) 184434

Minority gap in $Co_2Mn_{1-x}Fe_xSi$





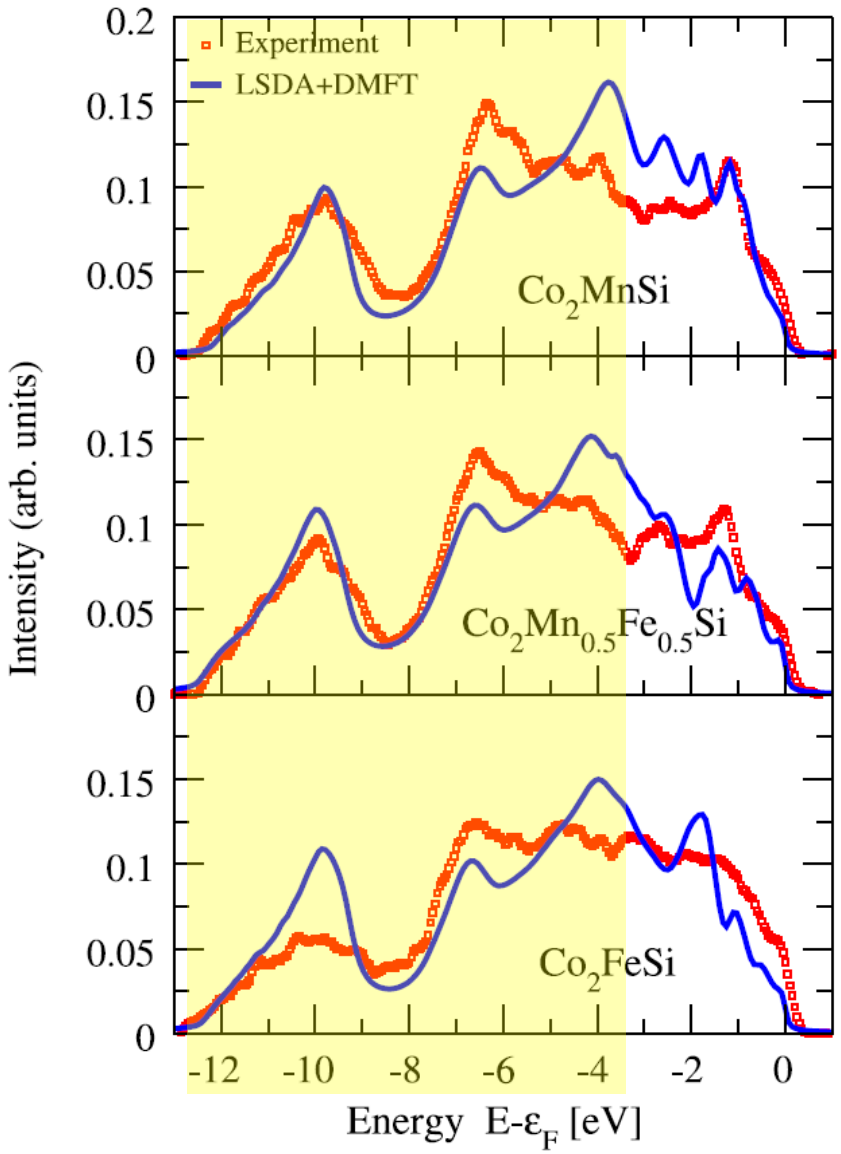
- U_{Co} = 1.9 eV
- U_{Mn} = 1.77 eV
- U_{Fe} = 1.785 eV
- LDA + EXX

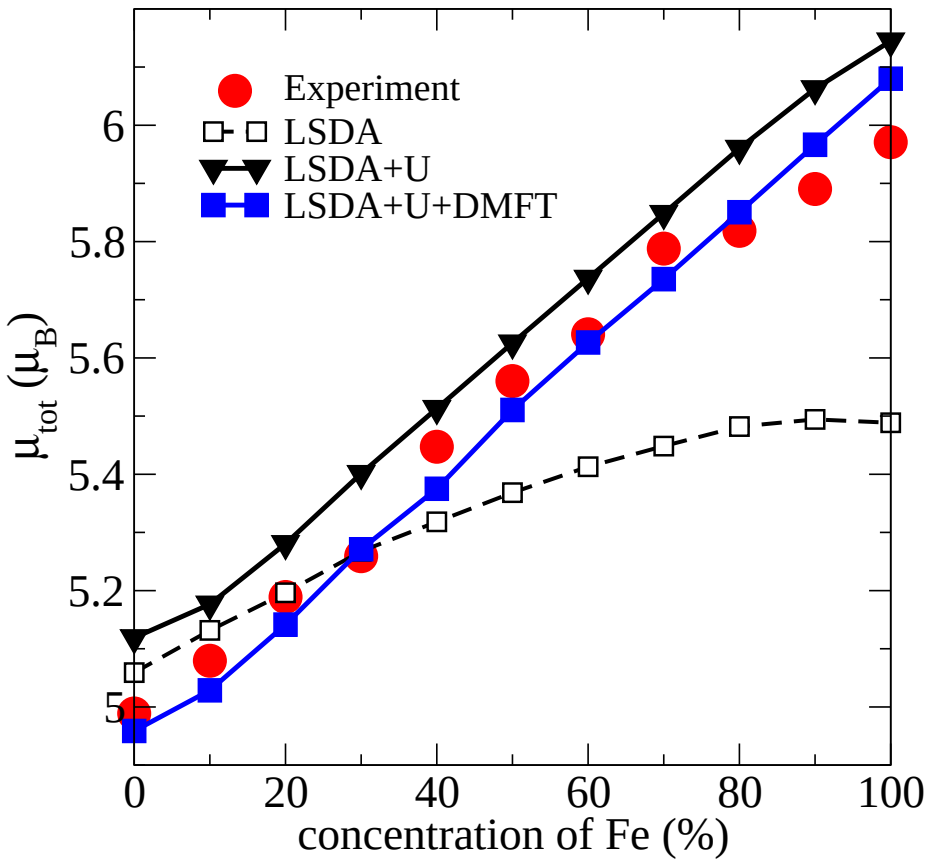
$$Exc(EXX, F\text{-}\alpha) = Exc(LDA) + \alpha\{Ex(HF) - Ex(LDA)\}$$

Wien2k: Tran et al., PRB **74** 2006 155108
KKR: Ködderitzsch et al. PRB **77** 2008 045101

Kandpal et al., PRB **73** (2006) 094422
Chadov et al. J. Phys. **D 42** 084002 (2009)

$Co_2Fe_{1-x}Mn_xSi$





Chadov et al. J. Phys. **D 42** 084002 (2009)

Summary

- HAXPES is a new tool to investigate the bulk properties of spintronics and thermelectric materials
- HAXPES of thin films can help to improve the film quality
- HAXPES of the valence band of tunnel junctions
- To describe the electronic structure of Heusler compounds ($L2_1$) correlations have to taken into account

SPINHAXPES and MCD will help to determine the spin polarization (with Claessen, Drube, Schoenhense, Kobayashi …)

Co-workers

Spring 8: Keisuke Kobayashi, Eiji Ikenaga, Jung-Jin Kim, Yuji Saitoh , Yukiharu Takeda , Shigenori Ueda, Yoshiyuki Yamashita, Hideki Yoshikawa, Ke Yang. JST-DFG

NIMS: K. Inomata et al. JST-DFG

Sapporo: M. Yamamoto JST-DFG

Sendai: Y. Ando et al. FG559

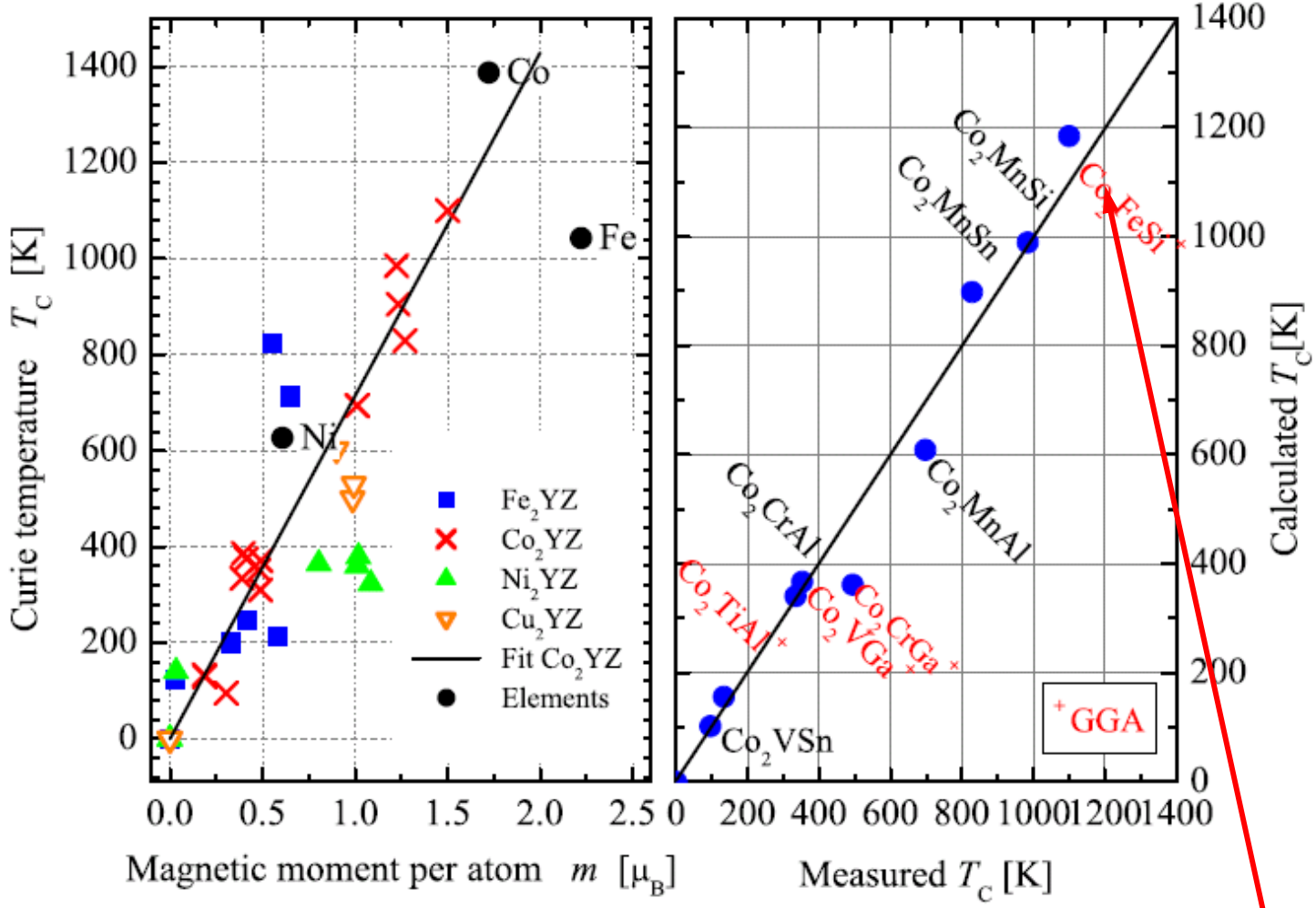
LMU: H. Ebert, J. Minar, J. Braun

BESSY, Berlin: Wolfgang Eberhardt, Marcel Mertin, Franz Schäfers, M. Gorgoi.

SPECS, Berlin: Sven Mähl, Oliver Schaff.

DFG-FG559, FE633, SP1166, BMBF: HAXPES, HEUSPIN, MULTIMAG

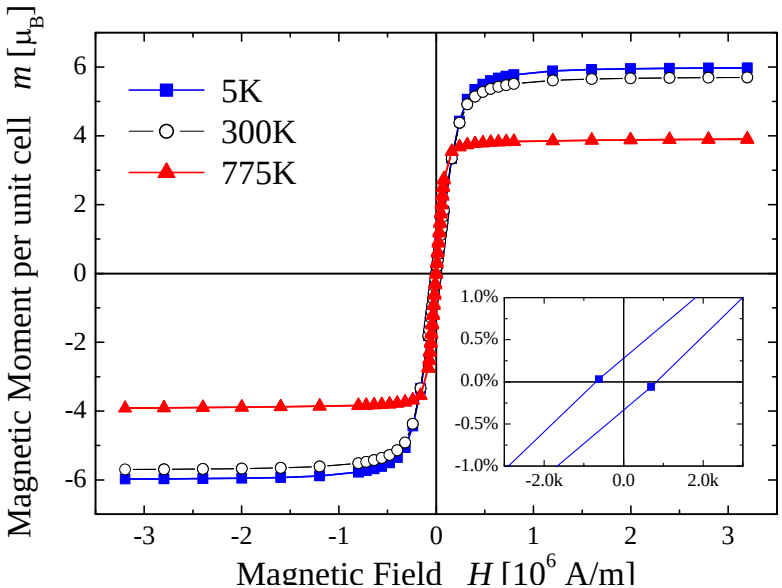
High Curie Temperatures

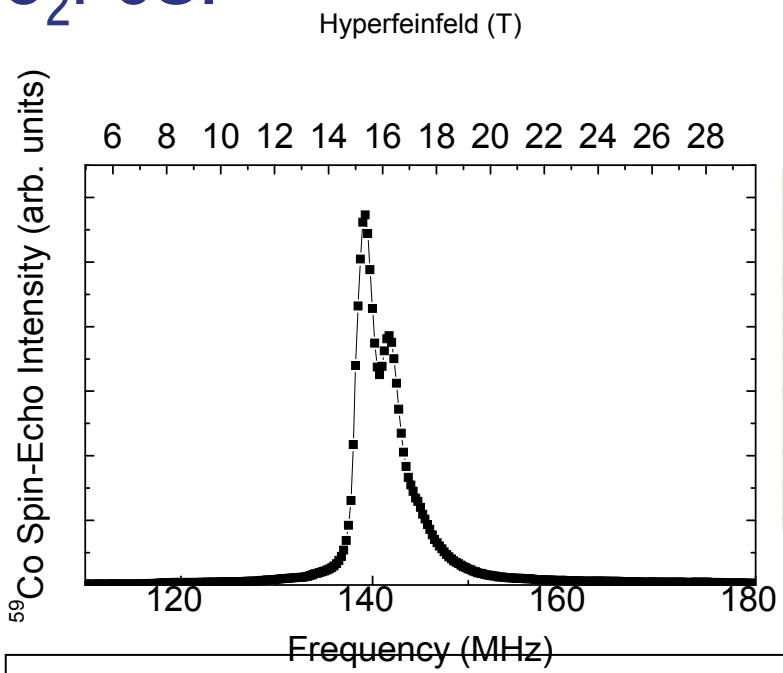


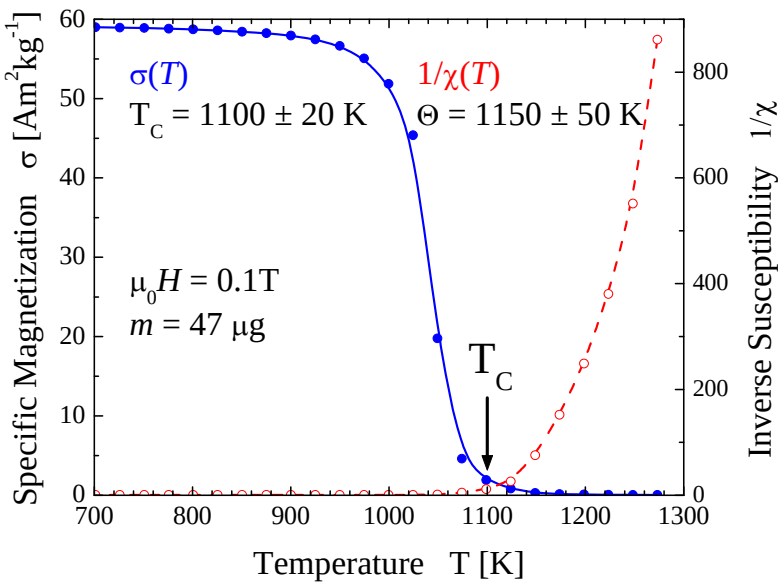
Expected Curie temperature for *Co_2FeSi* : > 1000K

Fecher, J. Appl. Phys. **99** (2006) 08J106
Kübler et al., Phys. Rev. **B 76** (2007) 024414

Co_2FeSi







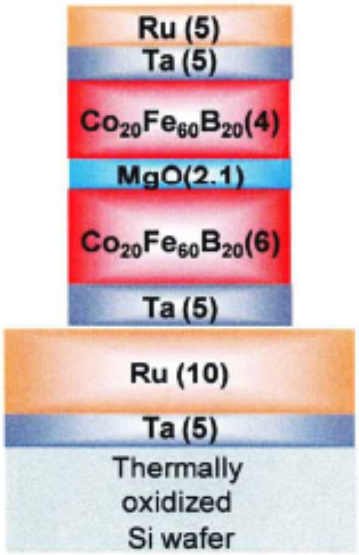
Magnetic moment in saturation: $5.97\mu_B \pm 0.1\mu_B$ at 5K

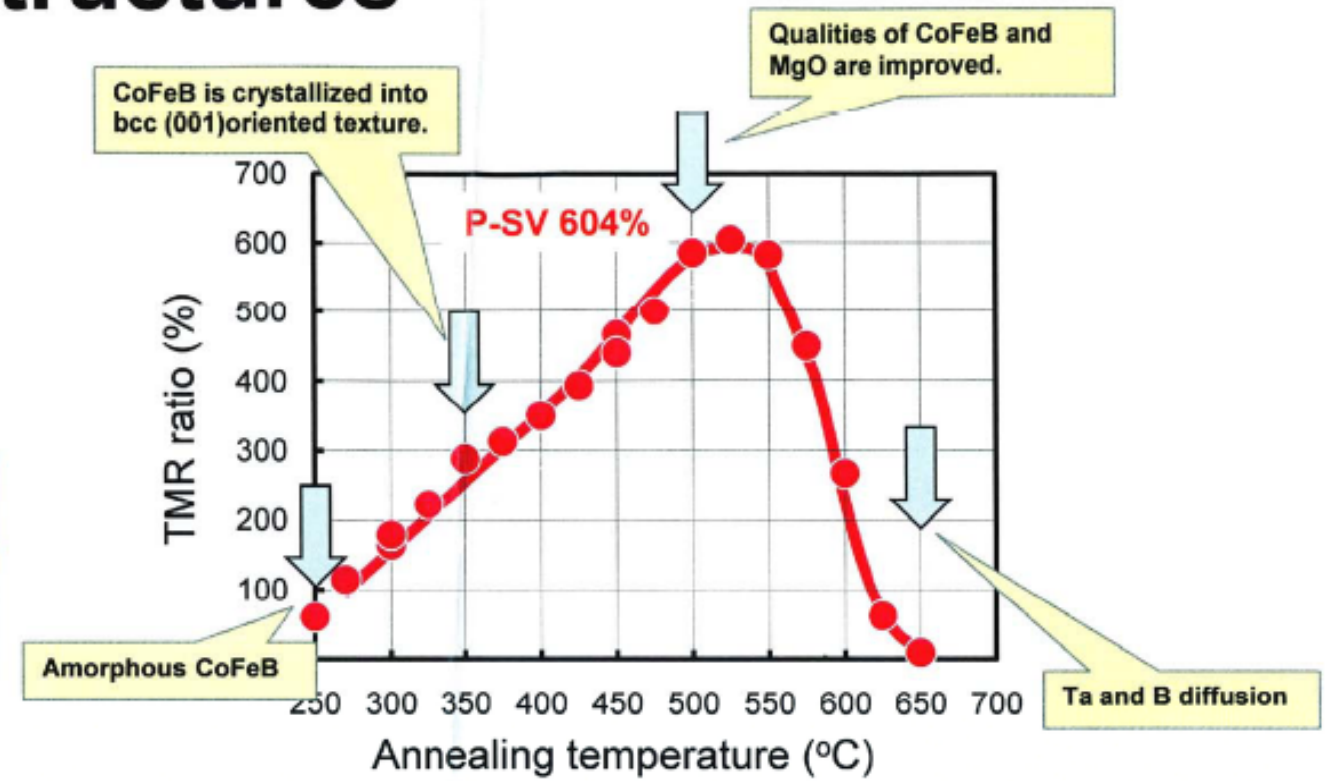
Extrapolation to 0K :Slater-Pauling rule: 6 μ_B

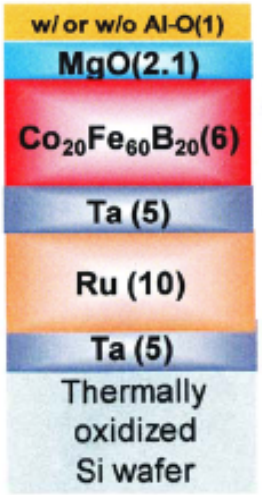
Curie Temperature 1120 K

Wurmehl, et al ., APL **88** (2006) 032502.
Wurmehl, et al ., Phys. Rev. B **72** (2005) 184434

Sample structures



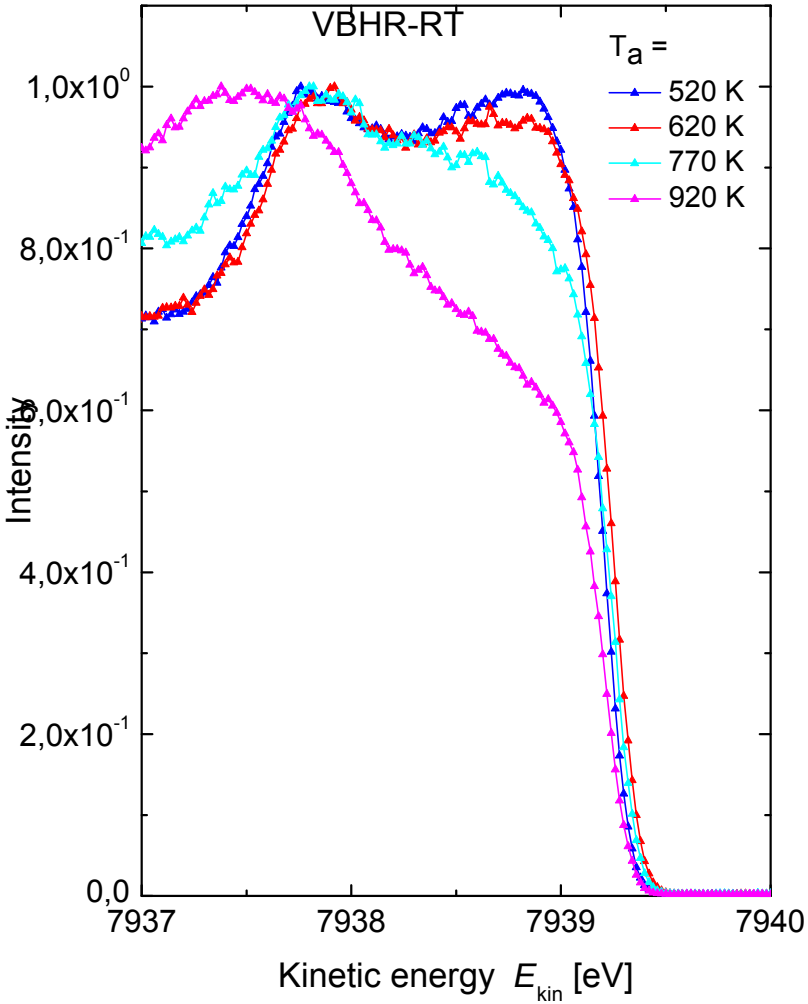


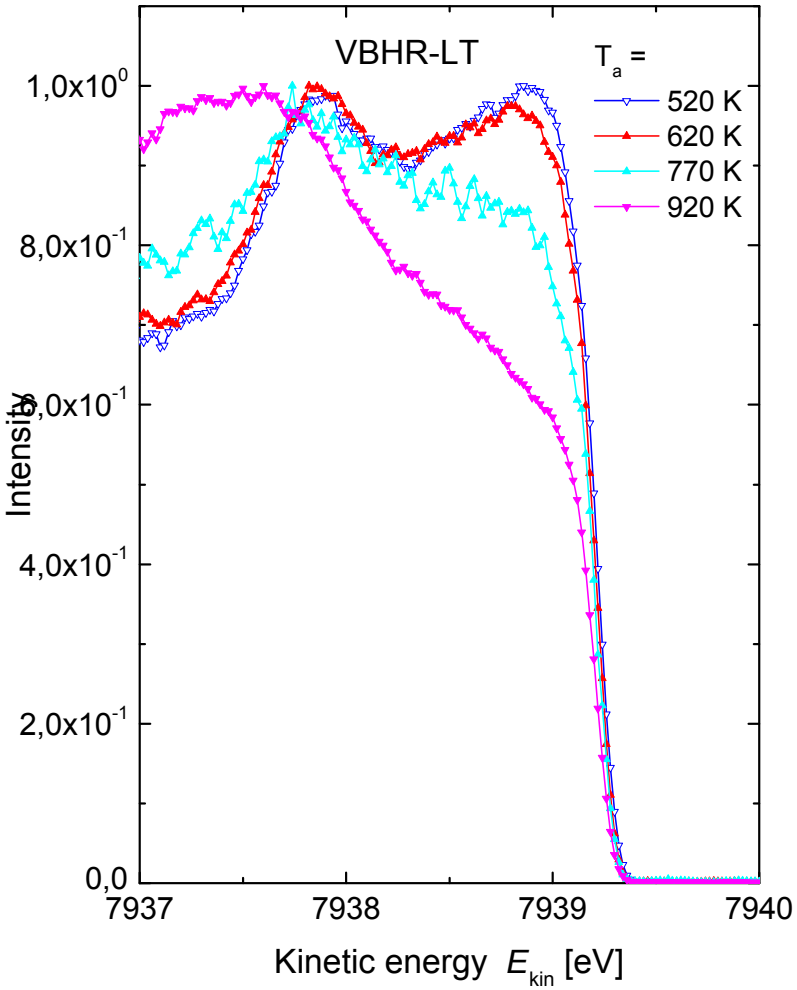


SP4018:Sub./Ta(5)/Ru(10)/Ta(5)/$Co_{20}Fe_{60}B_{20}$(6)/MgO(2)
SP4019:Sub./Ta(5)/Ru(10)/Ta(5)/$Co_{20}Fe_{60}B_{20}$(6)/MgO(2)/ AlOx(1)
SP4031:Sub./Ta(5)/Ru(10)/Ta(5)/$Co_{20}Fe_{60}B_{20}$(6)/MgO(20)/AlOx(1)
SP4032:Sub./Ta(5)/Ru(10)/Ta(5)/$Co_{20}Fe_{60}B_{20}$(6)/MgO(20)

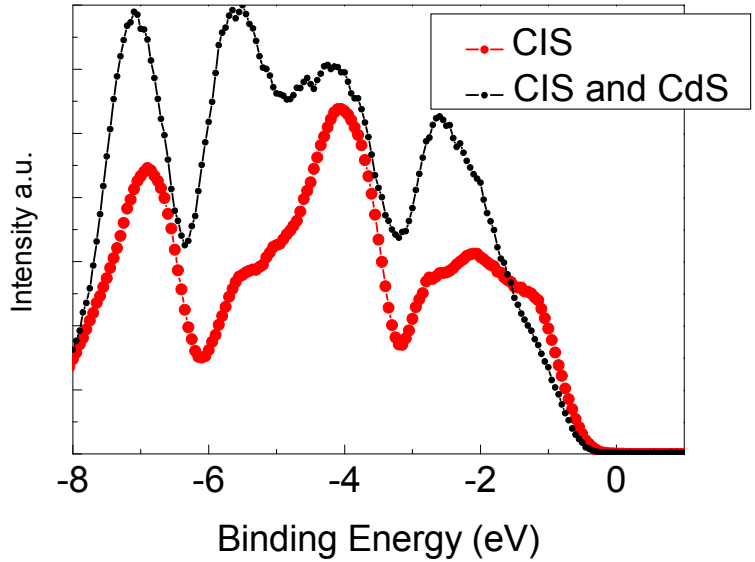
Annealed at 250, 350, 500, 650°C for 1hr in 4kOe
AlOx caps were deposited using other sputtering system after air exposure.

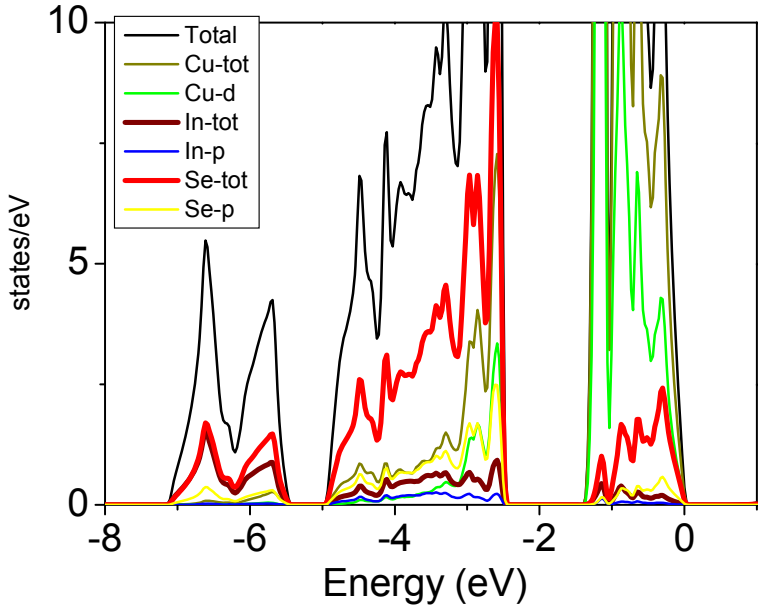
Valenceband





HAXPES of CIS

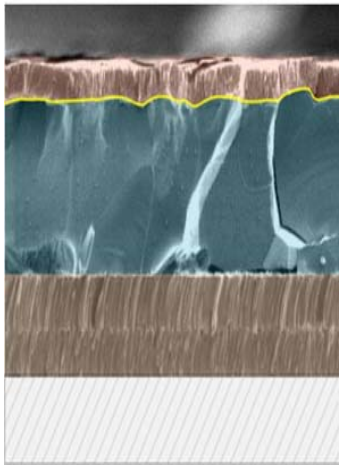




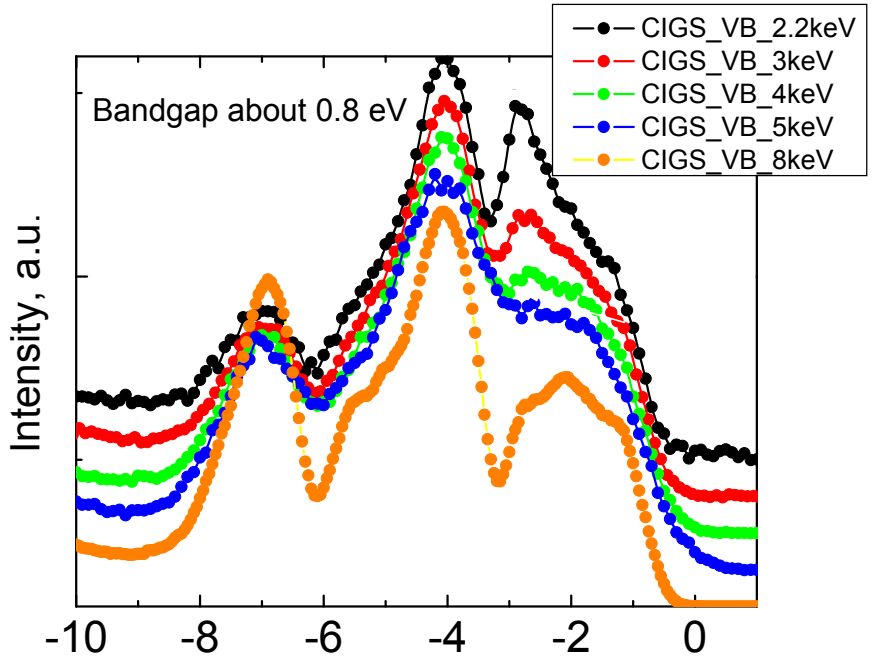
hν = 8 keV

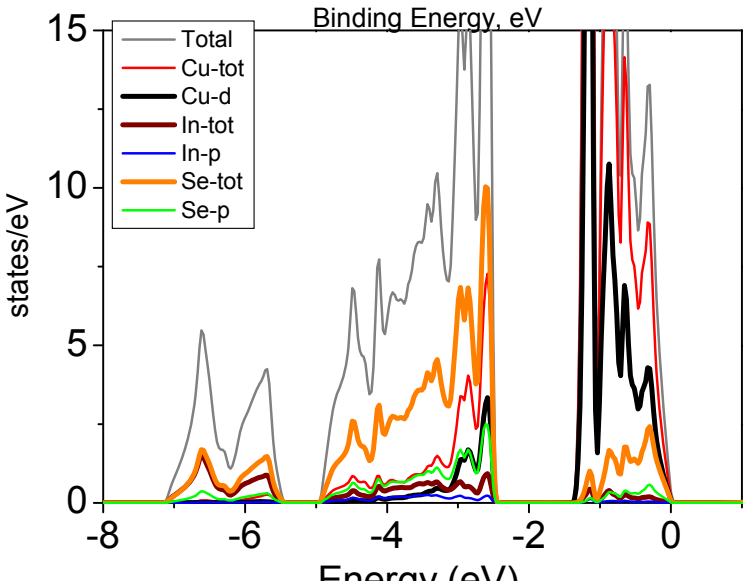
Cross section

Mainly s and p states



HAXPES: CIS

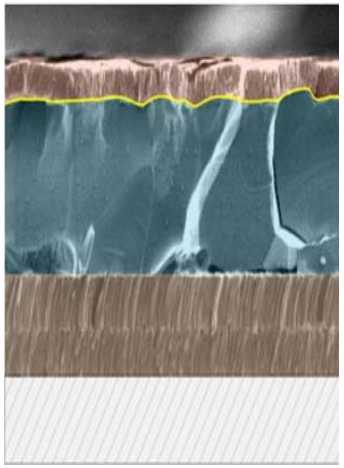
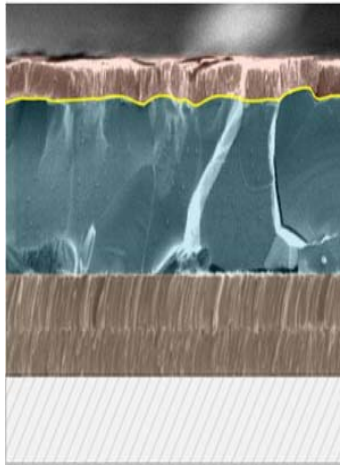
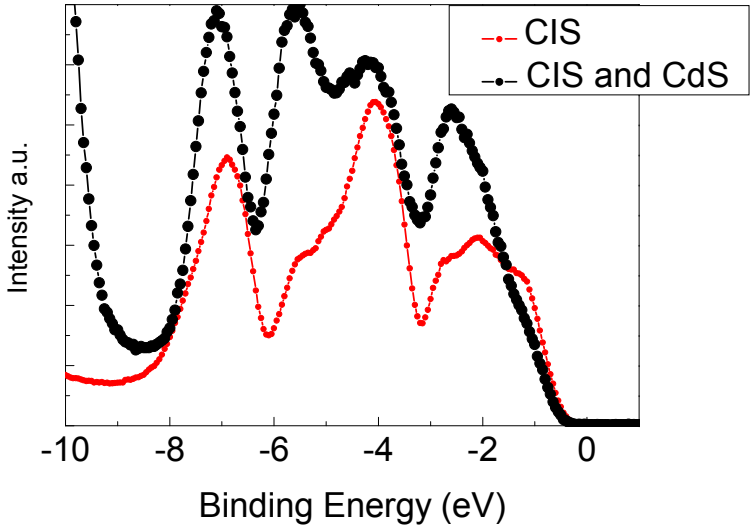
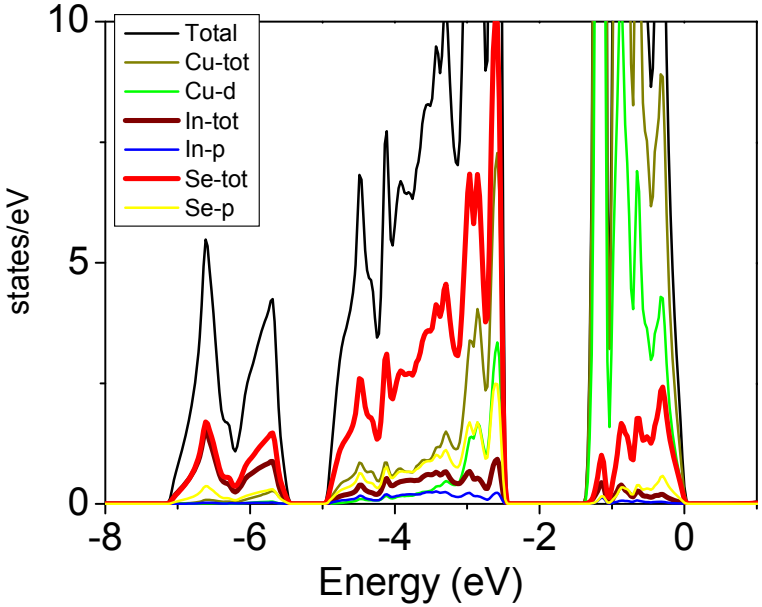
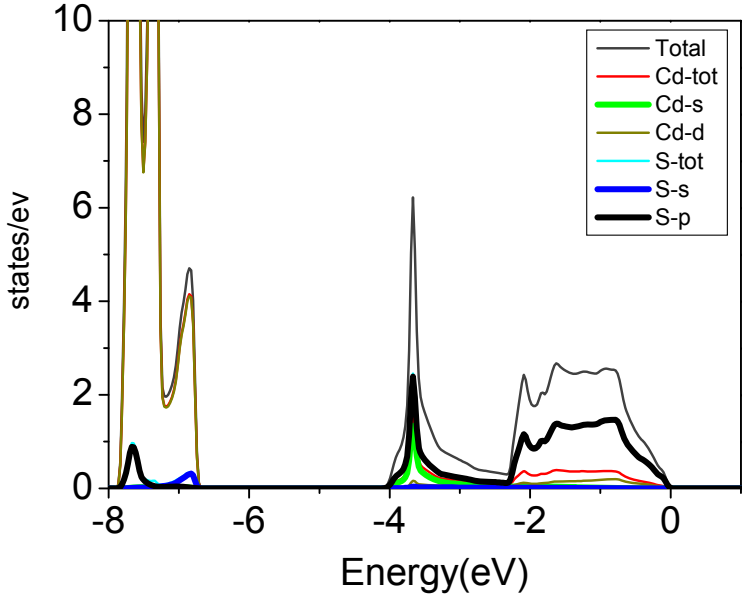




hν = 2 keV – 8 keV

Intensity depends on

Cross sections !



HAXPES of CIS +/- CdS