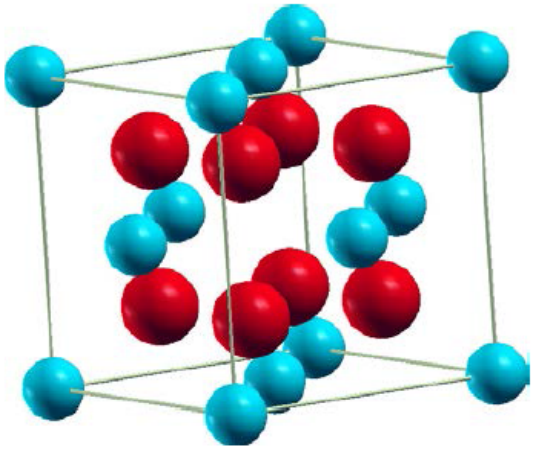
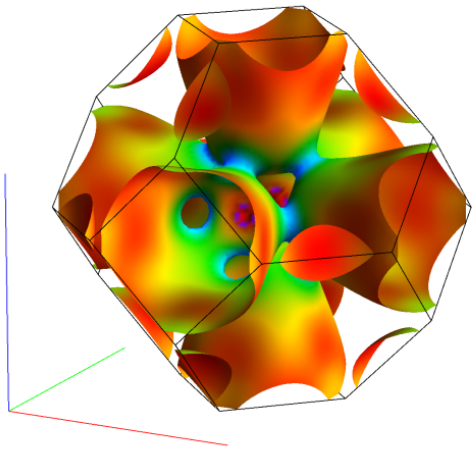
Struktura elektronowa a efektywność zjawisk konwersji energii w złożonych strukturach krystalicznych

Janusz TOBOŁA

KFMS WFIS AGH



$$G = G_0 + G_0 V G$$



Seminarium WFIS, 7 grudnia 2018, Kraków

PLAN

Energy conversion effects in solids

fundamental- quantum electrodynamics & thermodynamics
practical - search for energy recovering, storage and saving
complex phenomena – *thermoelectrics, magnetocalorics, ion-batteries*

Ab initio modelling: electronic structure (KKR & KKR-CPA)

electronic structure of realistic disordered systems
relativistic effects (spin-orbit interaction in transport)
electron transport via Boltzmann approach
densities of states vs. character of charge/discharge curves

Applications to thermoelectric materials

Effect of **band convergence** in Mg_2(Si-Sn-Ge) alloys
Effect of **spin-orbit coupling** on TE in p-doped Mg2X
Effect of **bands alignment** in half-Heusler phases

Applications to Li-/Na-ion battery systems

Electronic structure of NaxCoO2 and particular role of O vacancies
Electronic structure & magnetism of „fully disordered” Lix(Ni-Co-Mn)O2

Collaboration in TE materials

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Institut Jean Lamour CNRS, Universite de Lorraine, Campus Artem, NANCY, France

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Collaboration in 'battery' materials

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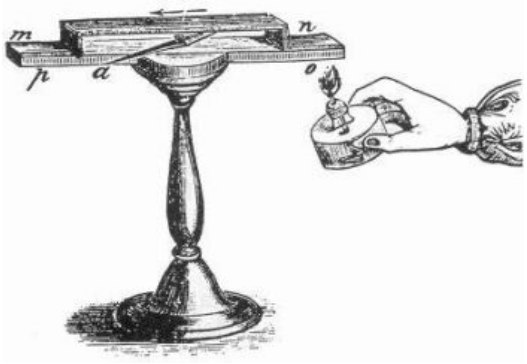
Partly supported by the Polish National Science Center (NCN)
Project **MAESTRO DEC-2011/02/A/ST3/00124**

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

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

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

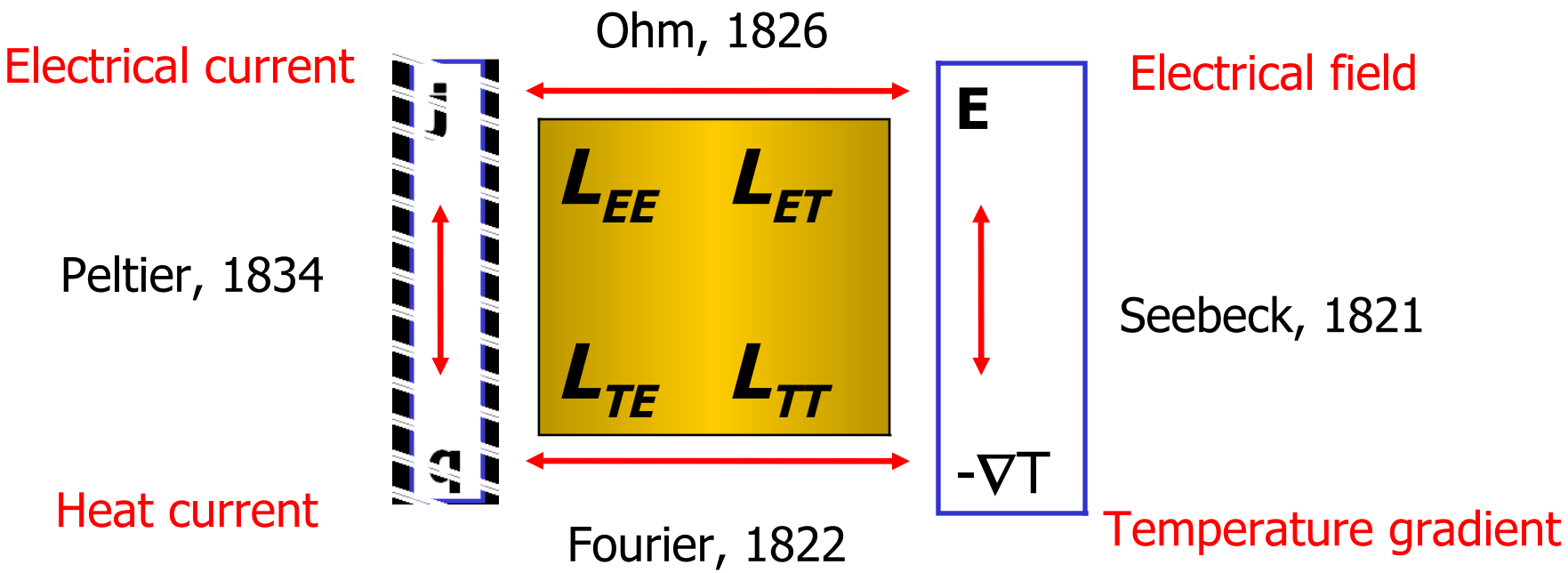
A.F. Ioffe

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

Lorentz factor

Thermal conductivity (phonons /electrons)

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), …

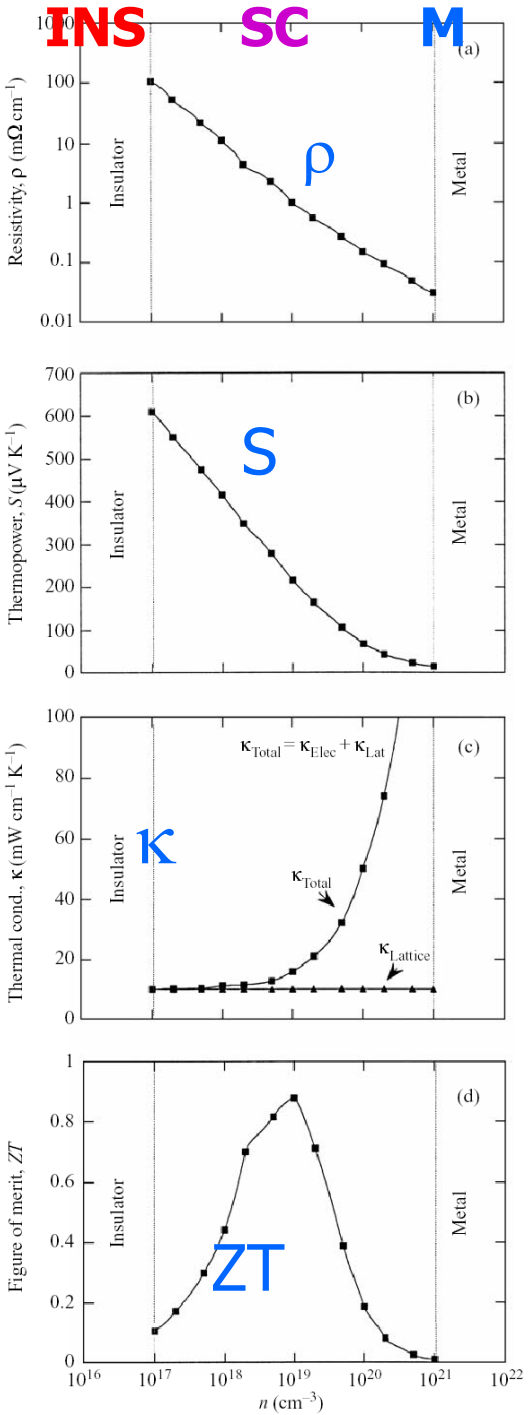
Thermoelectric properties

Resitivity

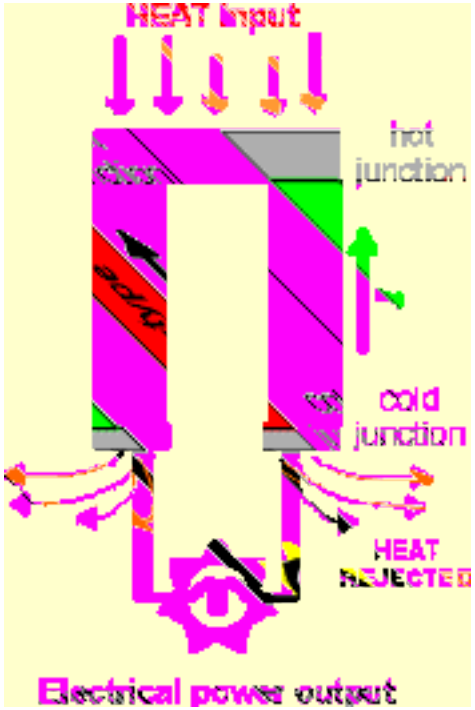
Thermopower

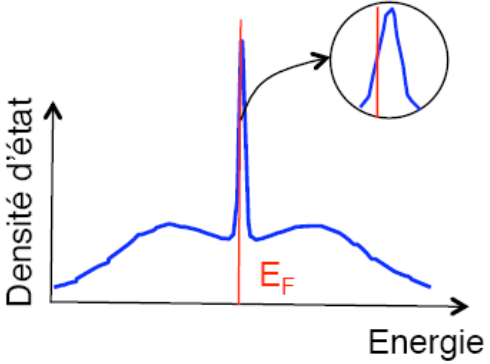
Thermal conductivity

ZT Figure of merit



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

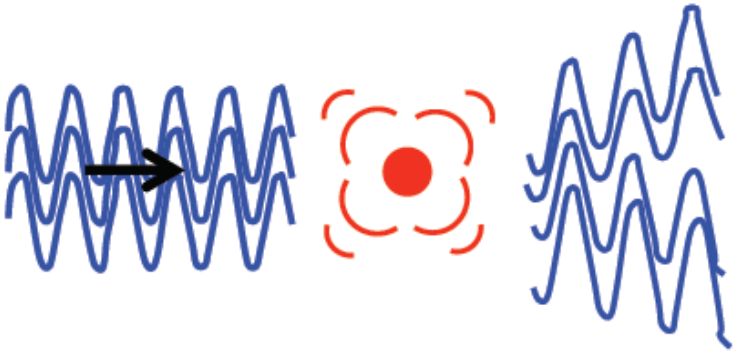


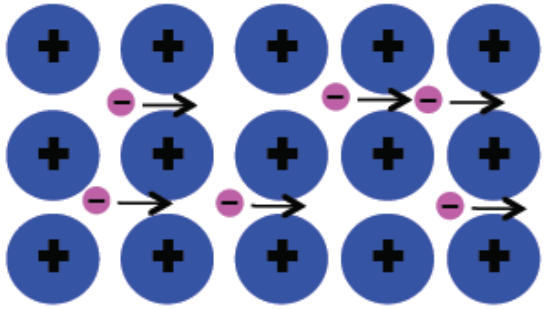


Concepts of ZT improvement

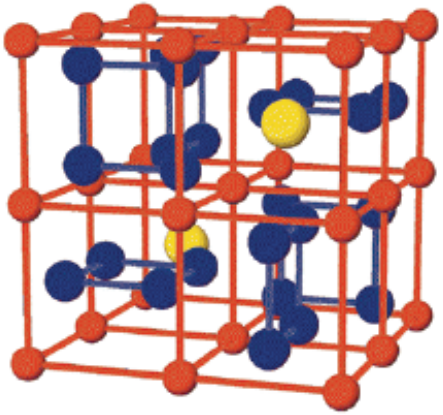
Sharp DOS (heavy fermions, QC, low dimension).

PGEC – „phonon glass" + „electron crystal" (Slack, '95)

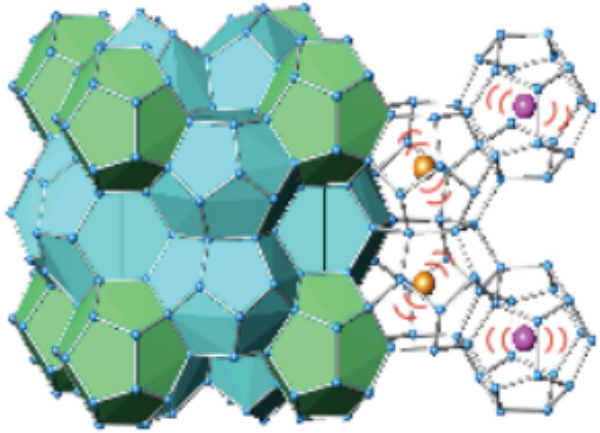




more complex structures + specific vibrations (rattling, phonon, magnon, ...)



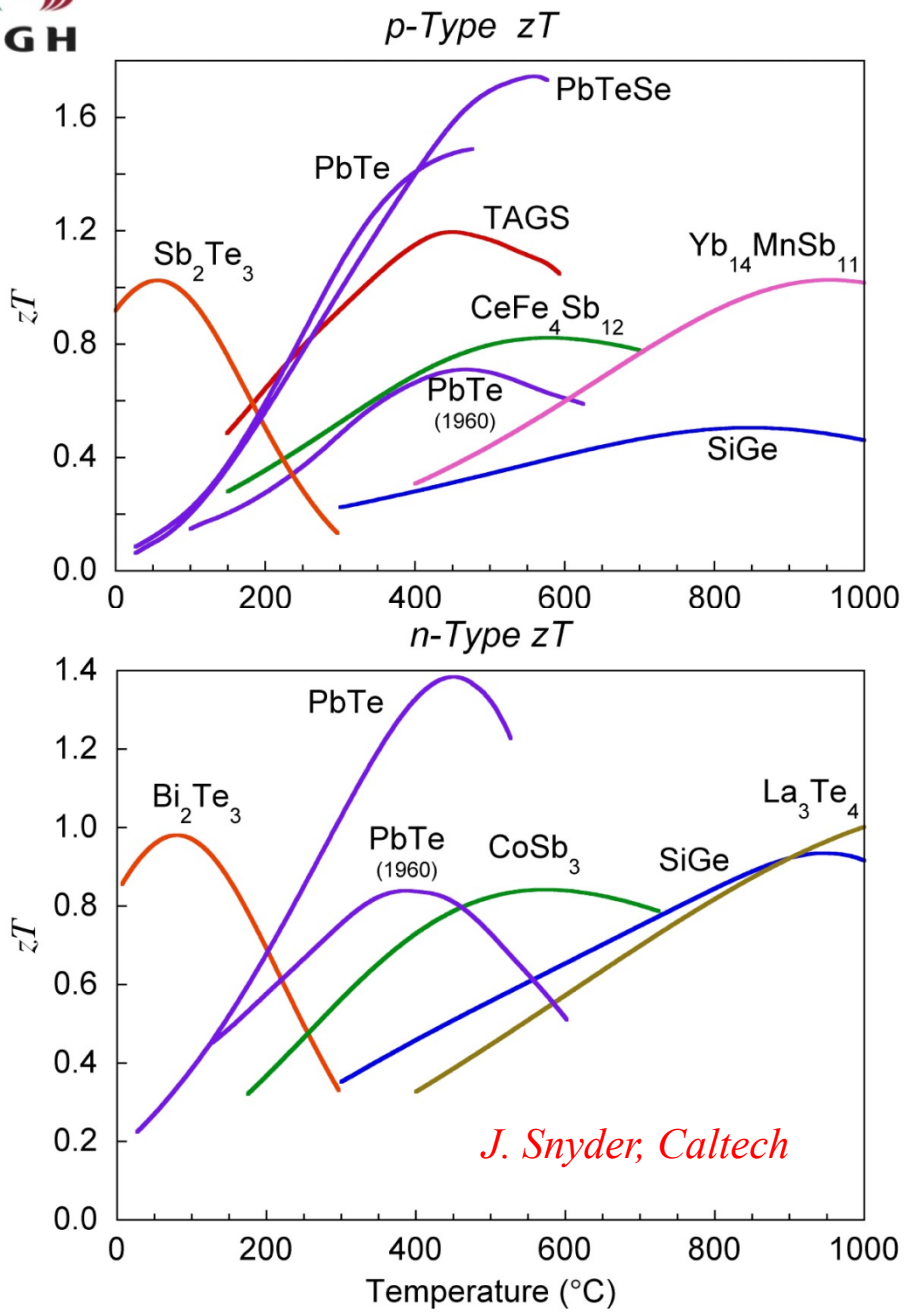
skutterudites

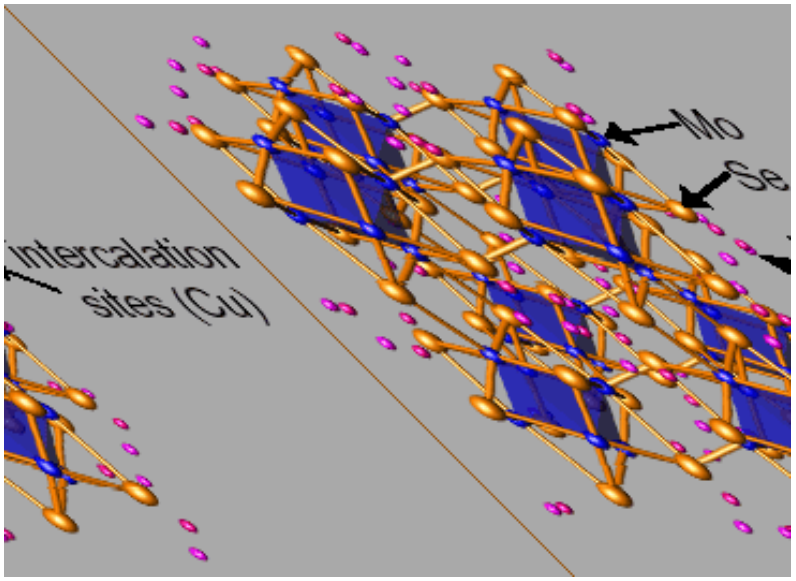


clathrates

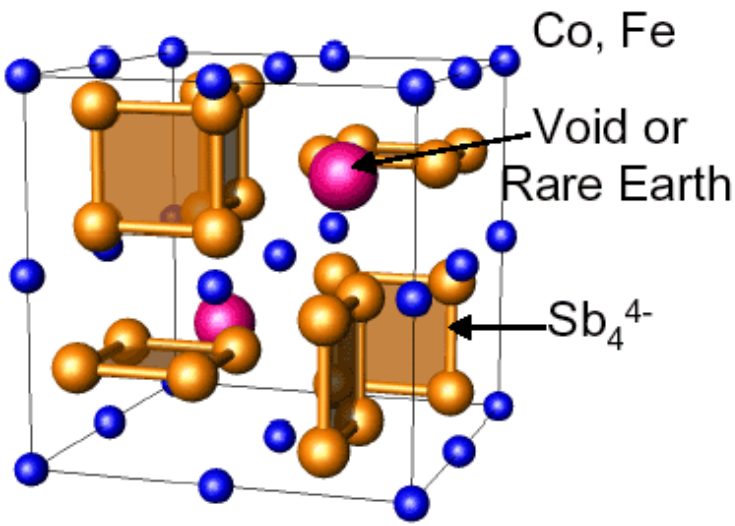
From Silke Paschen (2008)

Thermoelectric materials





Chevrel phases



Skutterudites

Mildred Dresselhaus

„Queen of nanoscience”

From Wikipedia, the free encyclopedia

Mildred Dresselhaus[1] (née **Spiewak**; November 11, 1930 – February 20, 2017),[2] known as the "queen of carbon science",[3] was the first female Institute Professor and professor emerita of physics and electrical engineering at the Massachusetts Institute of Technology.[4] Dresselhaus won numerous awards including the Presidential Medal of Freedom, the National Medal of Science, the Enrico Fermi Award and the Vannevar Bush Award.

Early life and education

Mildred was born Mildred Spiewak on November 11, 1930, in Brooklyn, the daughter of Ethel (Teichtheil) and Meyer Spiewak, who were Polish Jewish immigrants.[5][6]

Mildred Dresselhaus at the White House in 2012

Born	Mildred Spiewak November 11, 1930 Brooklyn, New York, U.S.
Died	February 20, 2017 (aged 86) Cambridge, Massachusetts, U.S.
Nationality	American
Fields	Applied physics
Institutions	Cornell · MIT
Alma mater	Hunter College · Cambridge University · Harvard University · University of Chicago

E. Fermi → M. Dresselhaus → J. Heremans

PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 M

Effect of quantum-well structures on the thermoelectric figure of merit

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(Received 3 December 1992)

PHYSICAL REVIEW B VOLUME 47, NUMBER 24 15

Thermoelectric figure of merit of a one-dimensional conductor

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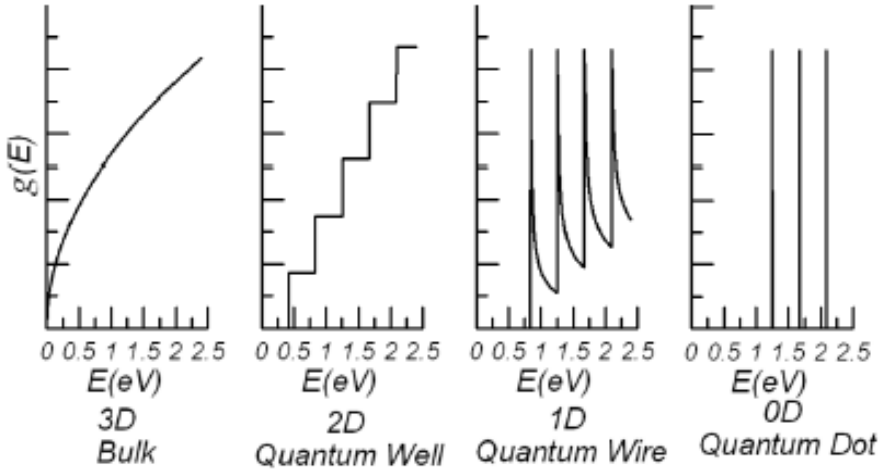
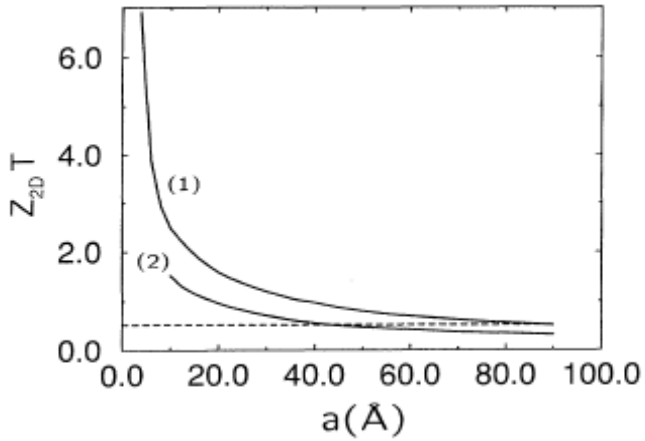
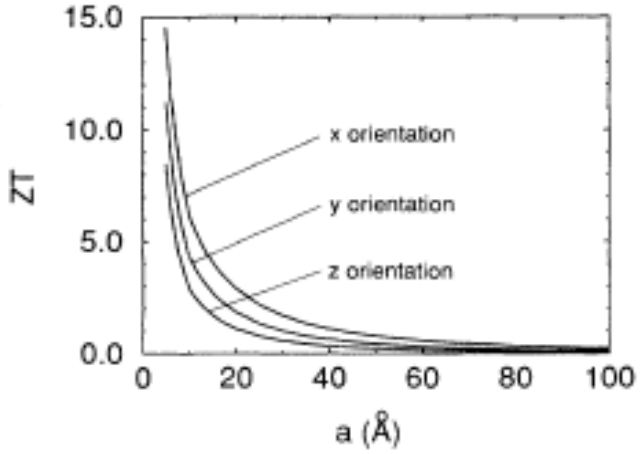
(Received 29 March 1993)



J. Heremans, Acta Phys. Pol. 108 (2005) 609

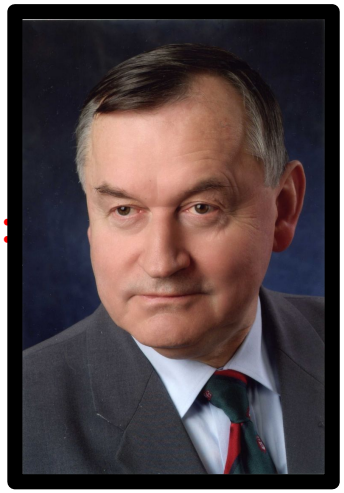




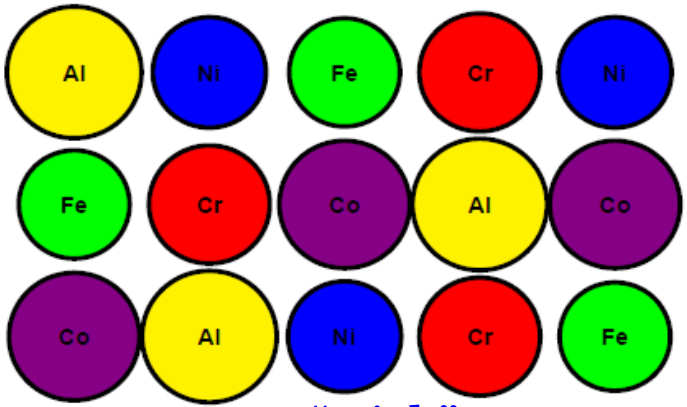
Mott's formula (thermopower)

$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{\mathrm{d}[\ln(\sigma(E))]}{\mathrm{d}E}\right\}_{E=E_F}$$

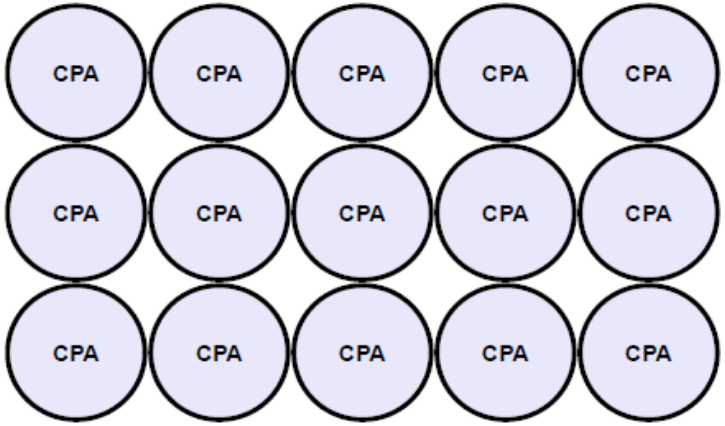
KKR-CPA method *(S. Kaprzyk 1948-2018)*



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



CPA "trick"



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

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.

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, Tobola, Phys. Rev. B (1999) conventional KKR

Full GF

Stopa, Kaprzyk, Tobola, 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 $\quad N(E_F)=Z$

Boltzmann equation

Electron system described by distribution function f in the (**r, k**) space. $\frac{1}{4\pi^3} f(k,r,t$

Fermi-Dirac function in equilibrium state

Electron density current $J(r,t) = \frac{e}{4\pi}$

Transport equation $\frac{df}{dt} = -\frac{dk}{dt} \cdot \nabla_k$ — —

Stationary condition $\frac{\partial f}{\partial t} = 0$ time-independent forces

Collision integral $\left(\frac{\partial f}{\partial t}\right)_{coll}$ Describes **e-e** scatterings/collisions , probability of exit outside the $d\mathbf{k}d\mathbf{r}$ volume

Relaxation time approximation $\left(\frac{\partial f}{\partial t}\right)_{coll} = \cdot$ ——

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

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

$$PF = S^2\sigma$$

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

$L(T,n)$

$PF(T,n)$

$ZT(T,n)$

Onsager-related functions

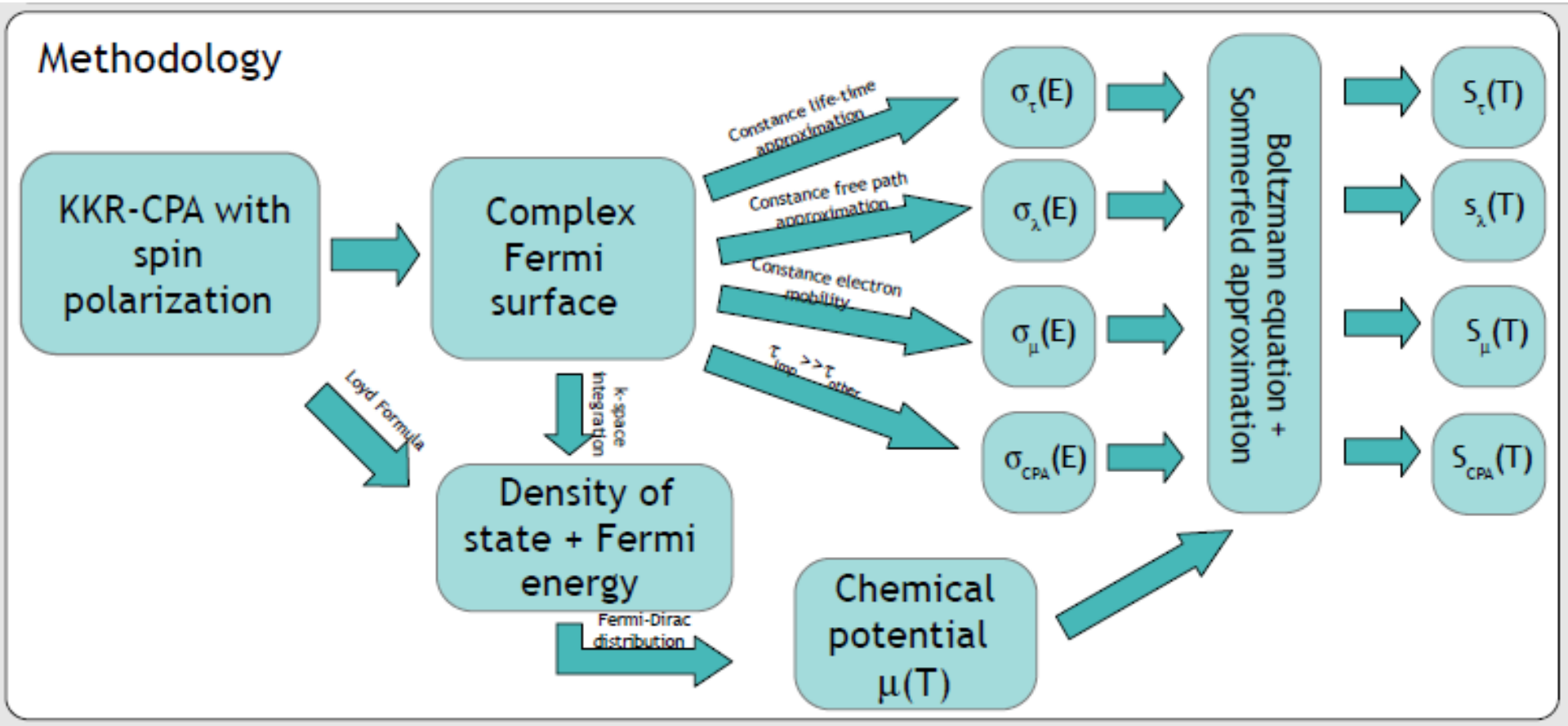
$$\mathscr{L}^{(\alpha)} = \int d\mathscr{E}\left(-\frac{\partial f}{\partial \mathscr{E}}\right)(\mathscr{E}-\mu)^{\alpha}\boldsymbol{\sigma}(\mathscr{E})$$

Transport functions (in general tensors)

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

Boltzmann transport & KKR-CPA calculations

of complex energy bands and thermopower



K. Kutorasinski, Ph.D. Thesis (2014)

Different approximations used

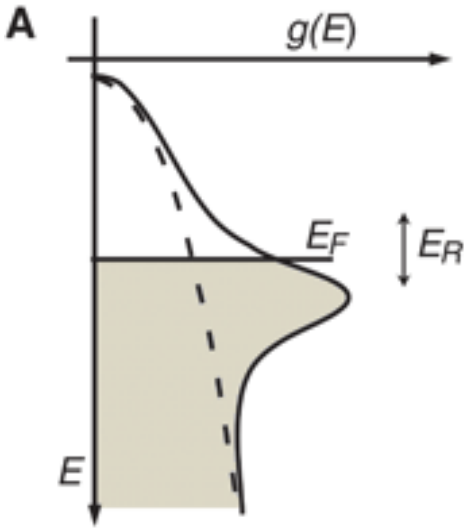
(1) τ = const; (2) λ = const; (3) μ = const; (4) CPA (velocity + life-time);

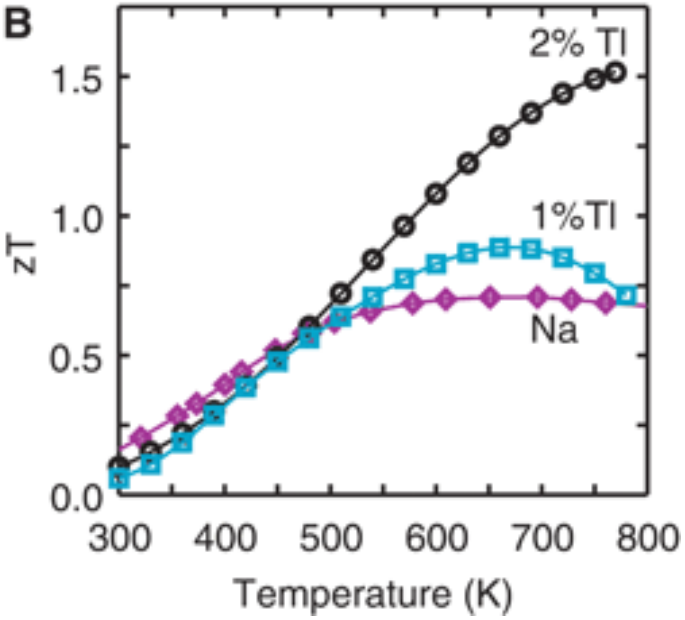
Enhancement of TE efficiency in **PbTe**

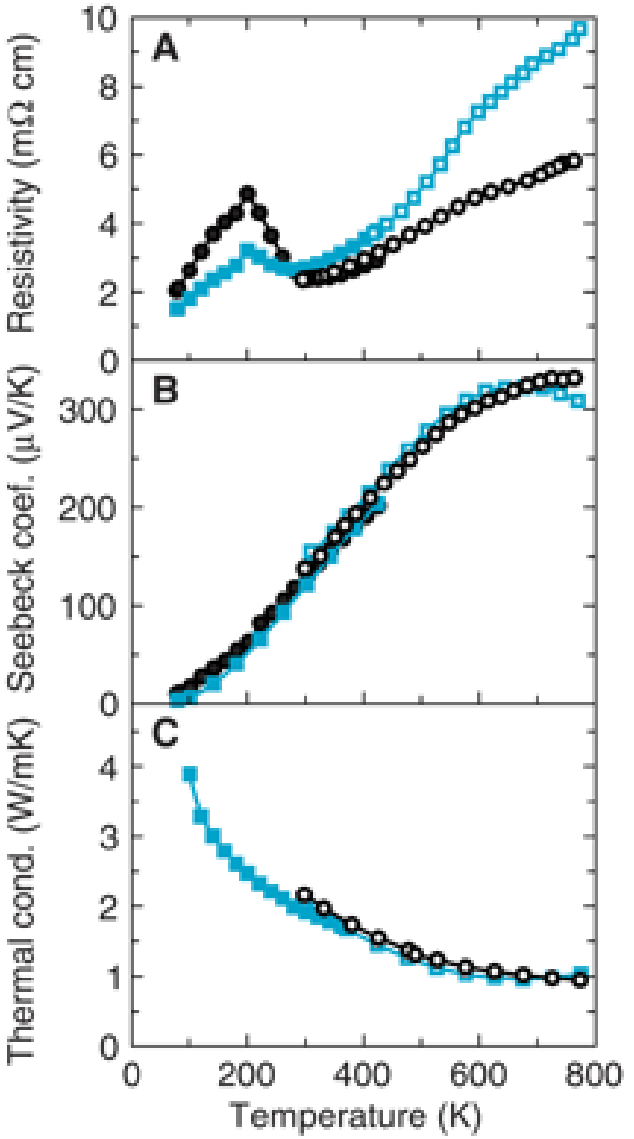
(distortion of electronic DOS)

S

Mott's formula for thermopower



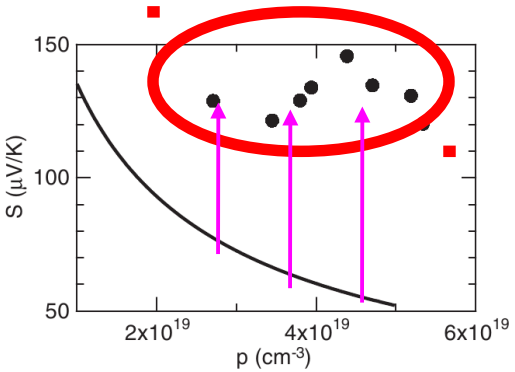




J. Heremans et al., Science **321** (2008) 544

Resonant levels (RL) in TE materials:

RL: increase in thermopower for given n, large PF and zT PbTe:Tl *Heremans et al, Science 321 (2008) 544*



Band structure results:

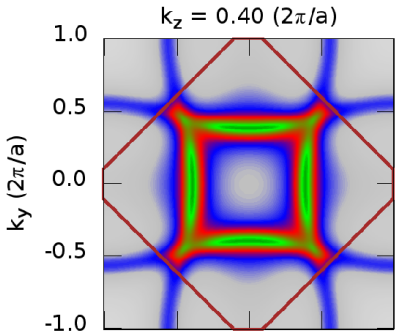
sharp peak in DOS from RL

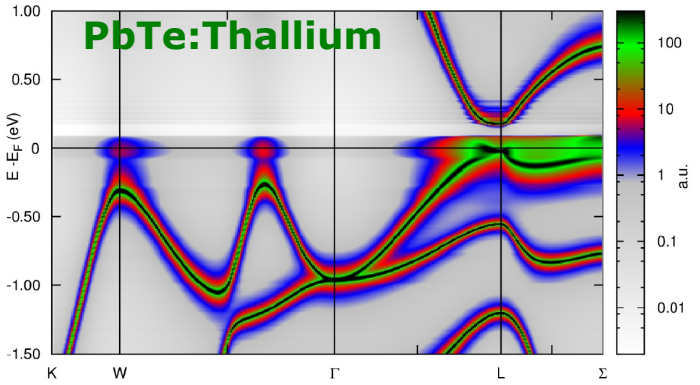
resonance from *s* electrons!

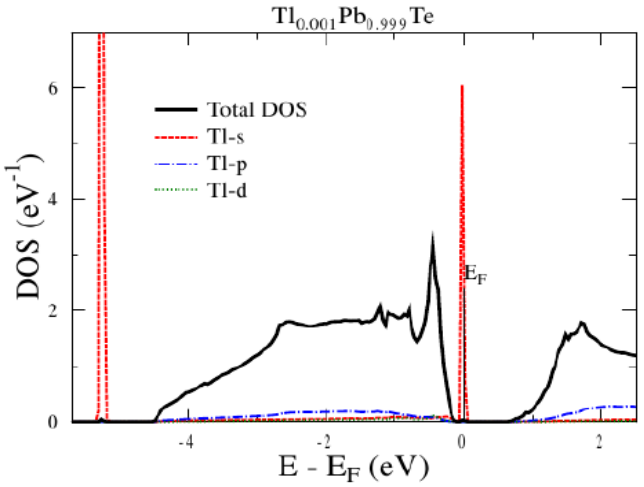
strongly disturbed bands

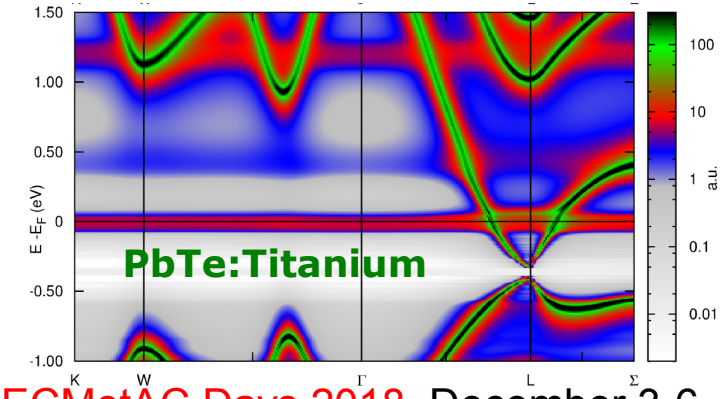
Fermi Surface: increase in number of states taking part in TE effects

PbTe:Tl





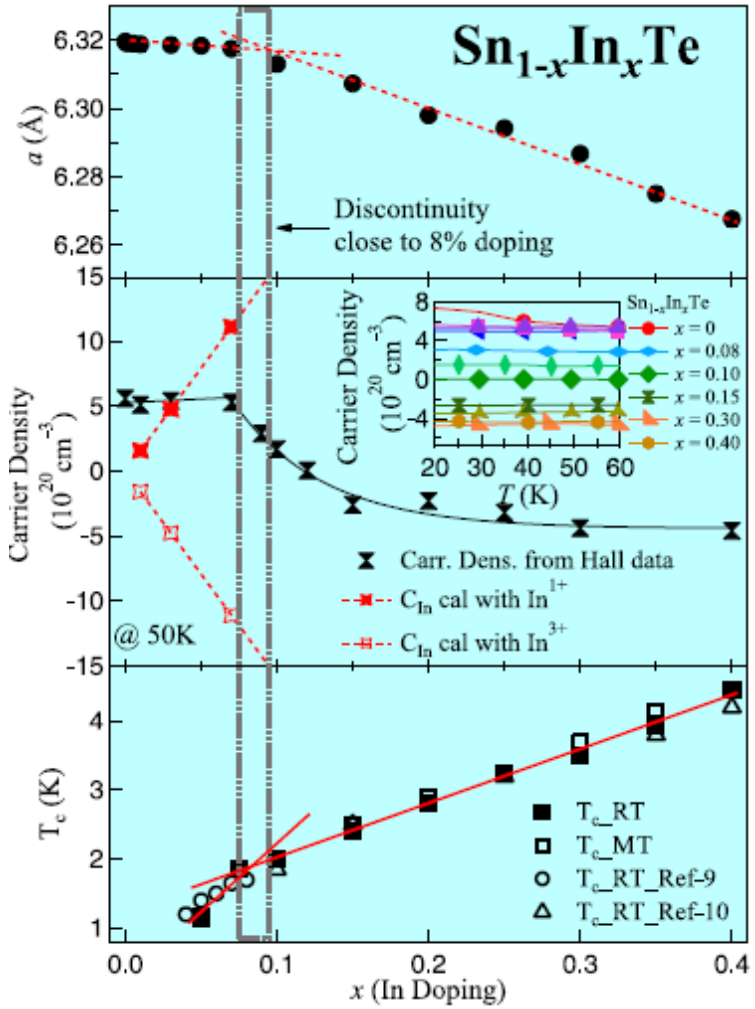




B. Wiendlocha, PRB 88 (2013) 205205.

Unusual physical properties of **SnTe**

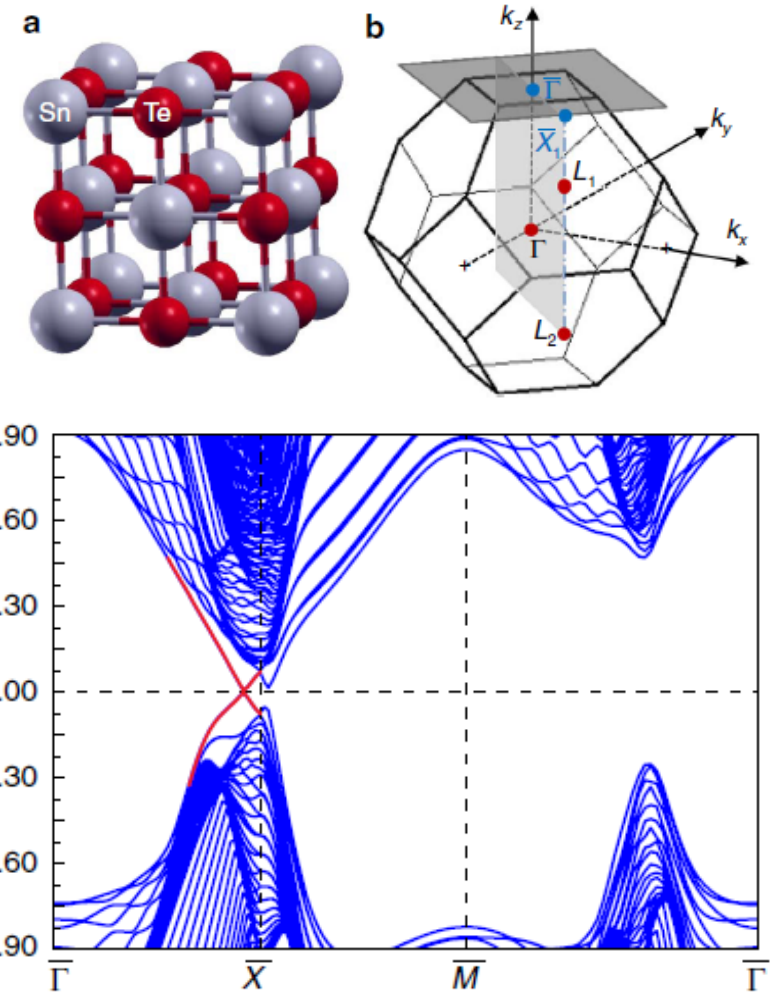
Superconductivity



Haldolaarachchige et al., Phys. Rev. 93 (2016) 024520

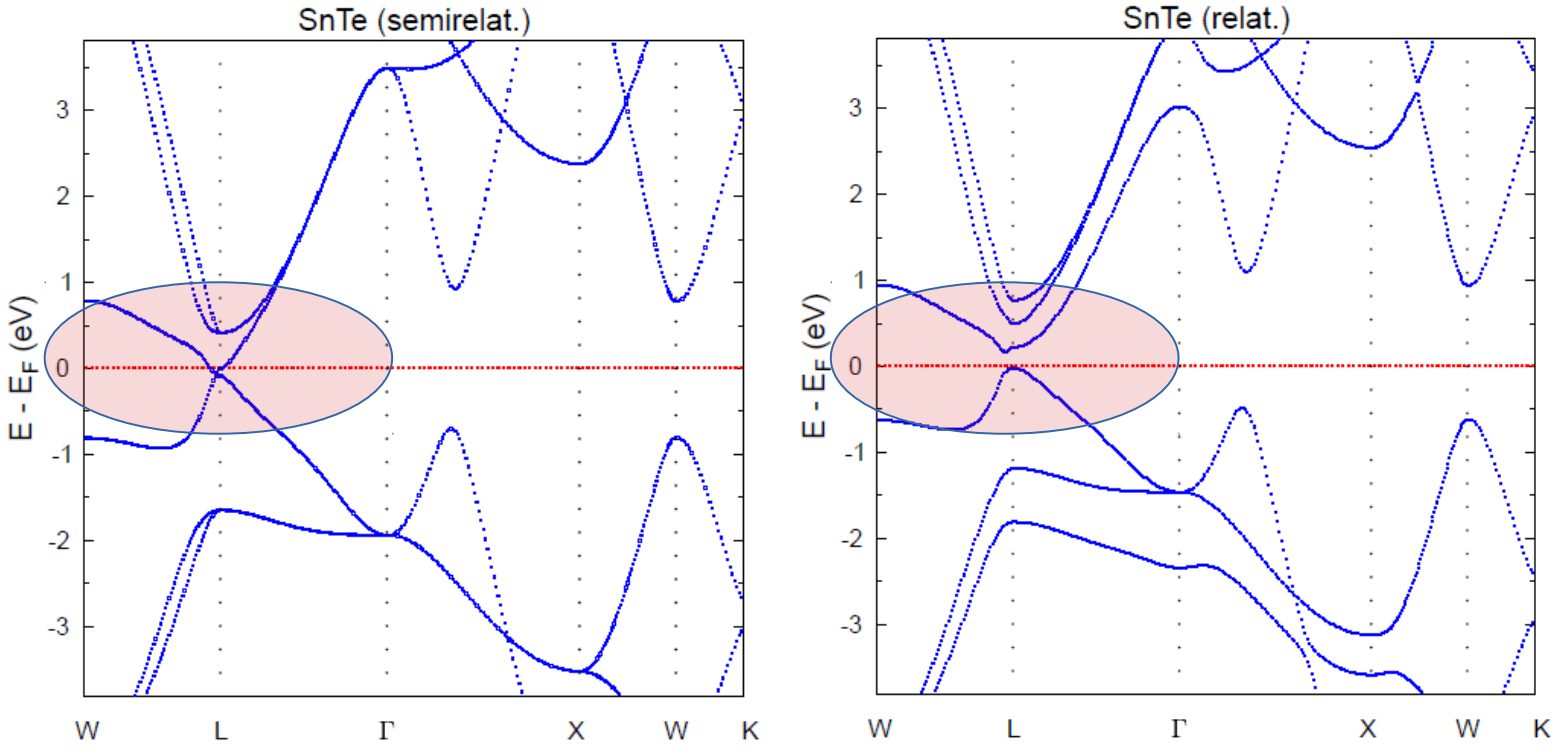
P. B. Allen and M. L. Cohen, Phys. Rev. **177**, 704 (1969).

Topological crystalline insulator

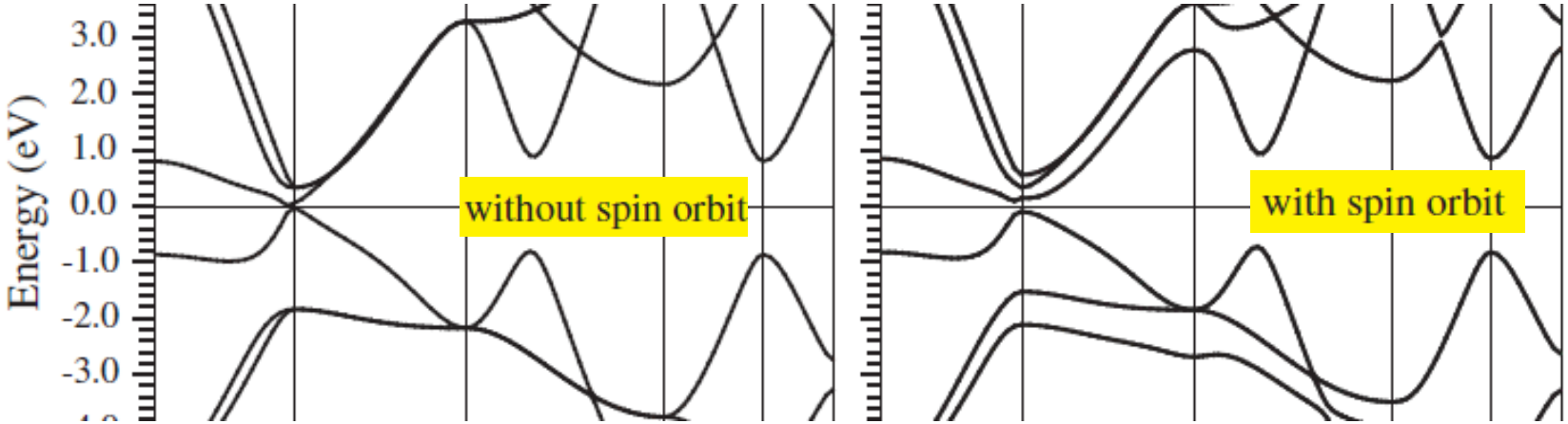


Hsieh et al., Nature Comm. (2016): DOI:10.1038/ncomms1969

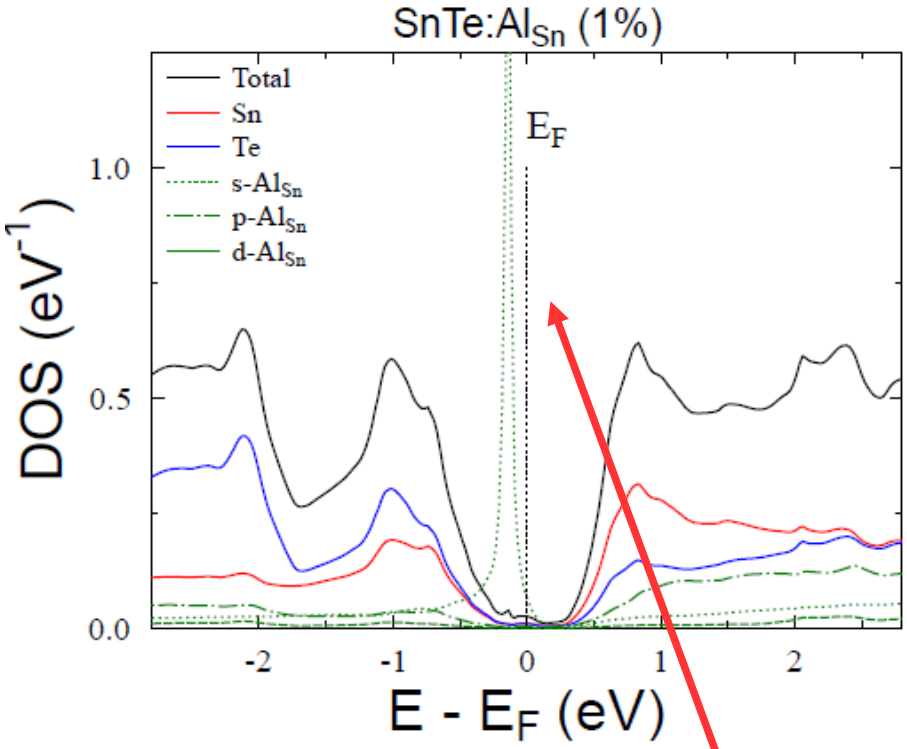
KKR (*relat. vs. semirel.*) dispersion curves in **SnTe**

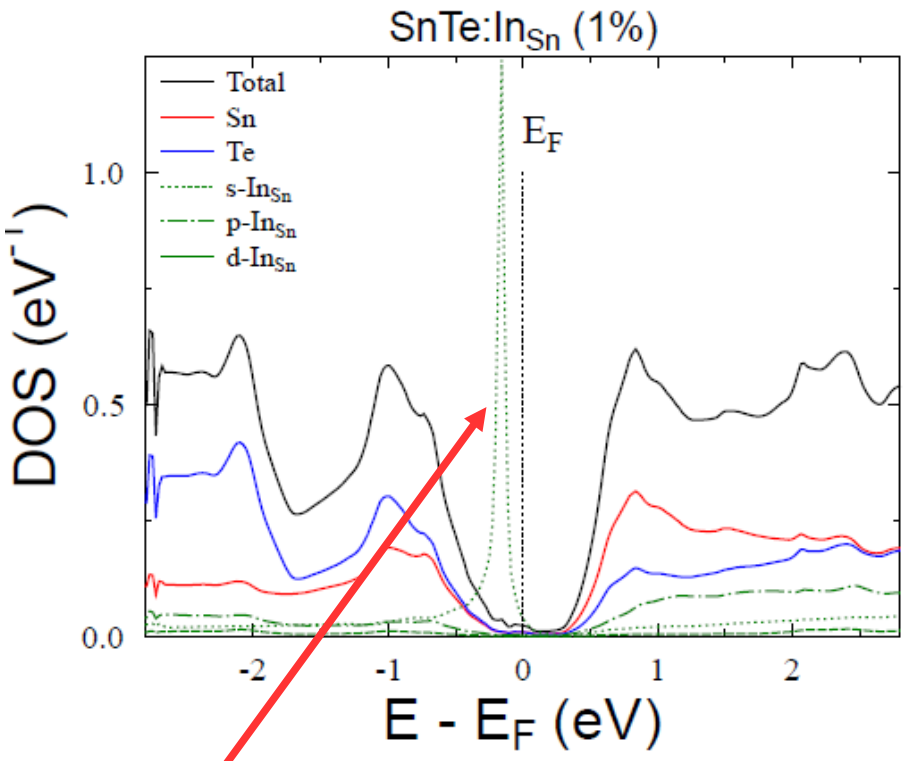


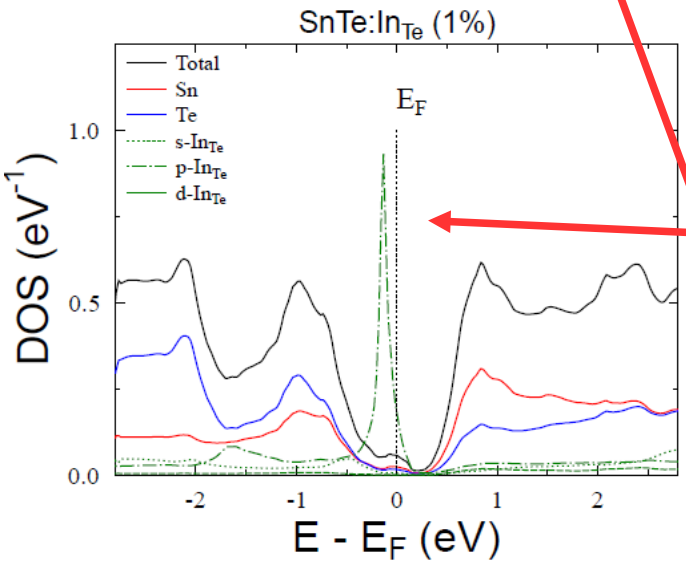
Liitlewood et al. PRL 105 (2010) 086404



DOS of **In** impurity in **SnTe**





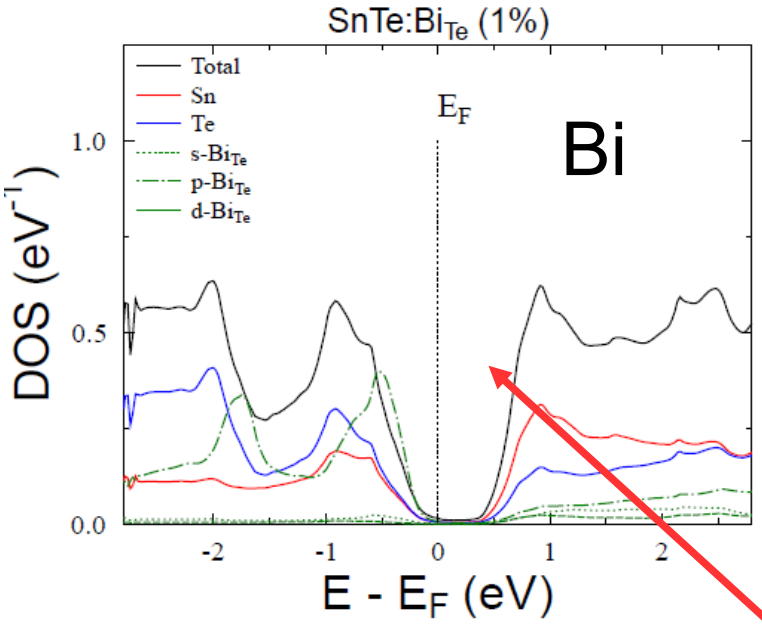


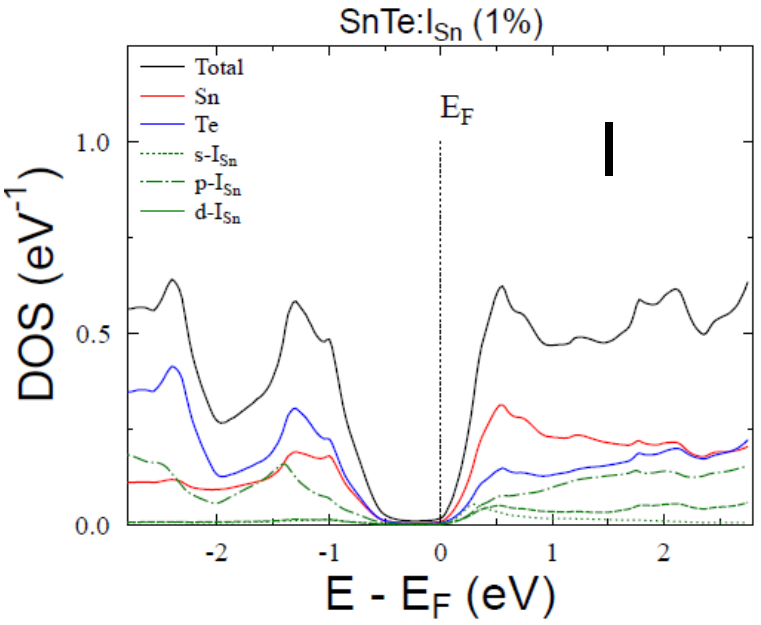
On Sn site huge s-In DOS peak appears at edge of valence states; resembles PbTe:Tl

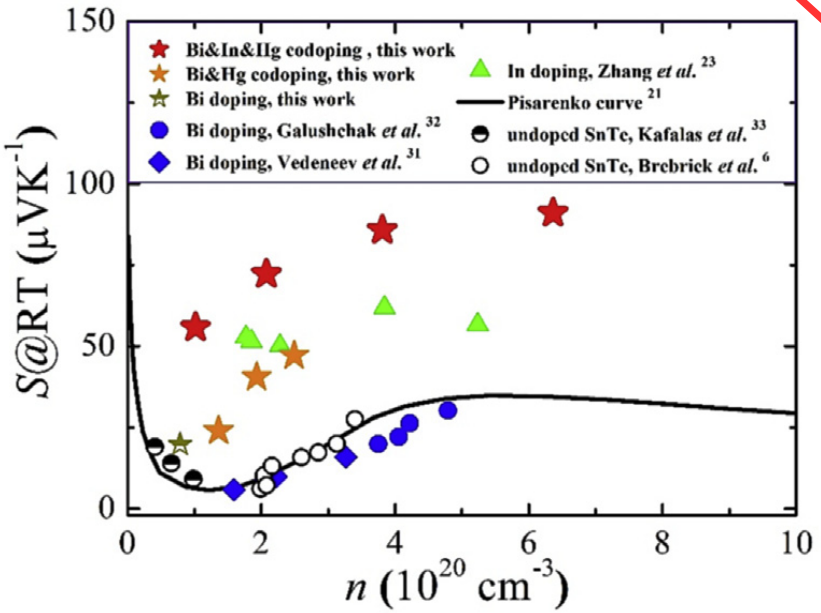
Conversely, In on Te site (less probable) would form much broadened p-DOS peak.

Isoelectronic Al also forms large s-DOS peak.

DOS of conventional dopants in **SnTe**







Tan et al., J. Materiomics 4 (2018) 62

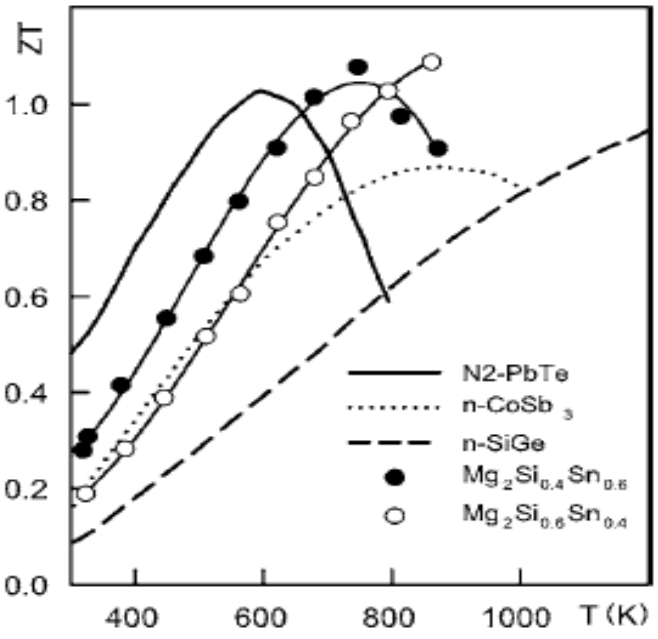
Bi on Te site → p-type

I on Sn site → n-type

depending on substituted sites some elements behave as conventional dopants, not disturbing DOS, only shifting in rigid band manner:

Mg_2X (X= Si, Ge, Sn) as thermoelectrics

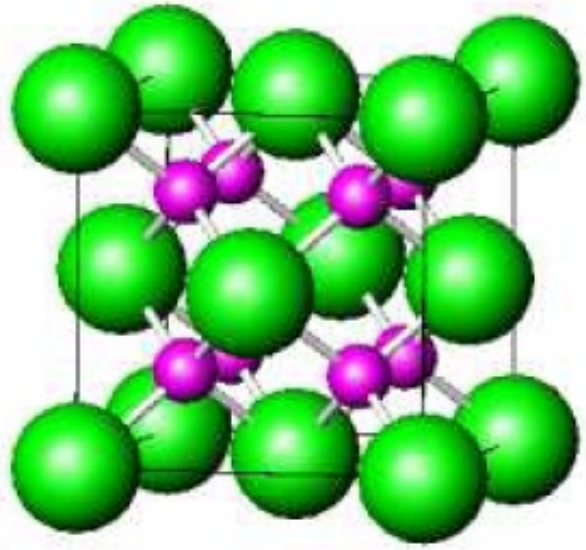
$$ZT = \frac{S^2\sigma}{\kappa}$$



Zaitsev et al., Phys. Rev. B 74 (2006) 045207

Light, non-toxic, rather cheap, large *ZT* of undoped compounds & alloys

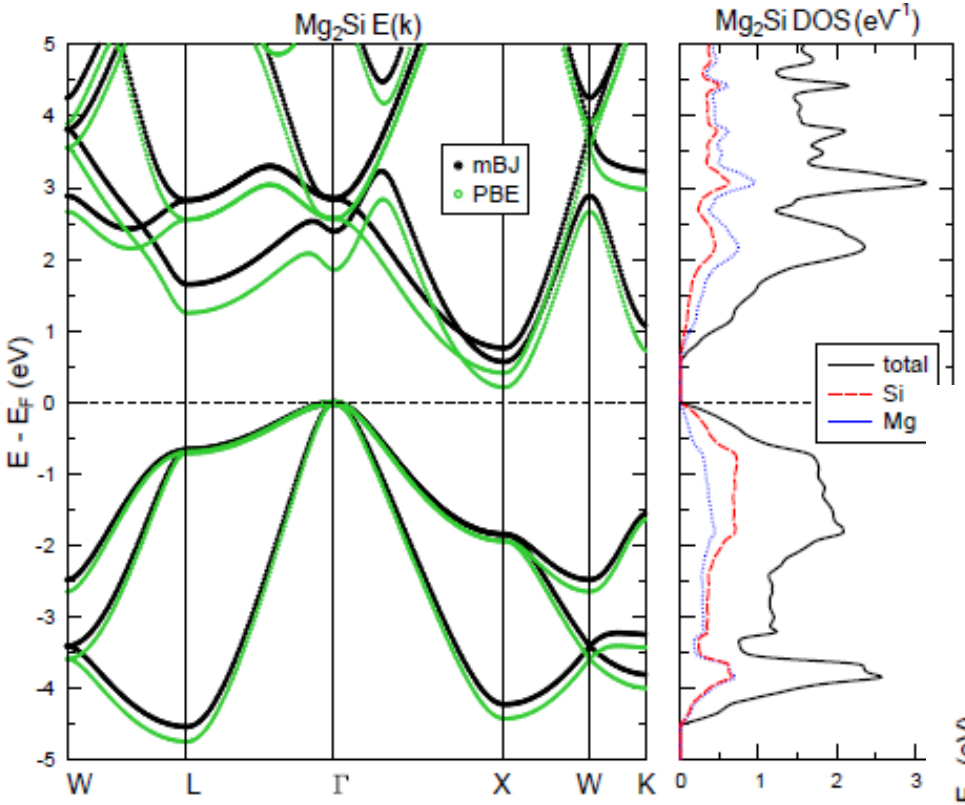
„Anti-fluorite" (CaF_2) structure



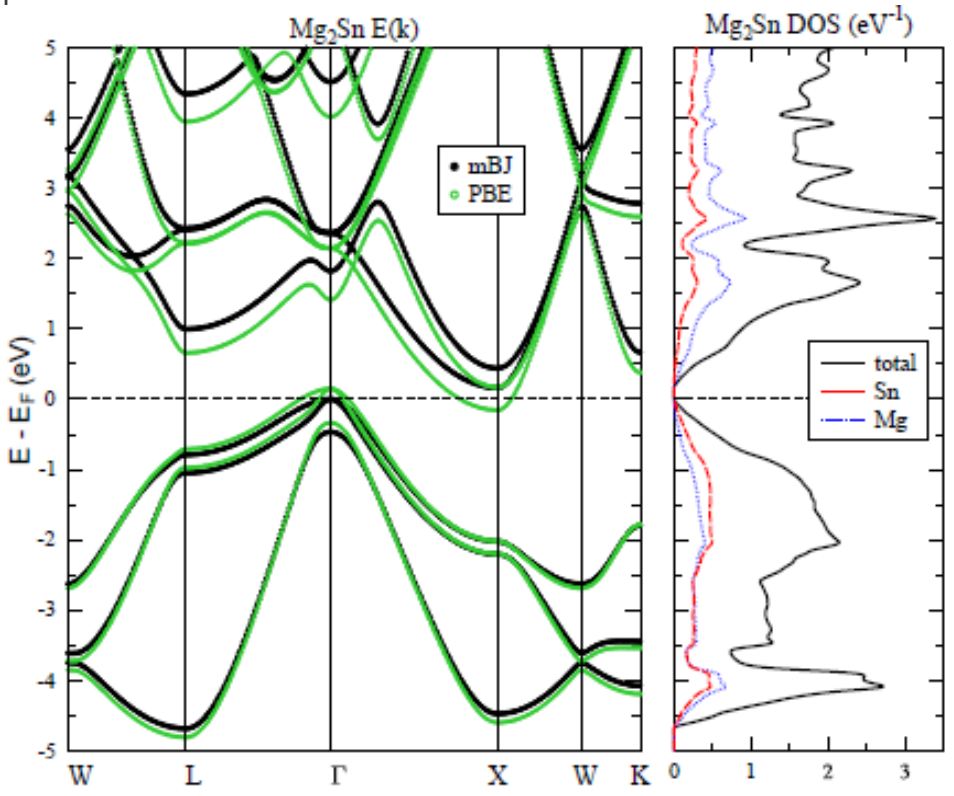
Mg: ¼ , ¼ , ¼
¾ , ¾ , ¾

X: 0, 0, 0,0
Si, Ge, Sn

More realistic treatment of “band gap problem”



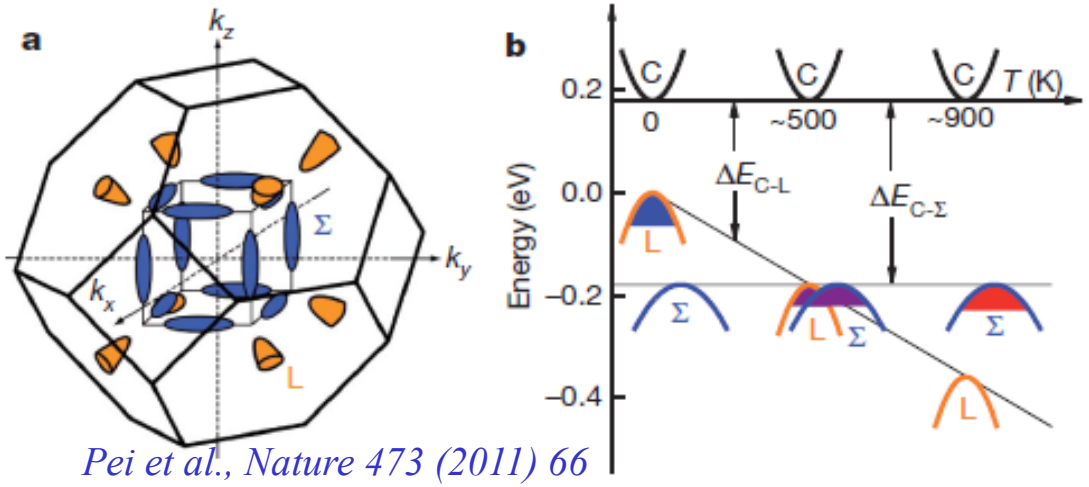
Application of more sophisticated exchange-correlation potential improves exp-theory agreement for band gap.



BUT the overall bands shape remains quite similiar -> important results for transport calculations based on LDA results

*J. Bourgois et a. (JT), Functional Mat. Lett. **6** (2013) 1340005.*

„Engineering” of band degeneracy to improve *zT*



Pei et al., Nature 473 (2011) 66

Pb(Te-Se)

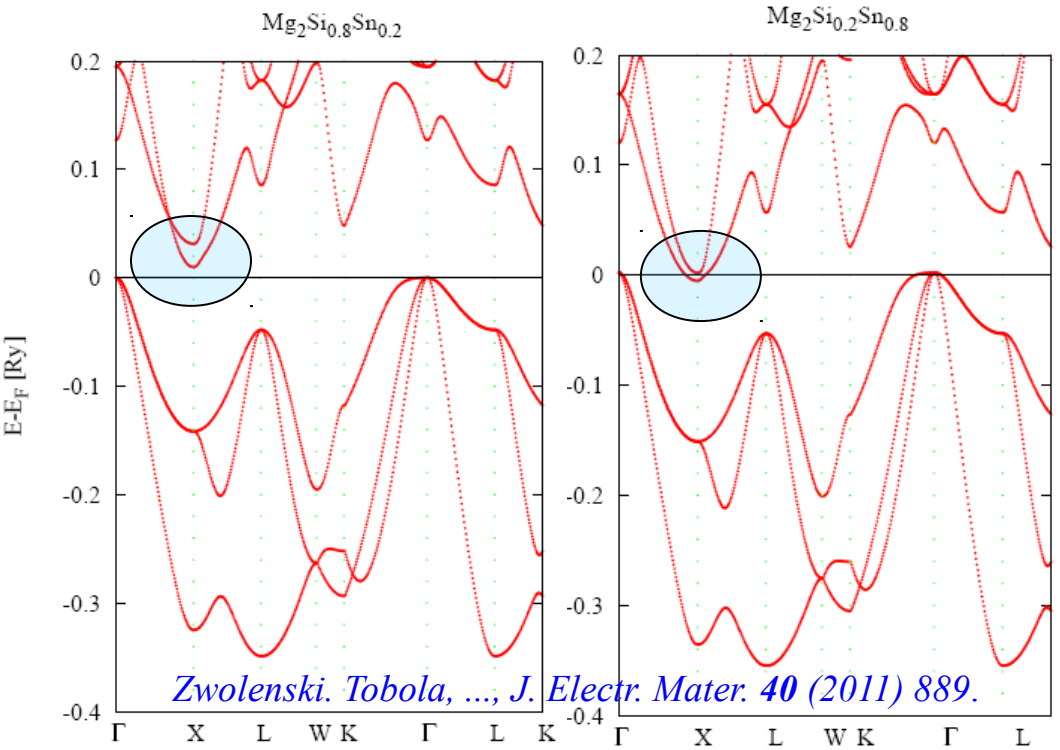
- similiar thermopower but higher electrical conductivity (more carriers) BUT p-type

~$Mg_2Si_{0.4}Sn_{0.6}$

- **Achievement of HIGH band** degeneracy – general strategy to improve TE properties in bulk materials **(n-type)**

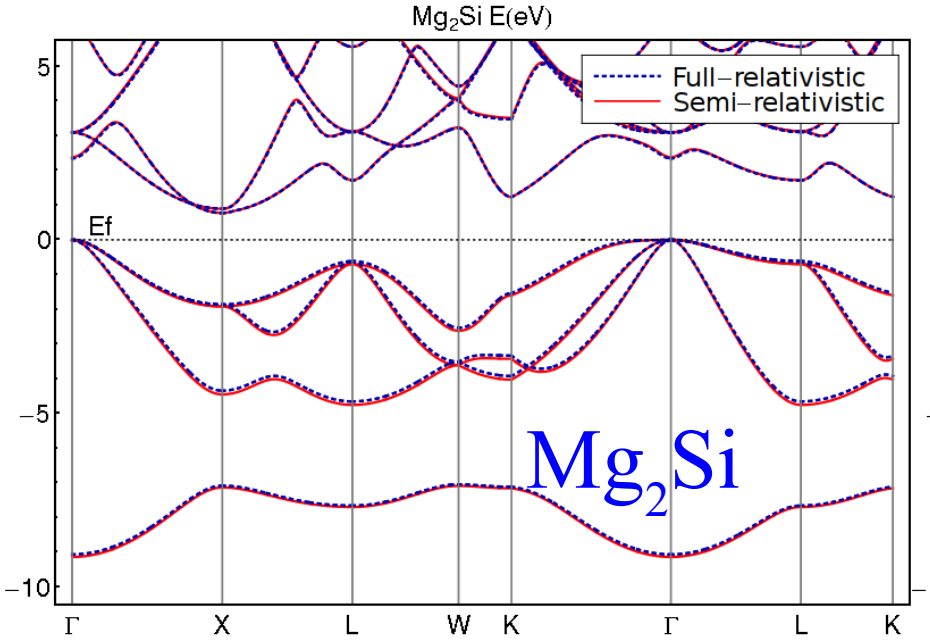
$Mg_2(Si\text{-}Sn)$

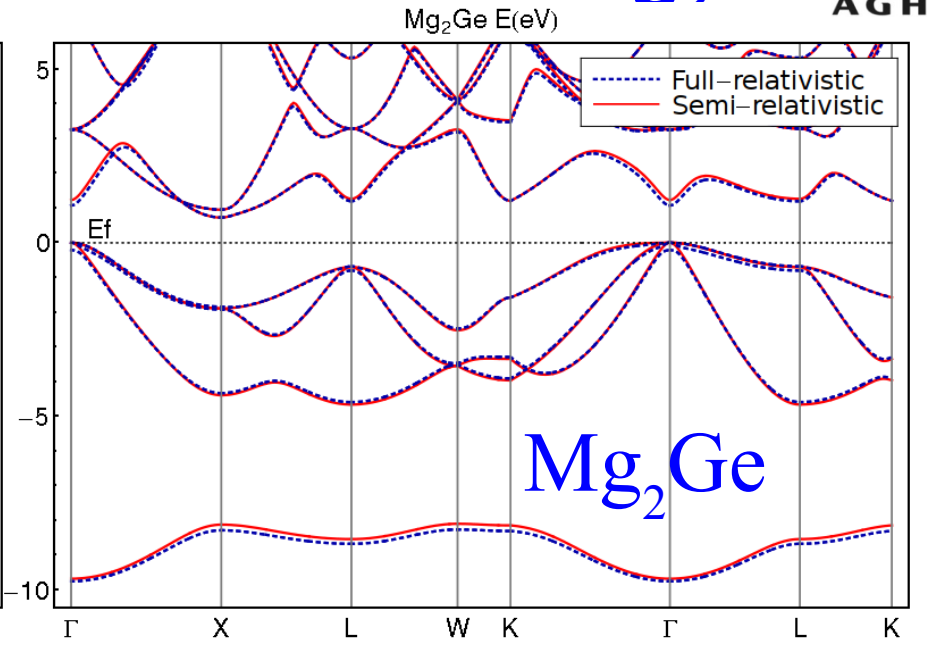
- **shrinking of band gap** and mutual shift of conduction bands near X : **not effect** of Si/Sn disorder, rather due to important variation of lattice constant

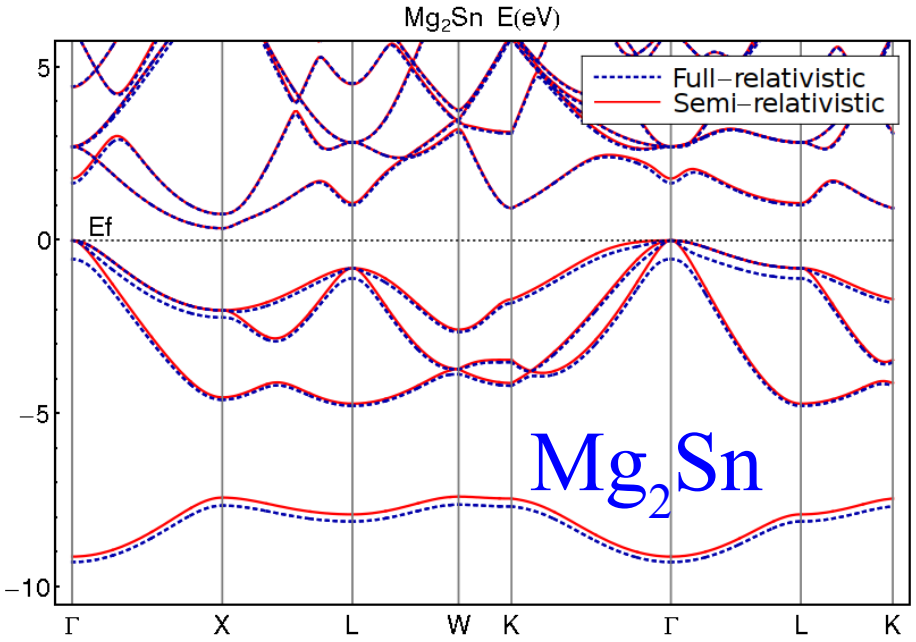


*Zwolenski. Tobola, ..., J. Electr. Mater. **40** (2011) 889.*

Convergence of conduction bands in Mg_2X







Conduction band degeneracy tends to increase thermopower in n-doped systems and is expected in $Mg_2(Si\text{-}Sn)$ alloys !

*Kutorasinski et al. (JT), Phys. Rev. B **87** (2013)195205.*

Complex energy Fermi surface

$Mg_2Si_{0.4}Sn_{0.6}$

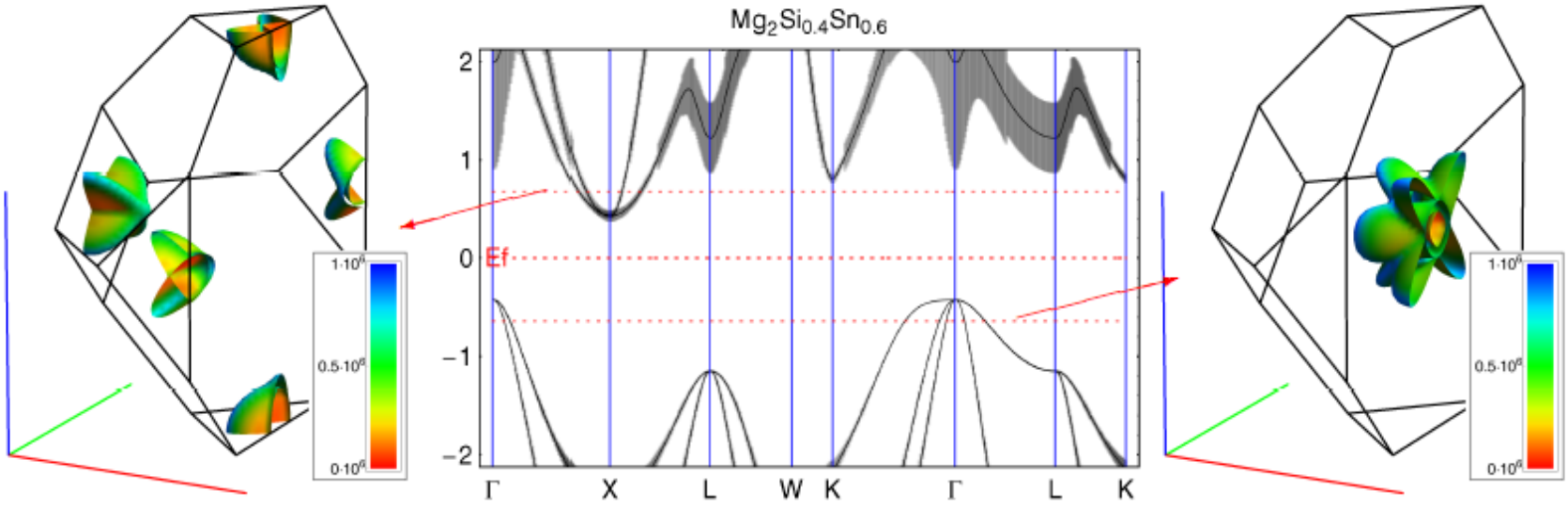


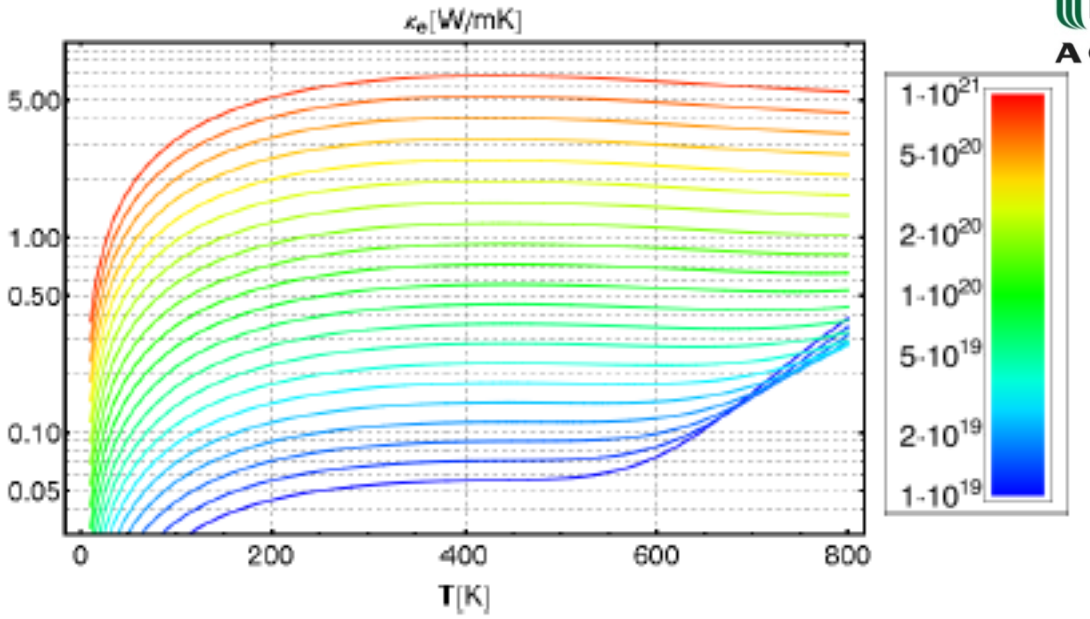
FIG. 1. Bands $Mg_2Si_{1-x}Sn_x$. Shadows around bands represent imaginary part of energy, enlarged 100 times to make them visible

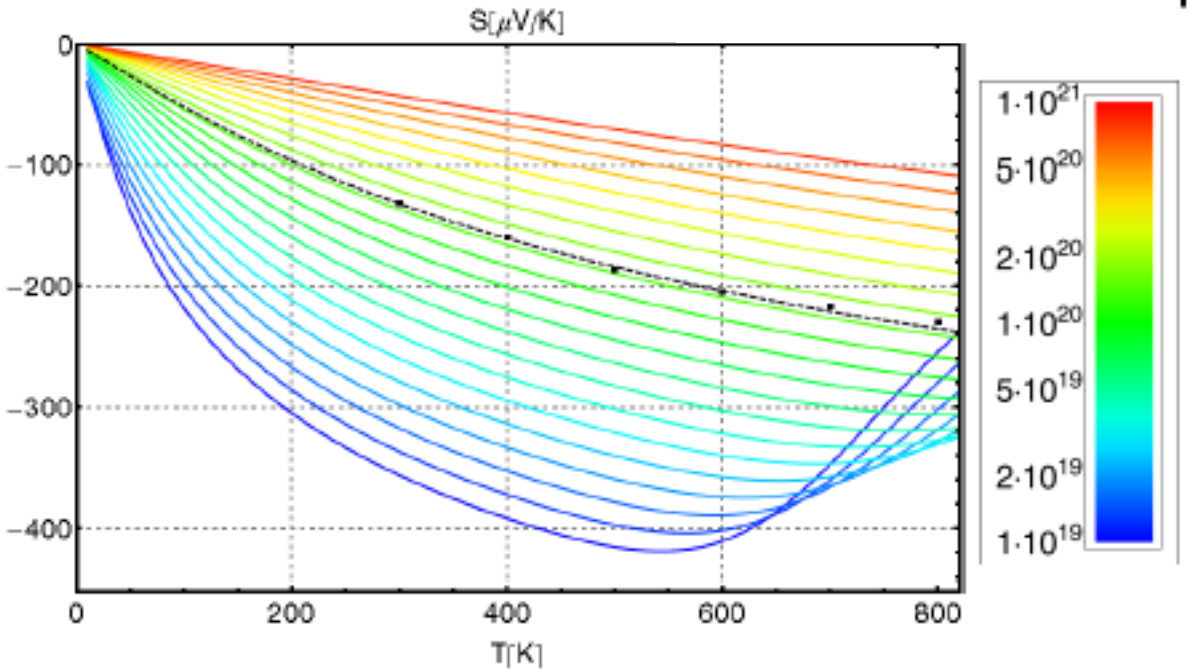
*Kutorasinski et al. (JT), Phys. Rev. B **87** (2013)195205.*

	a (Å)	E_g^{LDA}(eV) SR	E_g^{LDA}(eV) FR	E_g^{exp} (eV)
Mg_2Si	6.336	0.32	0.33	0.78
Mg_2Ge	6.385	0.21	0.23	0.72
Mg_2Sn	6.765	−0.17	−0.25	0.35

Electronic thermal conductivity

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





Seebeck coefficient

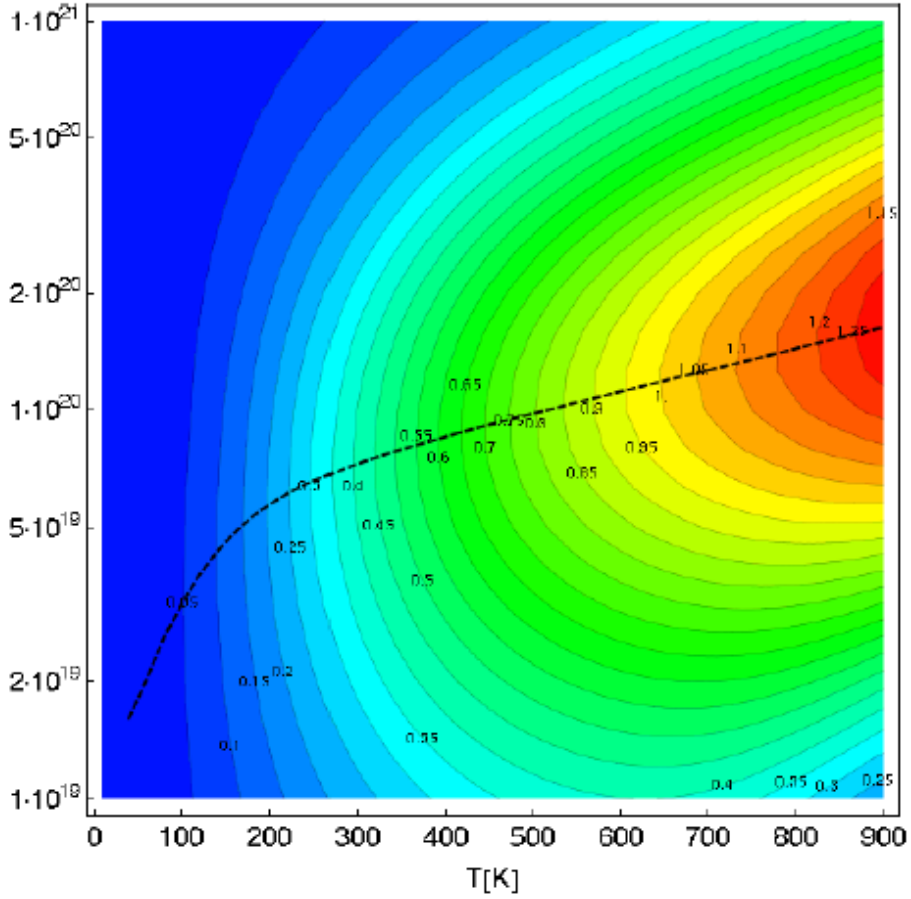
$$S = -\frac{1}{eT}\frac{\mathscr{L}^{(1)}}{\mathscr{L}^{(0)}},$$

TEST for relaxation time approach

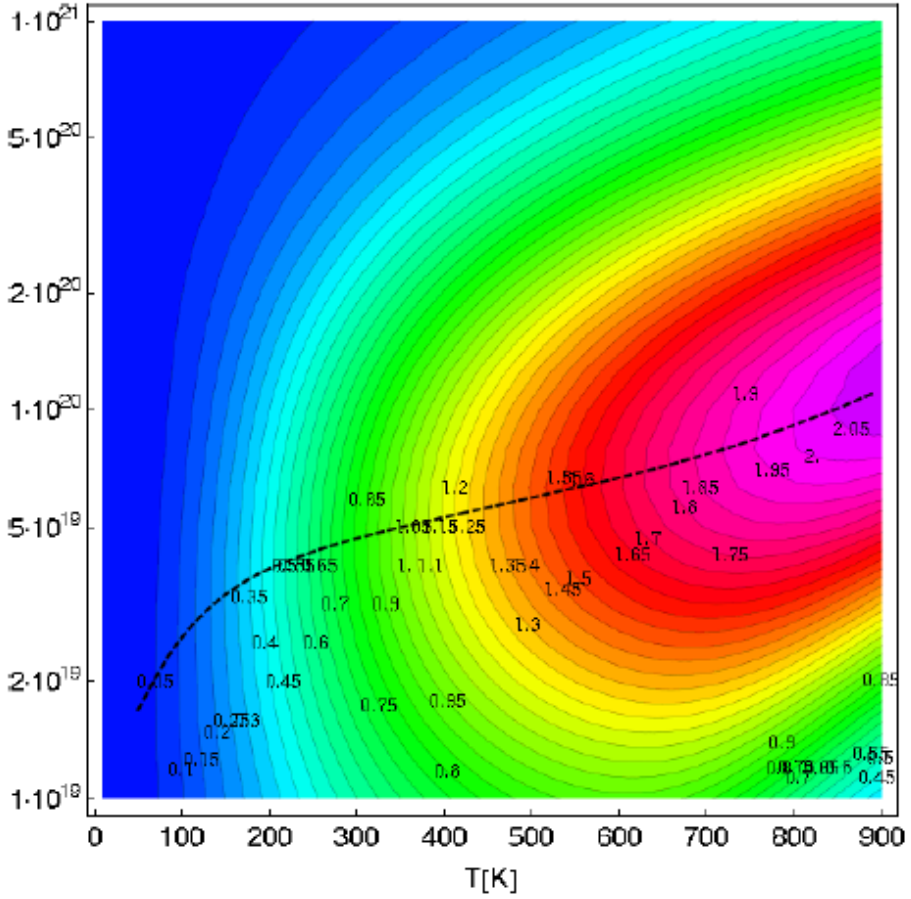
Kutorasinski et al. (JT), Phys. Rev. B **87** (2013)195205.

ZT *vs.* n/p & T

lattice thermal conductivity as parameter



$\kappa_l = 1.25$ W/mK



0.5 W/mK

Kutorasinski et al. (JT), Phys. Rev. B 87 (2013) 195205.

Relativistic KKR calculations

Full form of Dirac equation including four components

$$\left(\beta mc^2 + c(\alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3)\right)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

$$\begin{pmatrix} (mc^2 - E + e\phi) & c\sigma\cdot\left(p - \frac{e}{c}A\right) \\ -c\sigma\cdot\left(p - \frac{e}{c}A\right) & (mc^2 + E - e\phi) \end{pmatrix}\begin{pmatrix}\psi_+ \\ \psi_-\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix}$$

More readable: non-relativistic approach of Dirac equation

$$H = H_0 + H_{\text{kinetic}} + H_{\text{so}} + H_{\text{Darwinian}}$$

$$H_{so} = \frac{1}{2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\left(\frac{g_s}{2m_e^2c^2}\right)\frac{\vec{L}\cdot\vec{S}}{r^3}$$

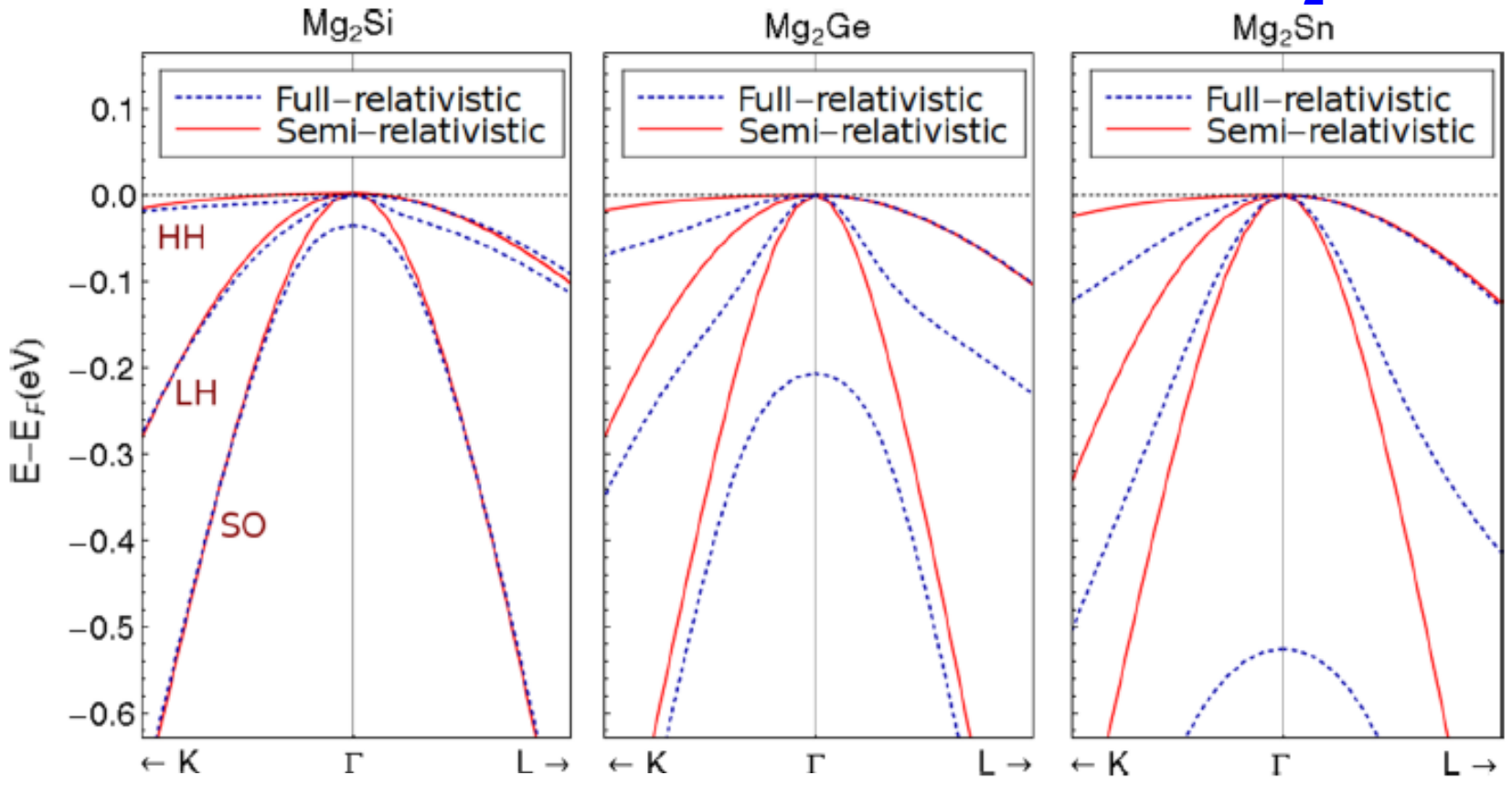
$$H_{\text{kinetic}} = -\frac{p^4}{8m^3c^2}$$

$$\langle H_{SO}\rangle = \frac{{E_n}^2}{m_e c^2}\left(n\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l\left(l+\frac{1}{2}\right)(l+1)}\right)$$

$$H_{\text{Darwinian}} = \frac{\hbar^2}{8m_e^2c^2}\,4\pi\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\delta^3(\vec{r})$$

SO splitting ~ $\dfrac{Z^4}{n^3(j+1/2)}10^{-5}$ eV

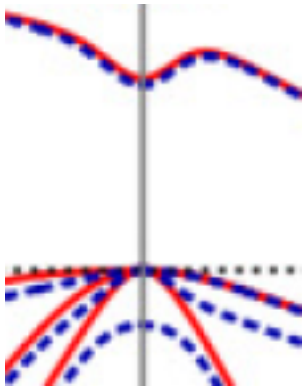
Effect of S-O on electronic bands in Mg_2X



	Mg_2Si	Mg_2Ge	Mg_2Sn
Calculated (meV)	36	208	525
Measured (meV)	30[a]	200[a]	480[a],600[b]

[11] F. Vazquez, A. R. Forman, and M. Cardonna *Phys. Rev.*, vol. 176, p. 905, 1968

[12] L. A. Lott and D. W. Lynch, Phys. Rev. 141, 681 (1965)

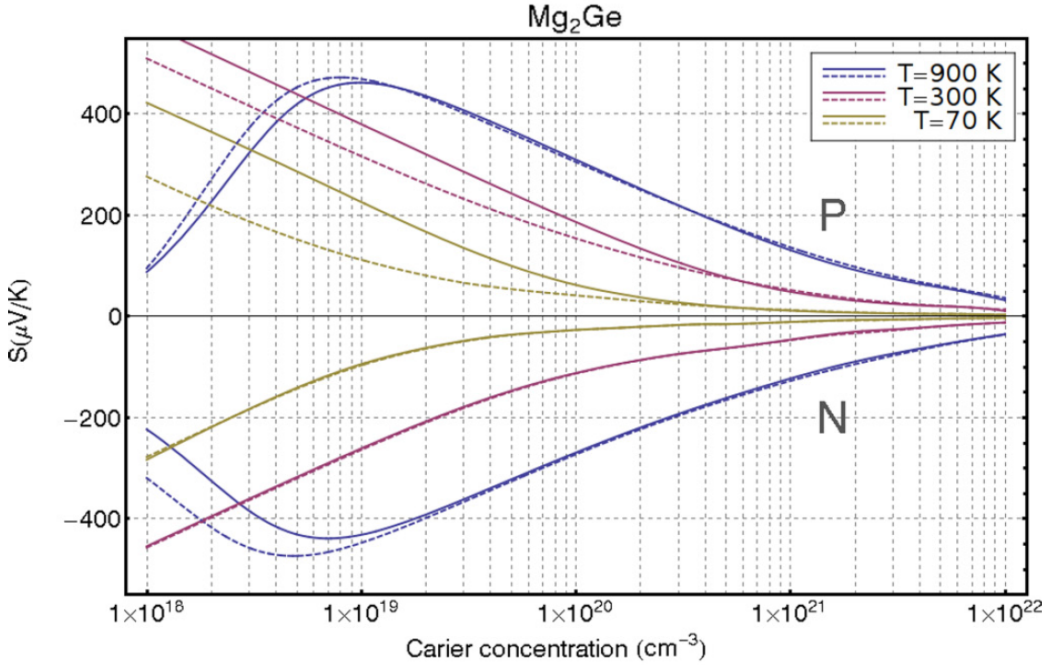


effect of S-O:

on CB – negligible
on VB – HUGE !

K. Kutorasinski, B. Wiendlocha, S. Kaprzyk, J. Tobola, Phys. Rev. B 89 (2014) 1152015.

Seebeck coefficient

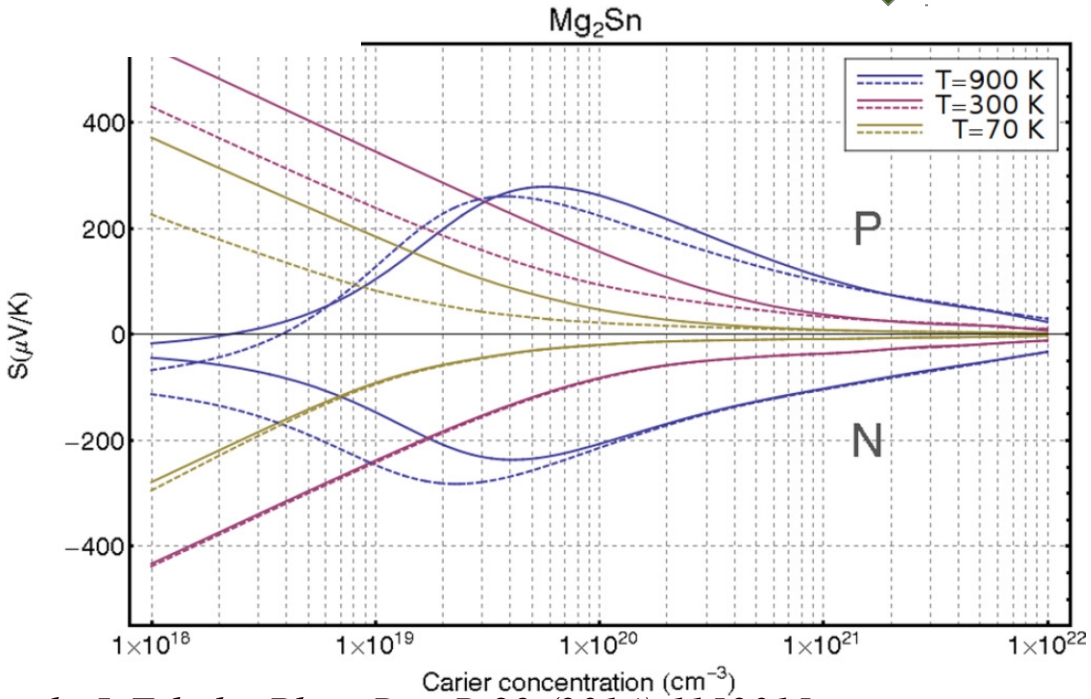


Mg_2Ge

Mg_2Sn

For p-type:
S-O decreases thermopower

For n-type:
paradoxally S-O increases themopower due to weakened bipolar effect



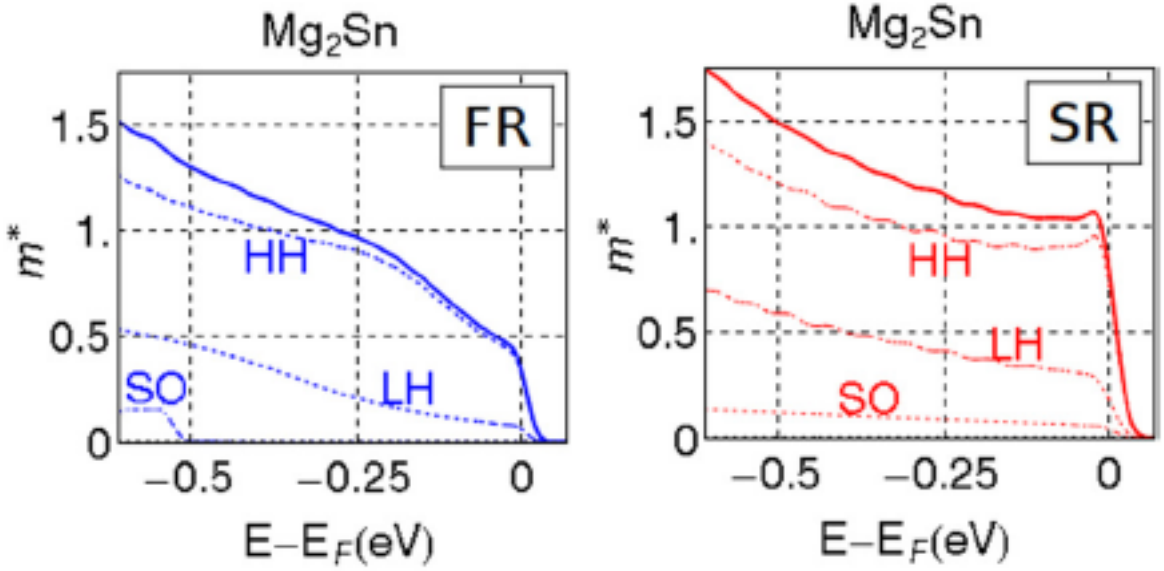
K. Kutorasinski, B. Wiendlocha, S. Kaprzyk, J. Tobola, Phys. Rev. B 89 (2014) 1152015.

Net effect of S-O on Seebeck coefficient

TABLE II: Seebeck coefficient at n=10^{20}cm^{-3} for different temperature and compound in Mg_2X.

		Si			Ge			Sn		
		70 K	300 K	900 K	70	300 K	900 K	70 K	300 K	900 K
n-type	$S_{FullRell}$ (μV/K)	-33.	-139.	-291.	-27.	-113.	-273.	-20	-84	-214.
	$S_{SemiRell}$ (μV/K)	-34.	-141.	-290.	-27.	-112.	-269.	-19.	-82.	-207.
	S_{FR}/S_{SR} (-)	98%	99%	100%	100%	101%	101%	103%	102%	104%
p-type	$S_{FullRell}$ (μV/K)	77.	208.	329.	41.	154.	305.	22.	94.	224.
	$S_{SemiRell}$ (μV/K)	65.	191.	314.	62.	189.	310.	47.	156.	263.
	S_{FR}/S_{SR} (-)	118%	109%	105%	67%	83%	98%	48%	60%	85%

Bands' contribution to hole effective mass



K. Kutorasinski, B. Wiendlocha, S. Kaprzyk, J. Tobola, Phys. Rev. B 89 (2014) 1152015.

Heusler phases X_2YZ, XYZ (1903)

Structure DO_3

Fm3m (type Fe_3Al)

X1: (0,0,0);(1/2,1/2,1/2)
X2: (3/4,3/4,3/4)
Z: (1/4,1/4,1/4)

Normal Heusler $L2_1$

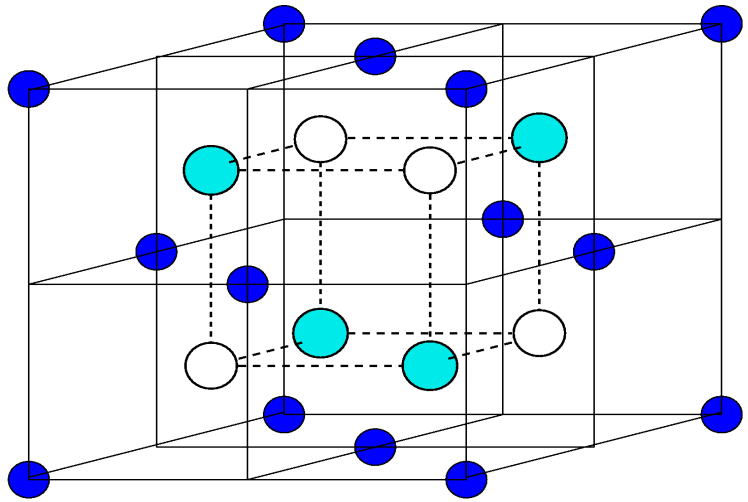
Fm3m (type Cu_2MnAl)

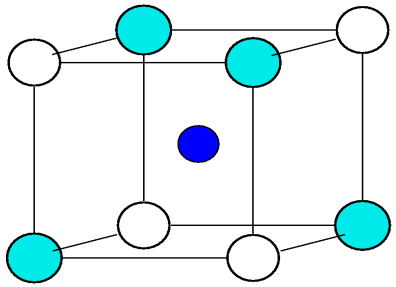
X : (0,0,0); (1/2,1/2,1/2)
Y : (3/4,3/4,3/4)
Z: (1/4,1/4,1/4)

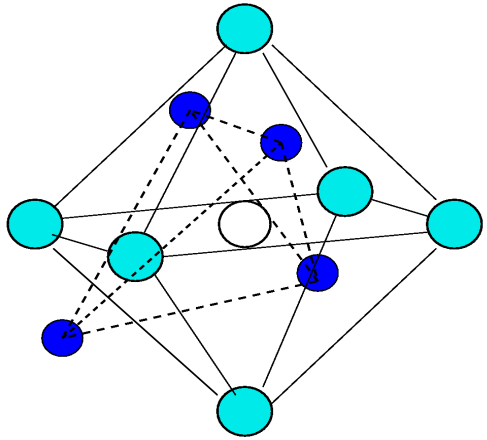
Half-Heusler $C1_b$

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

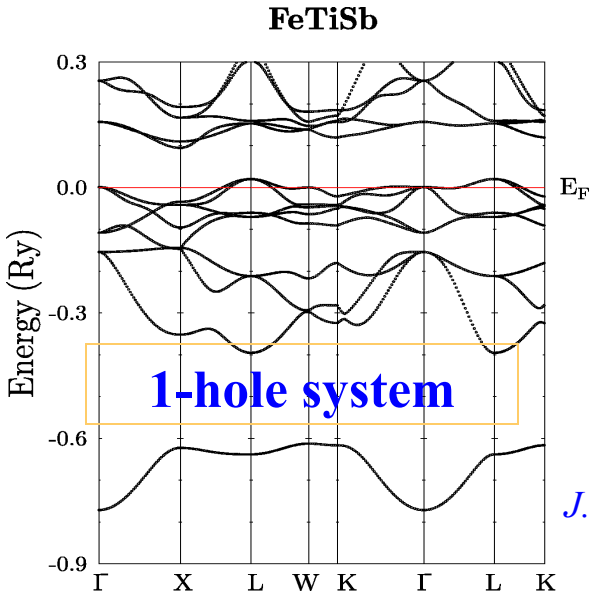






Crystal stability
orbitals *sp*³, *d*

Metal–semiconductor-metal crossovers



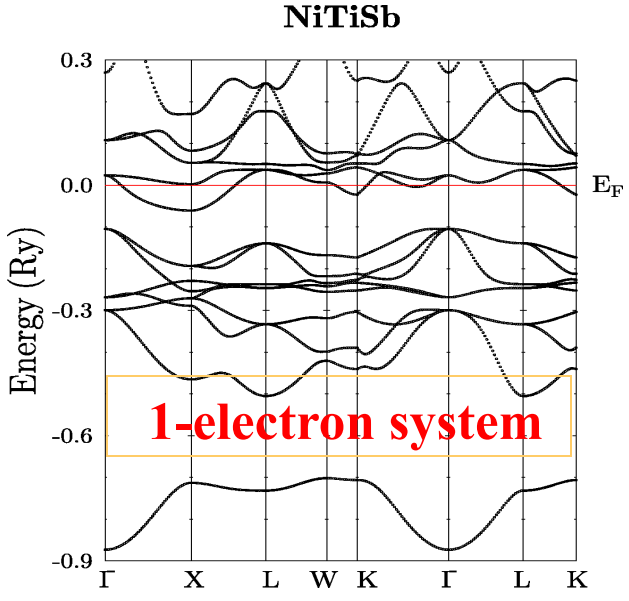
FeTiSb (VEC=17)

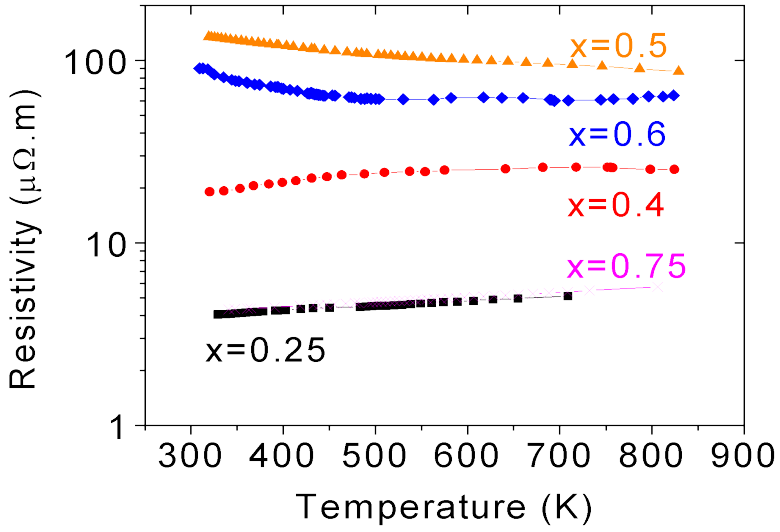
Curie-Weiss PM (~0.9μ_B)

NiTiSb (VEC=19)

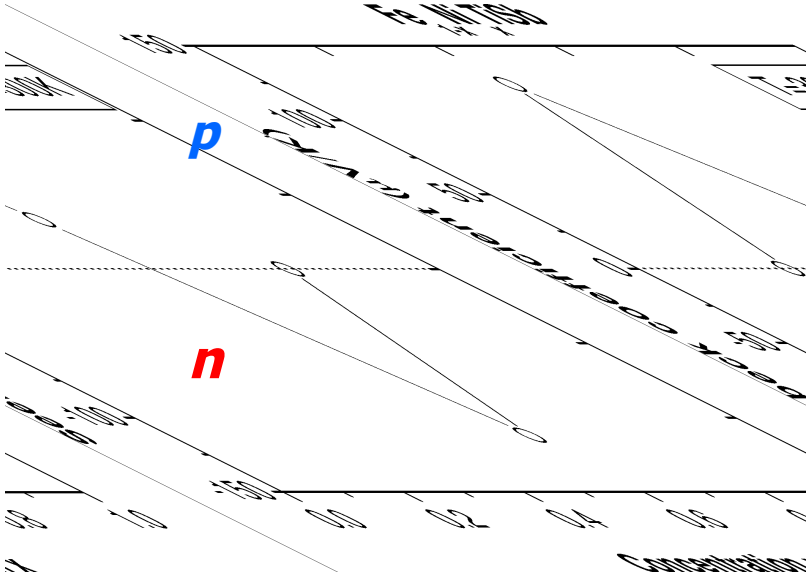
Pauli PM

*J. Tobola et al., PRB **64**, 155103 (2001)*





Resistivity (experiment)

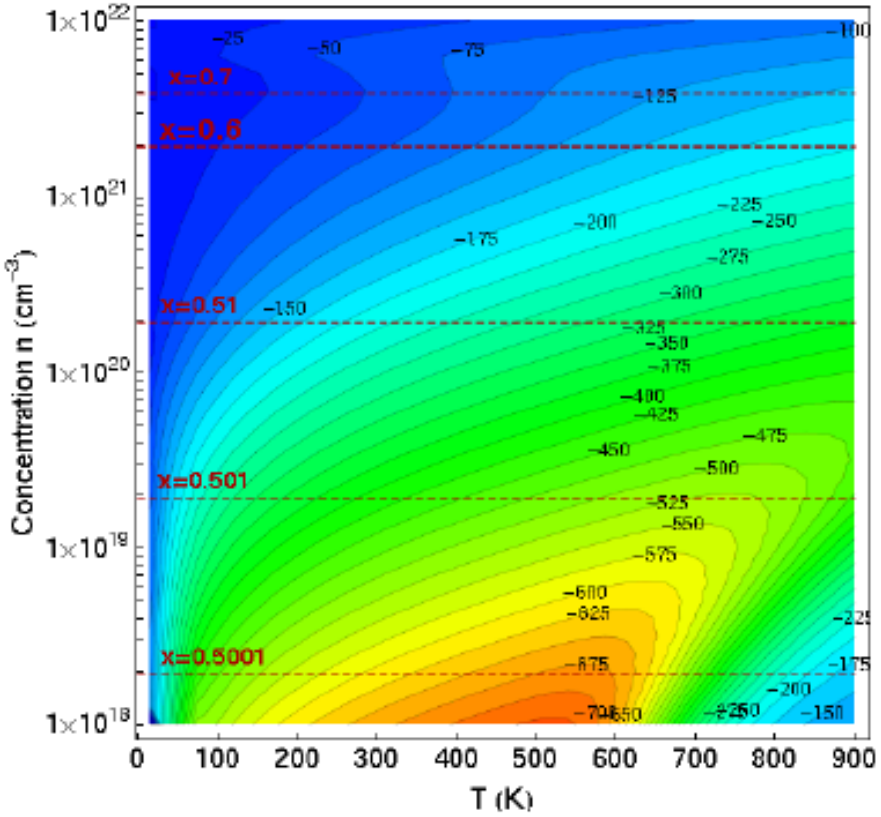


Thermopower (experiment)

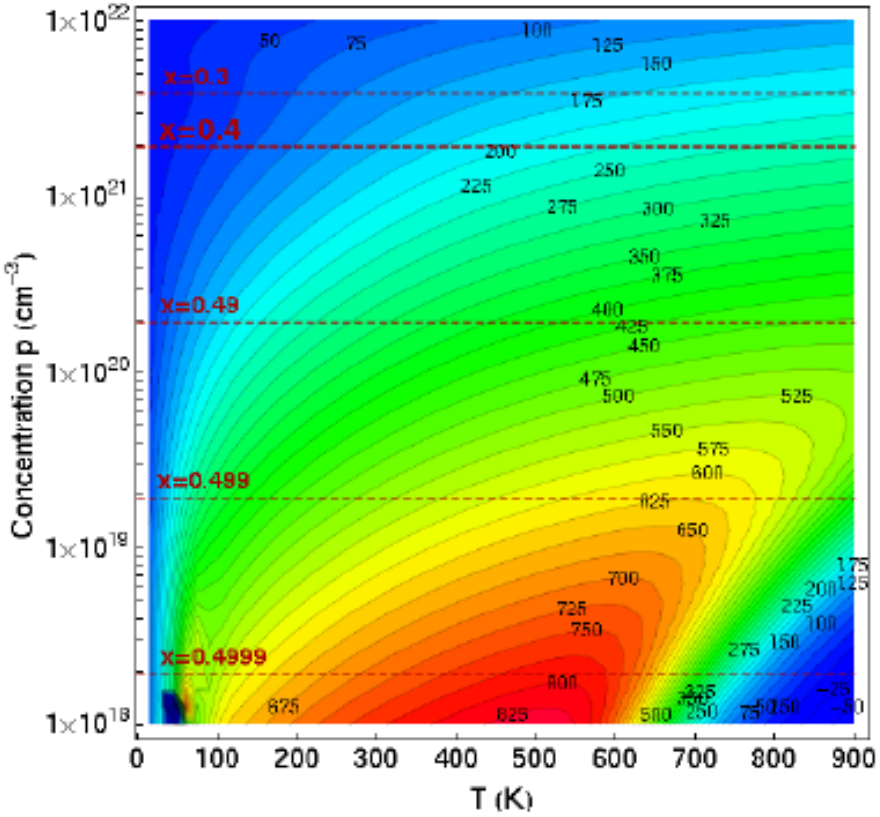
Seebeck coefficient *vs.*

temperature & carrier concentration

$TiFe_{1-x}Ni_xSb$

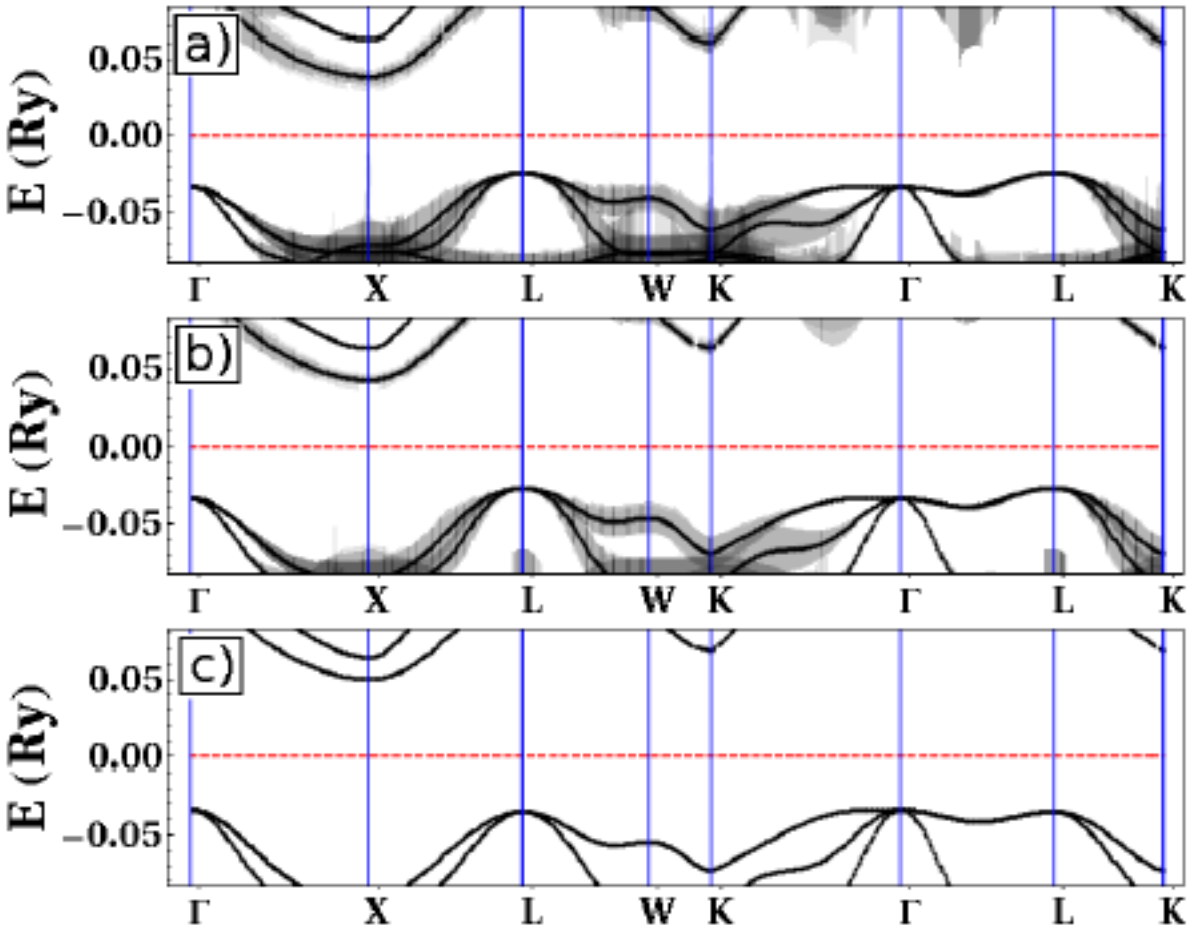


n-type



p-type

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

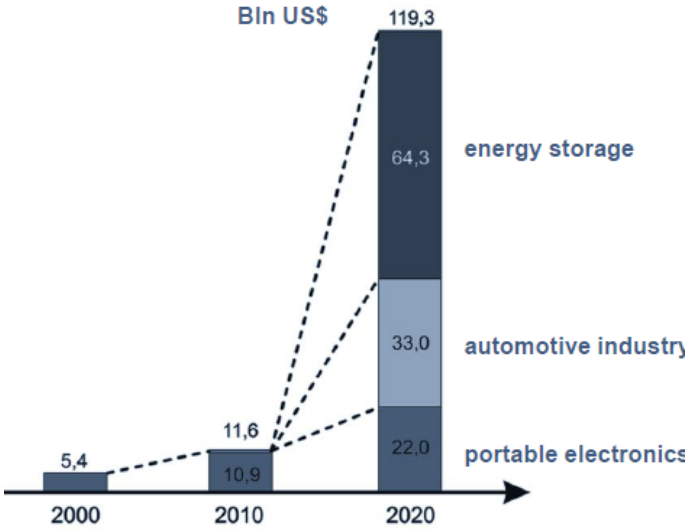
BUT it needs experimental proof whether TE properties are really improved

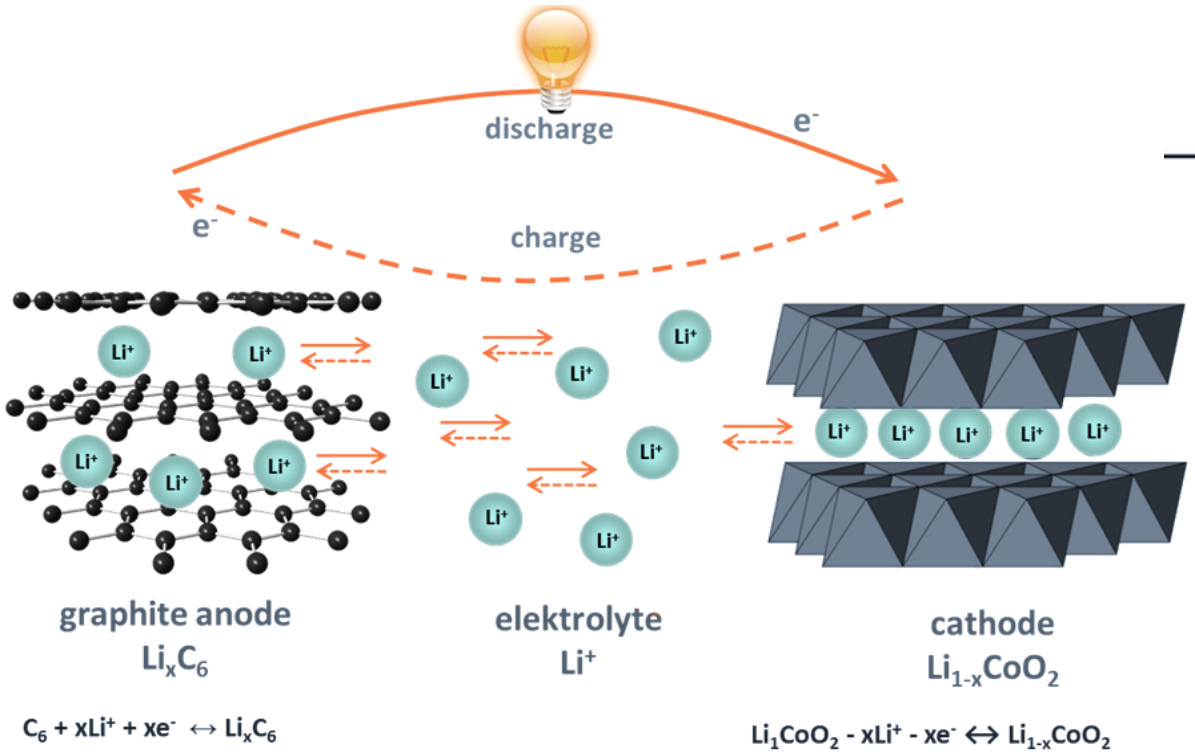
Kutorasinski et al. (JT), Phys. St. Sol. A ***211*** *(2014) 1229*

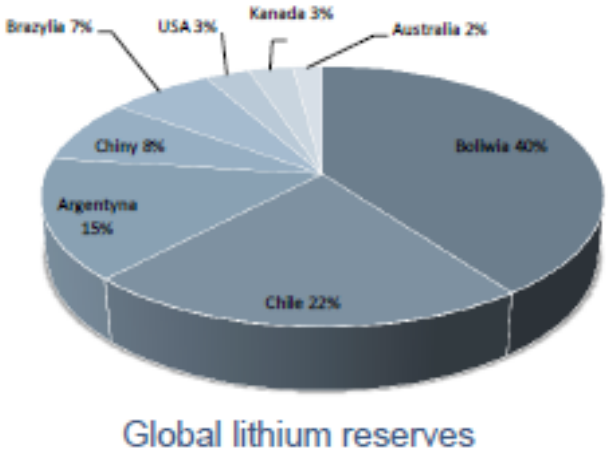
Li-ion battery cathode materials

Must be gradually replaced by Na-ion battery?

world's resources of Li likely insufficient...





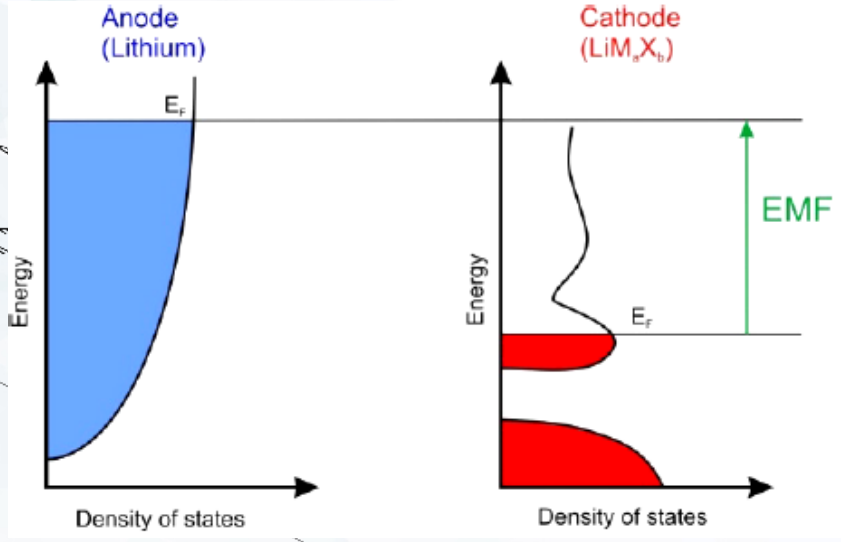


Kim et al. Adv. Energy Mater. 2 (2012) 860.

from J. Molenda

‘Electronic’ model of Li-intercalation process $Li/Li^+/Li_xM_aX_b$

$$xLi^+ + xe^- + MO_2 \Leftrightarrow Li_xMO_2$$

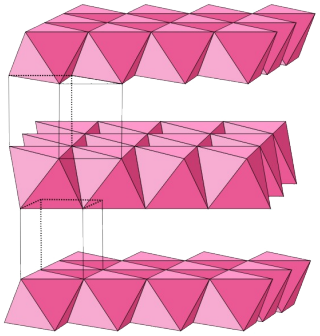


$$\Delta V_{OC} \approx \Delta E_F^{cathode}$$

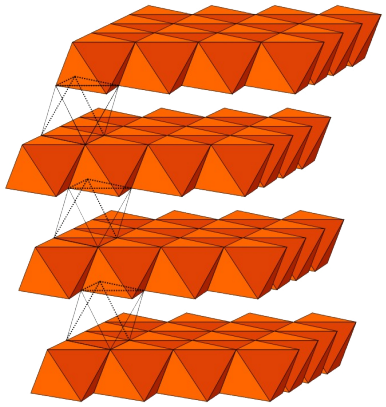
J. Molenda, Phys. Status Solidi B 165 (1991) 419
J. Molenda, Funct. Mater. Lett. 4 (2011) 107
J. Molenda *et al*. Phys. Chem. Chem. Phys. 16 (2014) 14845

Types of crystal structure capable for alkaline-ion intercalation

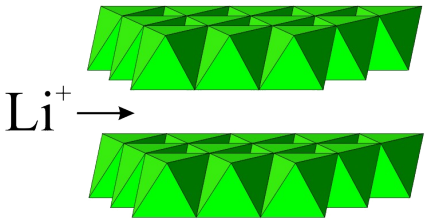
Na_xCoO_2



$LiCoO_2$

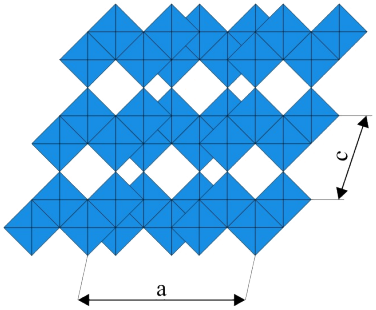


TiS_2

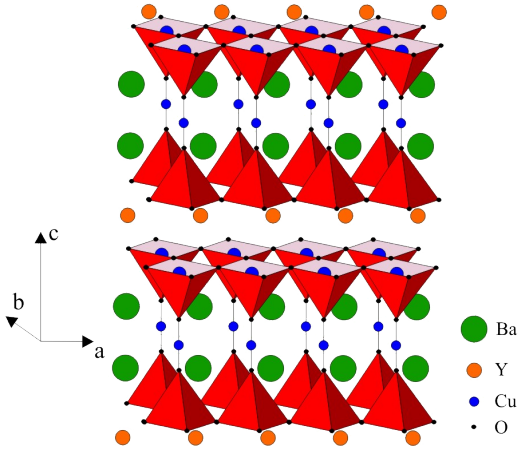


$xLi^+ + xe^- + M_aX_b \Leftrightarrow Li_xM_aX_b$ (M = transition metal, X = O, S)

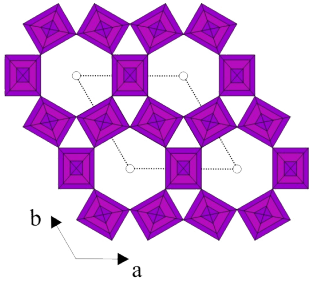
VO_2



$YBa_2Cu_3O_7$

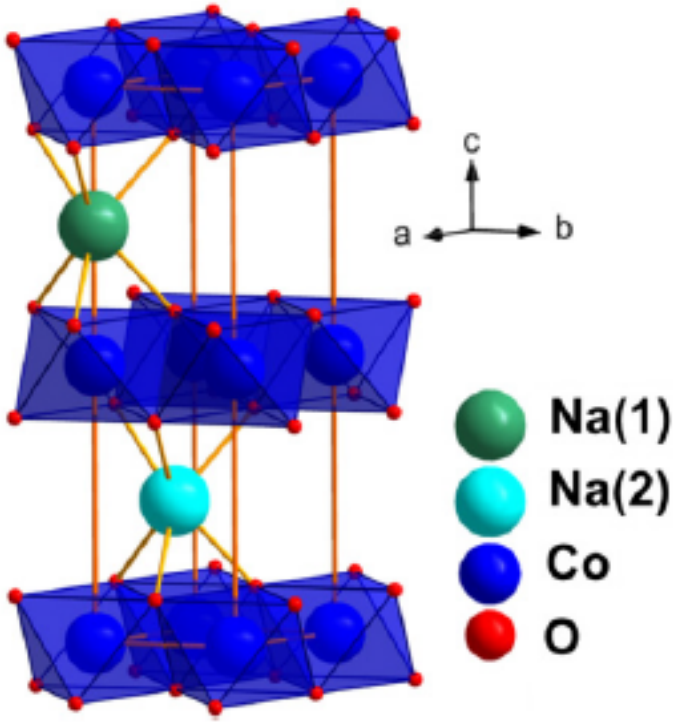


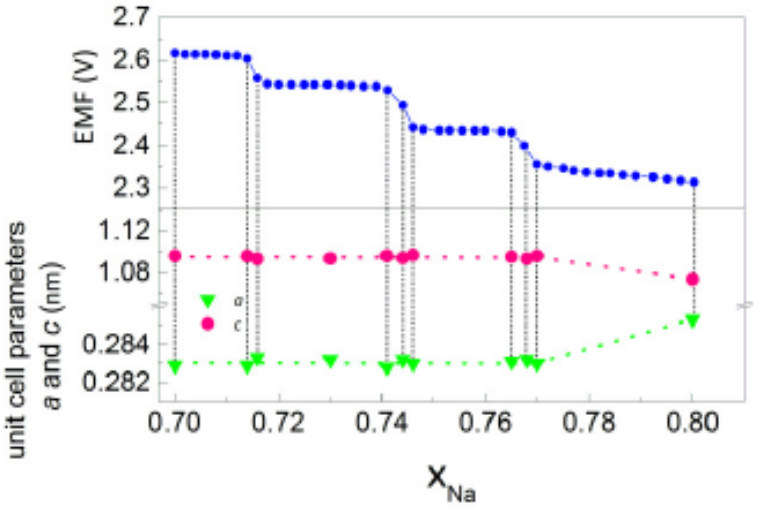
WO_3

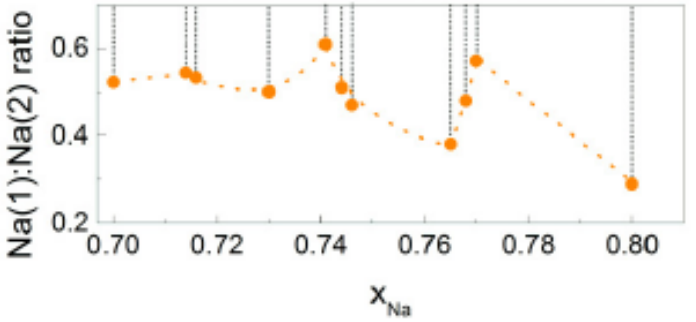


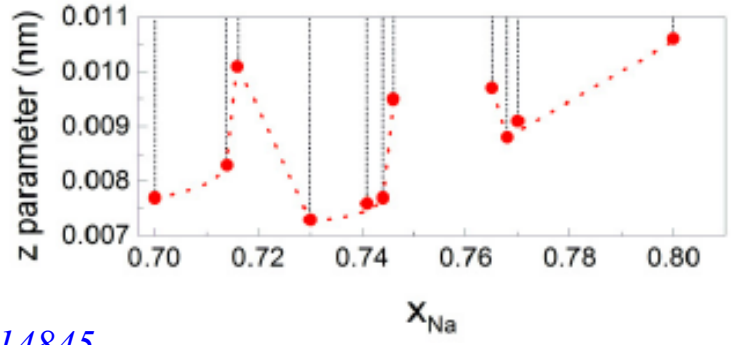
From J. Molenda

Important structural aspects in Na_xCoO_2







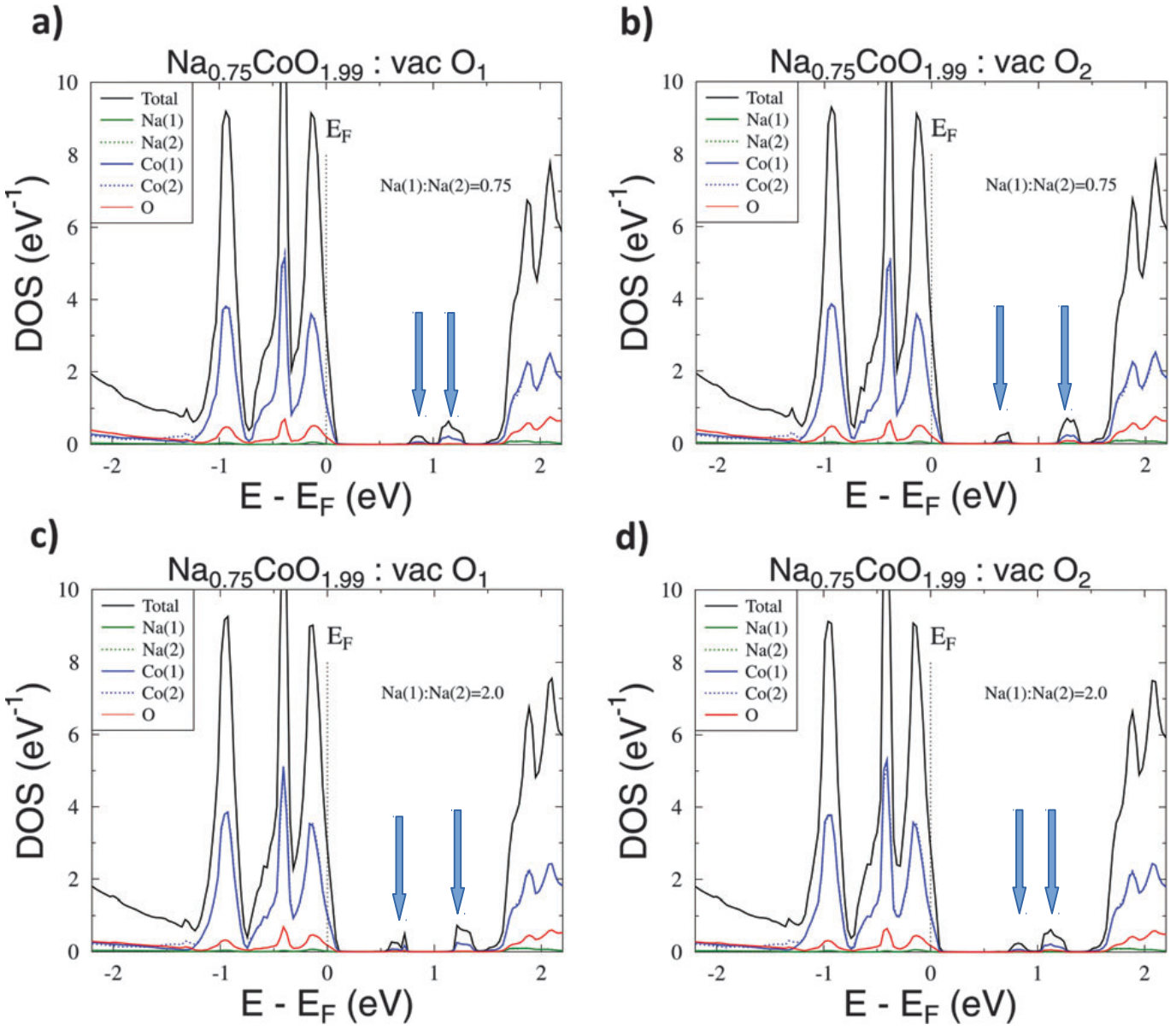


S.G. P63/mcm

- partial occupancy of Na(1) & Na(2) sites
- O atoms on 4f sites no more equivalent
- lattice constants change regularly, but z parameter defining O octahedron, irregularly.

Molenda et al. (JT), Phys. Chem. Chem. Phys., 9 (2014) 14845

O vacancy in Na_xCoO_2 → extra DOS peaks

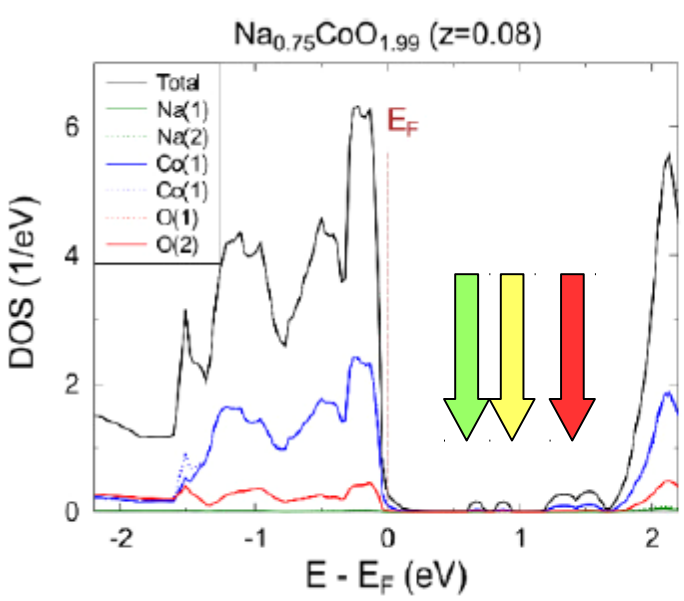


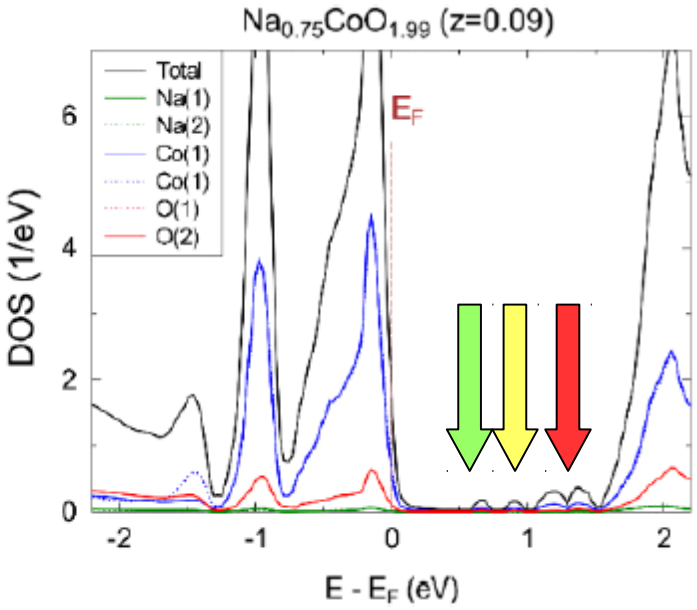
Vacancies on two pairs of O atoms generate extra DOS peaks inside bandgap in slightly different places, which comes from various occupancy of Na(1) & Na(2) sites.

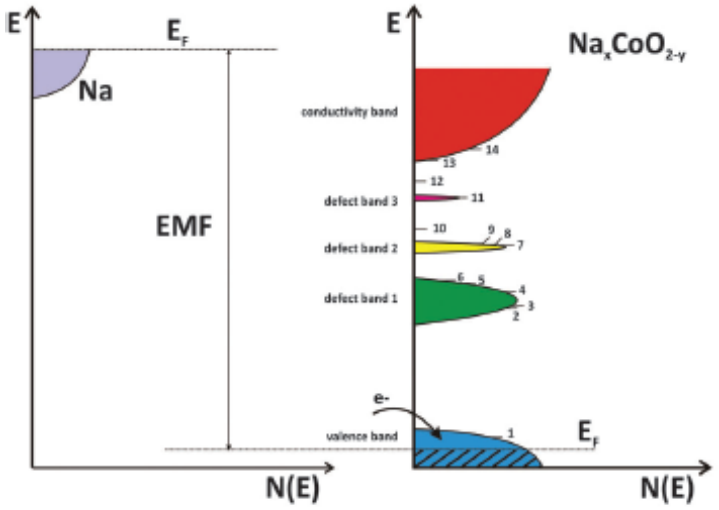
"Defect" peaks contain mostly *d*-states from the closest Co atoms, with some admixture of *p*-states of O.

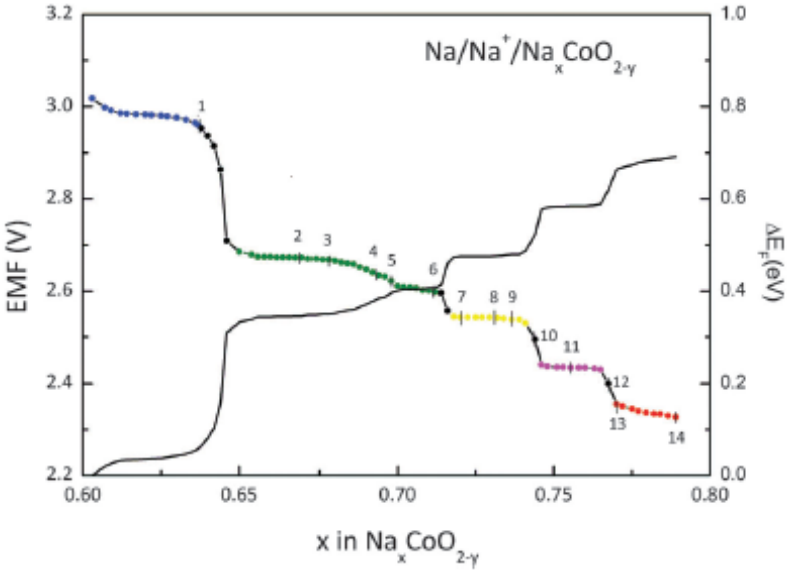
Molenda et al. (JT), Phys. Chem. Chem. Phys., 9 (2014) 14845

‘Defects bands’ versus of EMF character

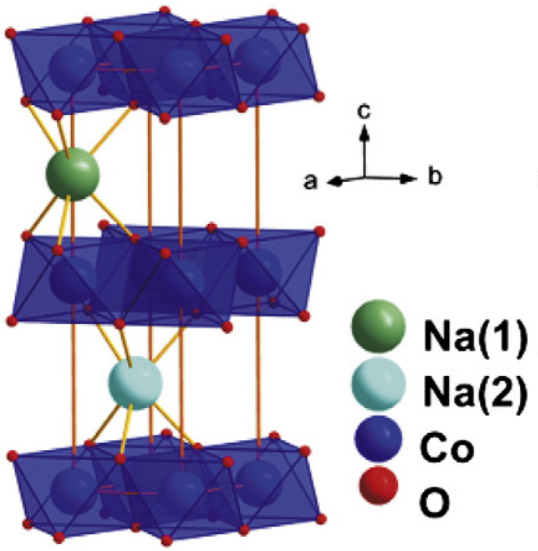


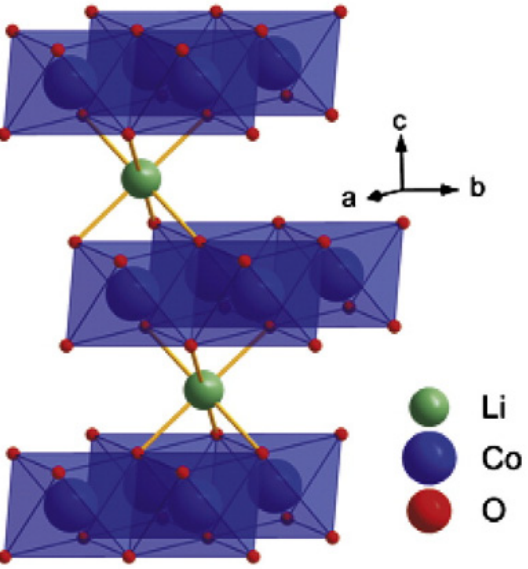


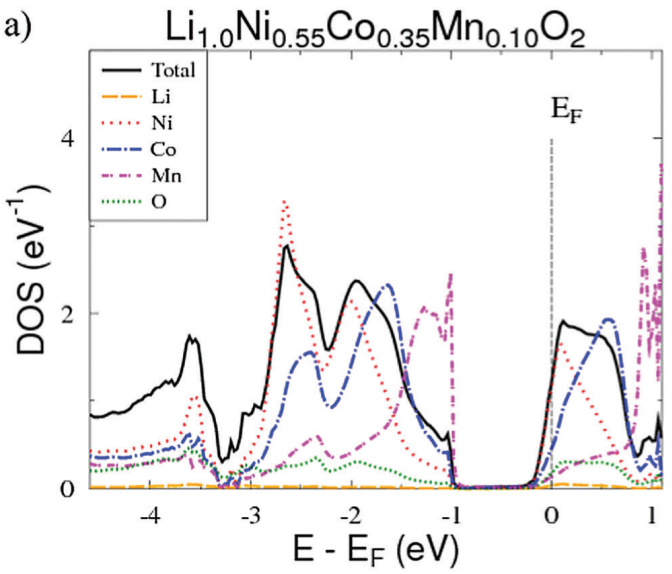


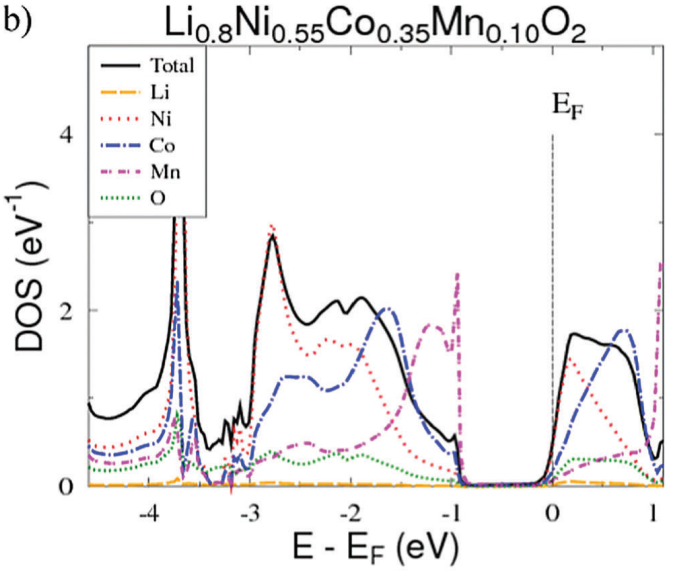


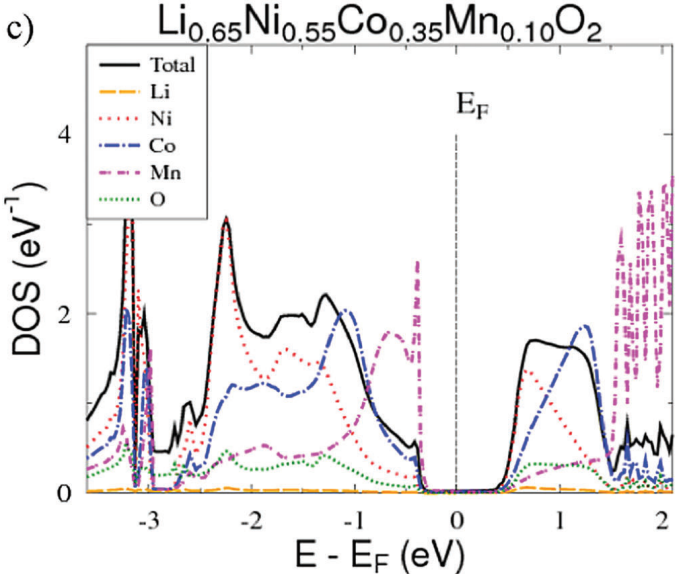
Electronic structure of $Li_x(Ni\text{-}Co\text{-}Mn)O_2$

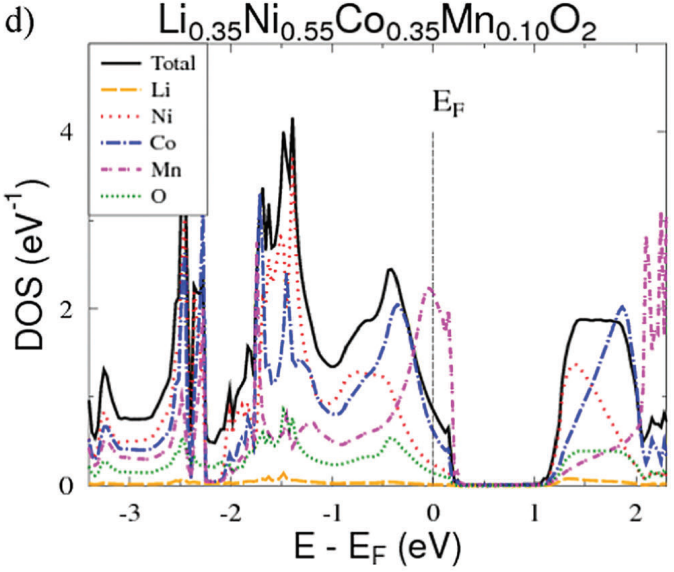






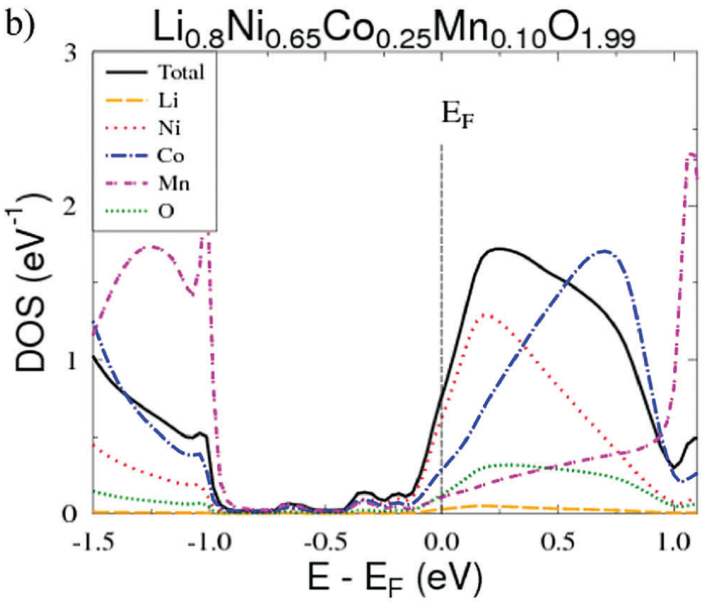


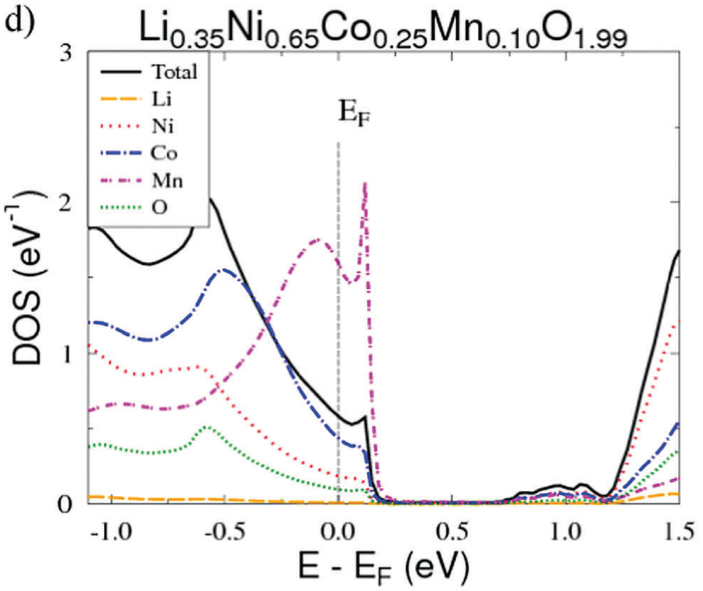


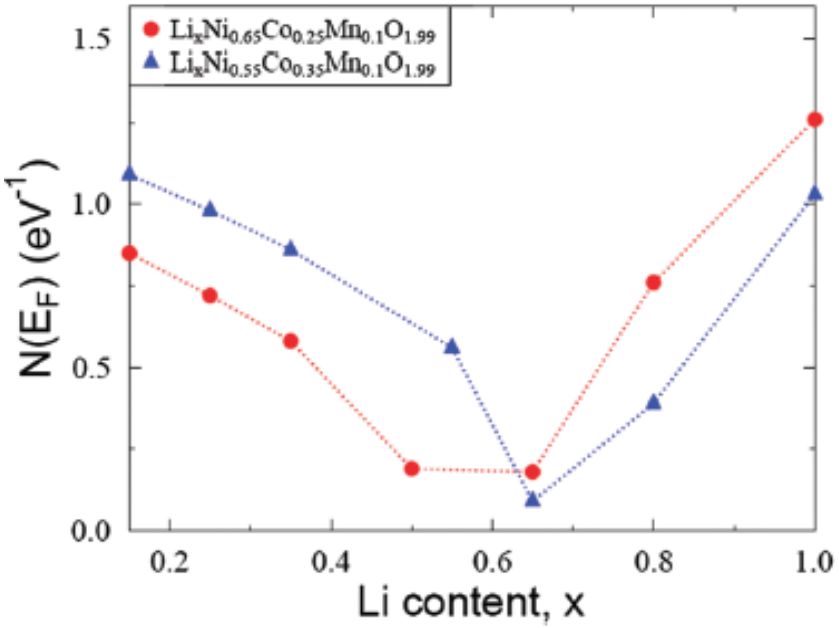


J. Molenda, A. Milewska, W. Zajac, M. Rybski, J. Tobola, Phys. Chem. Chem. Phys., 19 (2017) 25697

Electronic structure of $Li_x(Ni\text{-}Co\text{-}Mn)O_{2-y}$: + O vacancy







Strong effect of O vacancy which produces extra states inside the gap leading to its vanishing in view of KKR-CPA

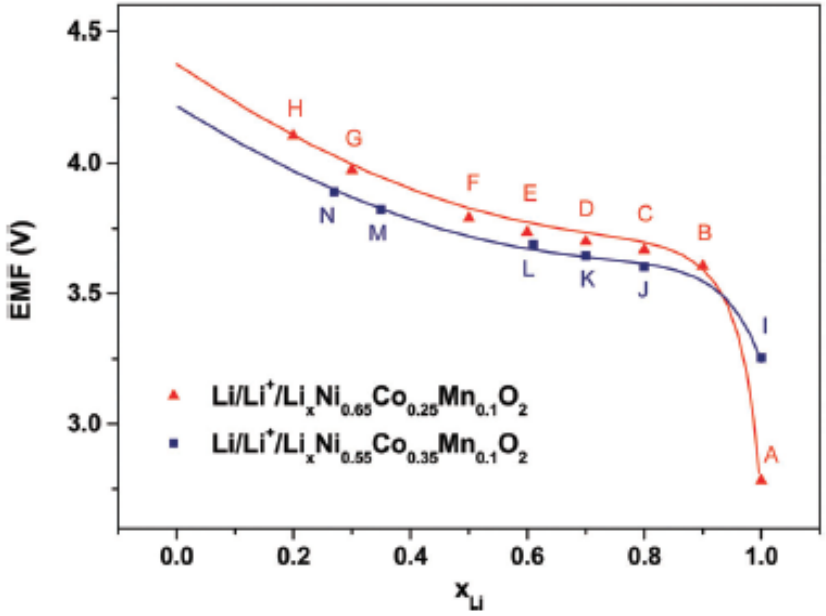
For lower Li content Fermi level falls into high DOS peak of d-states on Mn.

Without O-vacancies transport properties **can not be interpreted coherently.**

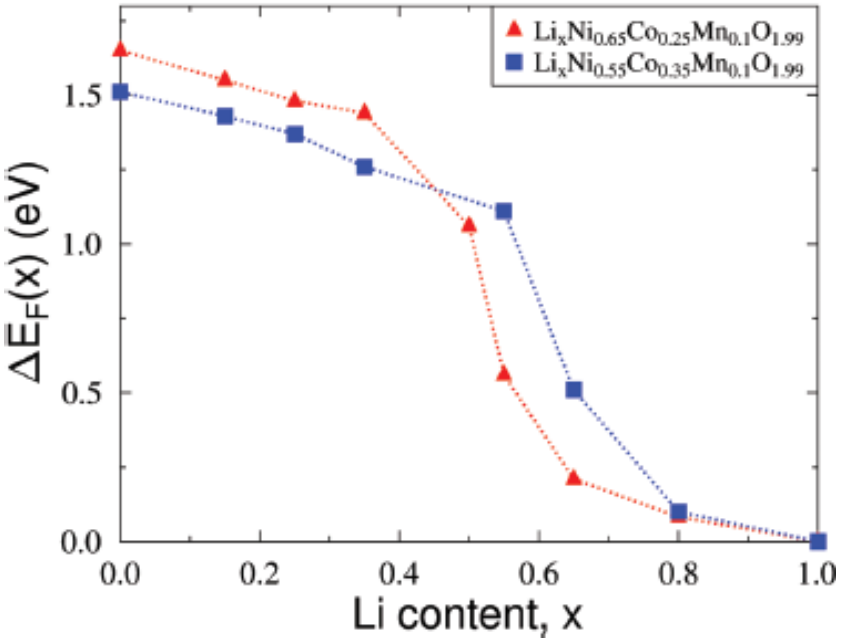
J. Molenda, A. Milewska, W. Zajac, M. Rybski, J. Tobola, Phys. Chem. Chem. Phys., 19 (2017) 25697

$Li_x(Ni\text{-}Co\text{-}Mn)O_{2-y}$: correlation of EMF & ΔE_F

Experimental EMF curve shows the voltage change of about **1.2-1.5 V**



More detailed computations would require analysis of **formation energy at finite T**.

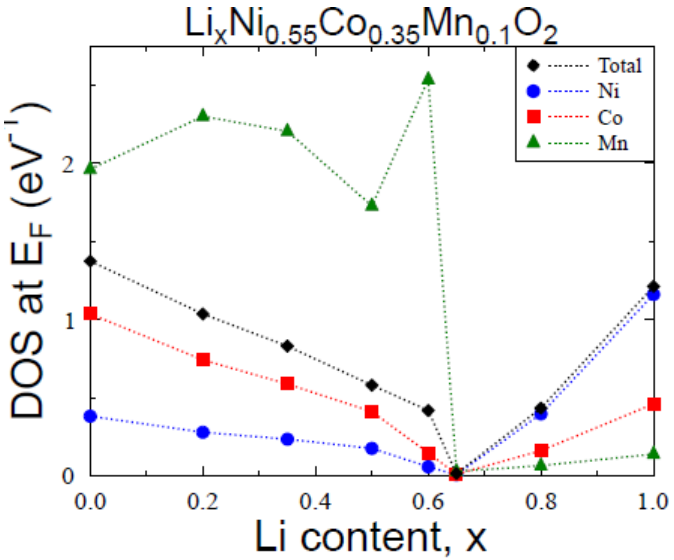


Variation of Fermi level from KKR-CPA calculations of about **1.5-1.6 eV** in reasonable agreement with EMF

To some extent it reflects change in chemical potential of cathode material,

J. Molenda, A. Milewska, W. Zajac, M. Rybski, J. Tobola, Phys. Chem. Chem. Phys., 19 (2017) 25697

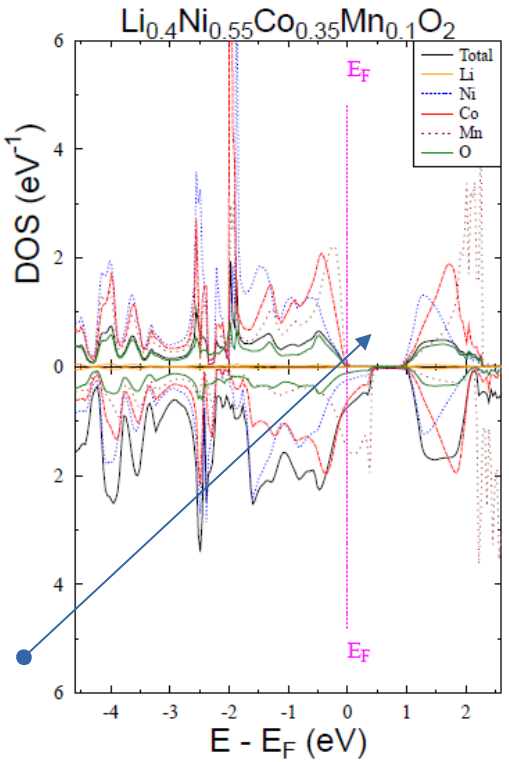
Prediction of magnetism in $Li_x(Ni\text{-}Co\text{-}Mn)O_{2-y}$

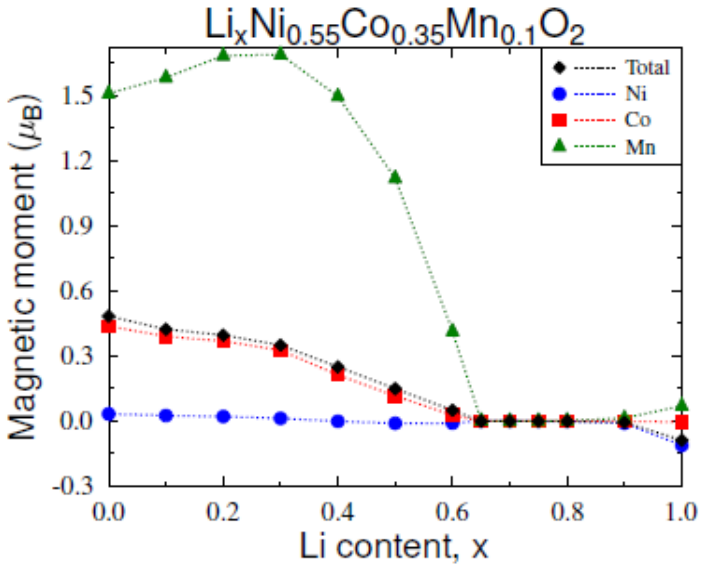


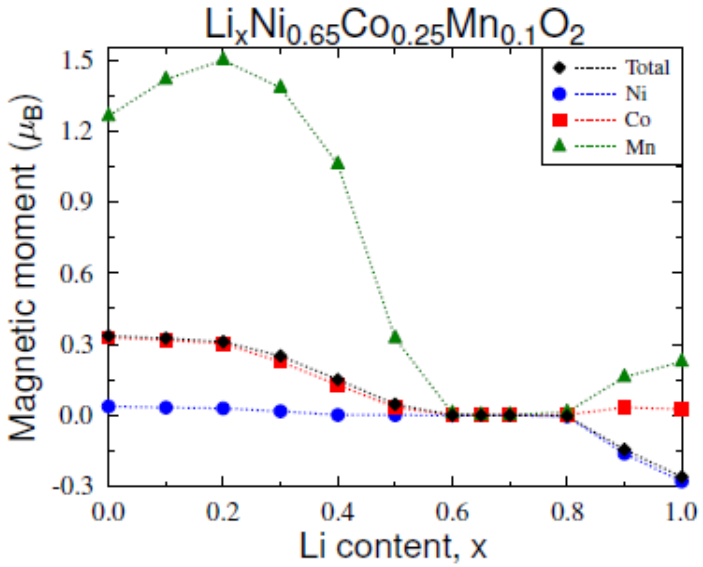
With decreasing Li content Magnetic moments can be born on TM atoms (Mn, Co).

It should have an effect on discharge curve if magnetic order present at battery operating T.

half-metallic state







M. Rybski, J. Tobola, J. Molenda, S. Kaprzyk, Solid State Ionics 321 (2018) 23

Summary

I Boltzmann approach combined with *ab initio* electronic structure calculations in disordered materials give reliable predictions of *T*-dependent & carrier concentration (n/p).

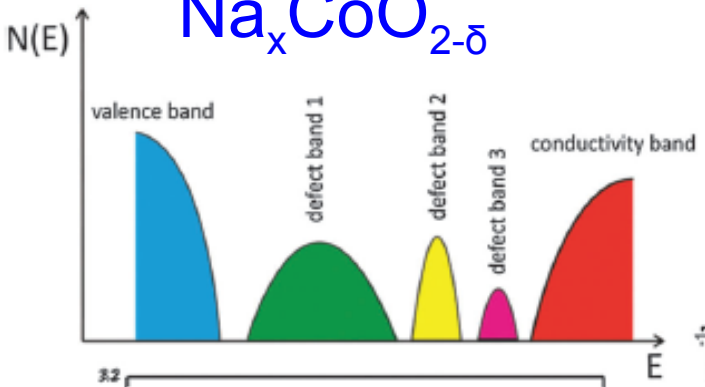
II Electronic structure calculations are helpful in electronic structure searching for band degeneracy or band alignment (complex energy bands) in alloys improving thermoelectric properties e.g. Mg_2(Si-Sn) or of strongly anisotropic, non-parabolic bands & Fermi surfaces etc.

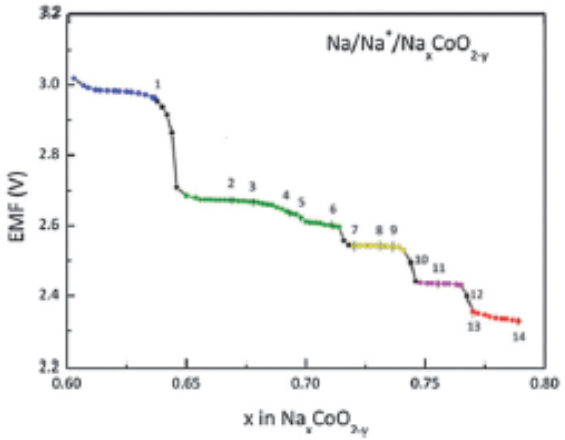
III KKR-CPA calculations accounting for realistic defects (alloying, vacancy defects) in battery systems as Lix(Co-Ni-Mn)O2 vs. NaxCoO2 show close correlation of variation of DOS near EF and character of EMF (more quantitative comparison needed to support this concept).

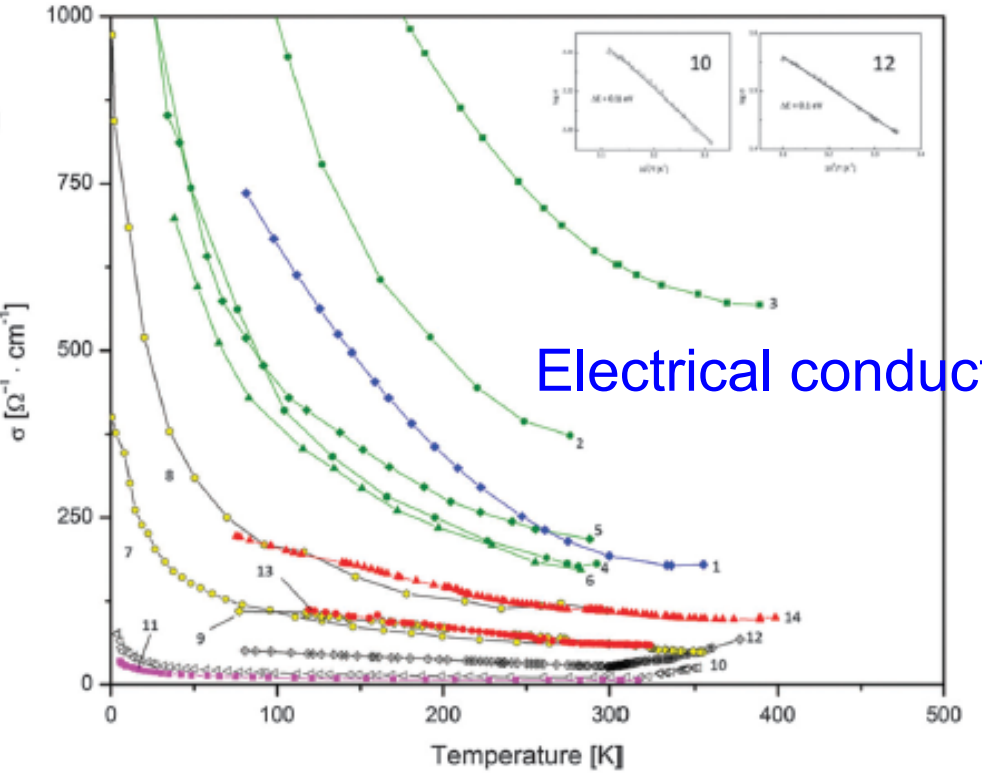
IV Relativistic effects (S-O coupling) and electron correlations play a important role in materials converting energy and should be accounted for calculations.

Supported by the Polish National Science Center (NCN)
Project **MAESTRO DEC-2011/02/A/ST3/00124**

$Na_xCoO_{2-\delta}$



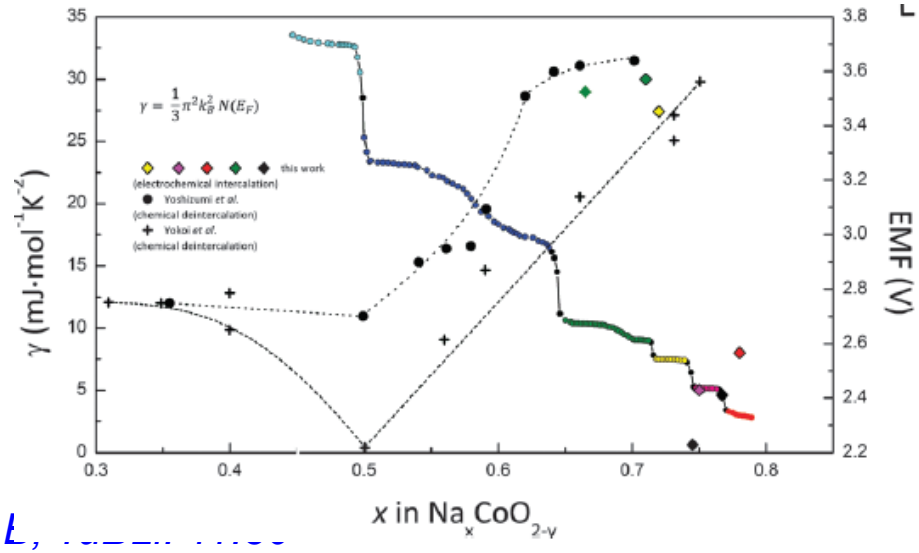




Electrical conductivity

Electronic specific heat

$$\gamma = \frac{1}{3}\pi^2 k_B^2 N(E_F)$$



SCTE'18, Vienna, March 27, 2018: *session L,*