AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY

Domieszki rezonansowe w materiałach termoelektrycznych – struktura elektronowa i własności transportowe.

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Seminarium Wydziałowe WFiIS AGH
Kraków, 12.10.2018

Postępowanie habilitacyjne: cykl 12 publikacji (2011-2018), dotyczących badania stanów rezonansowych w termoelektrykach

[**H1**] C. M. Jaworski, **B. Wiendlocha**, V. Jovovic and J. P. Heremans, "Combining alloy scattering of phonons and resonant electronic levels to reach a high thermoelectric figure of merit in PbTeSe and PbTeS alloys" Energy & Environmental Science **4**, 4155 (2011).

[**H2**] C.M. Orovets, A.M. Chamoire, H. Jin, **B. Wiendlocha** and J.P. Heremans, "Lithium as an Interstitial Donor in Bismuth and Bismuth-Antimony Alloys", Journal of Electronic Materials **41**, 1648 (2012).

[**H3**] J. P. Heremans, **B. Wiendlocha** and A. M. Chamoire "Resonant levels in bulk thermoelectric semiconductors" Energy & Environmental Science **5**, 5510 (2012).

[**H4**] **B. Wiendlocha**, "Fermi surface and electron dispersion of PbTe doped with resonant Tl impurity from KKR-CPA calculations", Physical Review B **88**, 205205 (2013).

[**H5**] **B. Wiendlocha**, "Localization and magnetism of the resonant impurity states in Ti doped PbTe", Applied Physics Letters **105**, 133901 (2014).

[**H6**] S. Kim, **B. Wiendlocha**, H. Jin, J. Tobola, J.P. Heremans, "Electronic structure and thermoelectric properties of p-type Ag-doped Mg_2Sn and $Mg_2Sn_{1-x}Si_x$ $(x = 0.05, 0.1)$", Journal of Applied Physics **116**, 153706 (2014).

[**H7**] H. Jin, **B. Wiendlocha** and J. P. Heremans, "P-type doping of elemental bismuth with indium, gallium and tin: a novel doping mechanism in solids" Energy & Environmental Science **8**, 2027 (2015).

[**H8**] **B. Wiendlocha**, K. Kutorasiński, S. Kaprzyk, J. Tobola, "Recent progress in calculations of electronic and transport properties of disordered thermoelectric materials", Scripta Materialia **111**, 33 (2016).

[**H9**] **B. Wiendlocha**, "Resonant Levels, Vacancies, and Doping in Bi_2Te_3, Bi_2Te_2Se, and Bi_2Se_3 Tetradymites", Journal of Electronic Materials **45**, 3515 (2016).

[**H10**] J.P. Heremans, **B. Wiendlocha**, H. Jin, Thermoelectric Materials with Resonant States, rozdział rozdział 11.3 (strony 441 - 451) w monografii *Advanced Thermoelectrics: Materials, Contacts, Devices, and Systems*, ed. Z. Ren, Y. Lan, Qi. Zhang, CRC Press, Taylor & Francis Group, Boca Raton, FL (USA), 2018.

[**H11**] **B. Wiendlocha**, J-B. Vaney, C. Candolfi, A. Dauscher, B. Lenoir, and J. Tobola, "An Sn-induced resonant level in β-As_2Te_3", Physical Chemistry Chemical Physics **20**, 12948 (2018).

[**H12**] **B. Wiendlocha**, "Thermopower of thermoelectric materials with resonant levels: PbTe:Tl versus PbTe:Na and $Cu_{1-x}Ni_x$", Physical Review B **97**, 205203 (2018).

Plan wystąpienia

0. Krótkie wprowadzenie – metody, materiały termoelektryczne

1. Stan rezonansowy (RL) na przykładzie Cu-Ni i PbTe:Tl.

Kontrowersje wokół RL, wpływ na strukturę elektronową, problem

pasma domieszkowego i lokalizacji, termosiła

2. RL jako nowy mechanizm domieszkowania (Bizmut + In, Ga, Sn)

3. Poszukiwanie nowych domieszek rezonansowych: stop Bi-Sb,

tetradymity (Bi2Te3), Mg2Sn

NARODOWE CENTRUM NAUKI

Prace finansowane w ramach grantów **NCN**: **MAESTRO** (2011/02/A/ST3/00124) i **Sonata Bis 7** (2017/26/E/ST3/00119)
oraz **USA AFOSR-MURI** *"Cryogenic Peltier Cooling"* (#FA9550-10-1-0533)

Collaboration

- Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków, Poland:
  prof. **Janusz Toboła**
  prof. **Stanisław Kaprzyk**
  (KKR-CPA calculations)
- Department of Mechanical & Aerospace Engineering, Ohio State University, Columbus, Ohio (USA): prof. **Joseph P. Heremans** and his group
  (experiment)
- Institut Jean Lamour, Nancy (France): prof. **Bertrand Lenoir** and his group
  (experiment)

Methods: DFT

• **DFT – density functional theory –** single-partice description of the electronic structure of solids. *Ab iniito* calculations, input = crystal structure parameters.

$$\mathcal{H}\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = E\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) \quad \Rightarrow \quad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\Psi(\vec{r}) = E\Psi(\vec{r})$$

• Schrödinger equation (+ relativistic corrections & spin-orbit coupling) with the effective potential, which is a functional of electrons' density.

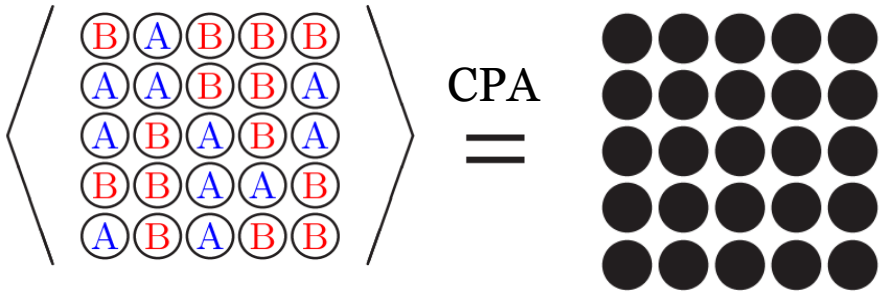
• $V = V_{jon} + V_{el/gaz} + V_{xc}$ all the difficult terms in the exchange-correlation (XC) potential, which is expected to be smaller, than other terms

• XC treated in the local density approximation (LDA) $E_{xc} \propto n(r)^{\alpha}$
or generalized gradient approximation (GGA) $E_{xc} \propto [n(r)^{\alpha}, \nabla n(r)]$

DFT implementations: KKR-CPA & LAPW

• **KKR-CPA method** (Korringa-Kohn-Rostoker with Coherent Potential Approximation) computer codes: Krakow AGH-UST, S. Kaprzyk and Munich SPRKKR, H. Ebert)

• Doped crystal: no periodicity - CPA:



Green function of the „CPA atom" (self-consistent)

$$\langle G \rangle = x_A G^A + x_B G^B$$

No additional scattering on average if "CPA atom" replaced by A/B

CPA: brings back the periodicity - No supercells

any concentration 0-100% of impurity in the same primitive cell

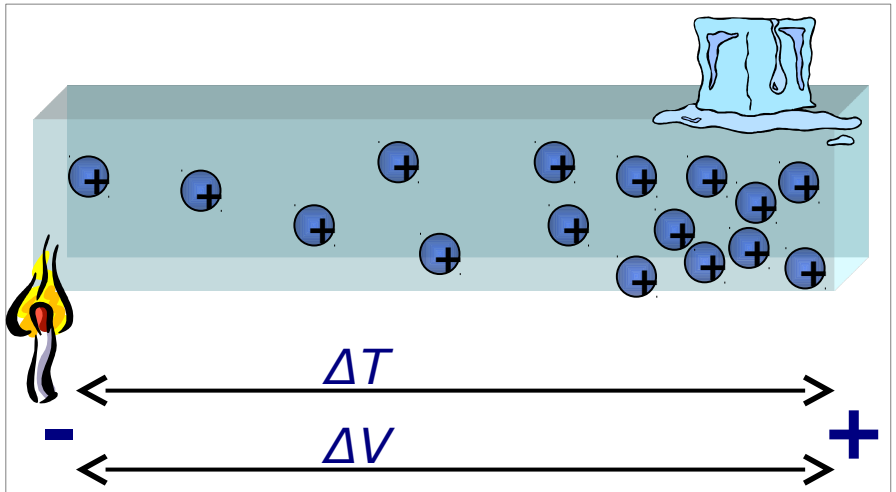
From GF we can get many single-particle properties (DOS, BSF,..)

• **Complementary calculations & relaxation effects:** FP-LAPW method, pure crystals (possible doping via supercells), Wien2k code (P. Blaha et al, Vienna)

Introduction – thermoelectric materials

Seebeck effect - potential gradient from temperature gradient

Peltier effect – cooling of one side due to current flow



$$Seebeck\ Coef. \equiv S \equiv -\frac{E}{\nabla T} = \frac{\Delta V}{\Delta T}$$

$$S = -\frac{1}{eT}\frac{L^{(1)}}{L^{(0)}} \qquad L^0 = \sigma$$

$$\mathsf{L}^n = \int dE \left(-\frac{\partial f}{\partial E}\right)(E-\mu_c)^n \sigma(E)$$

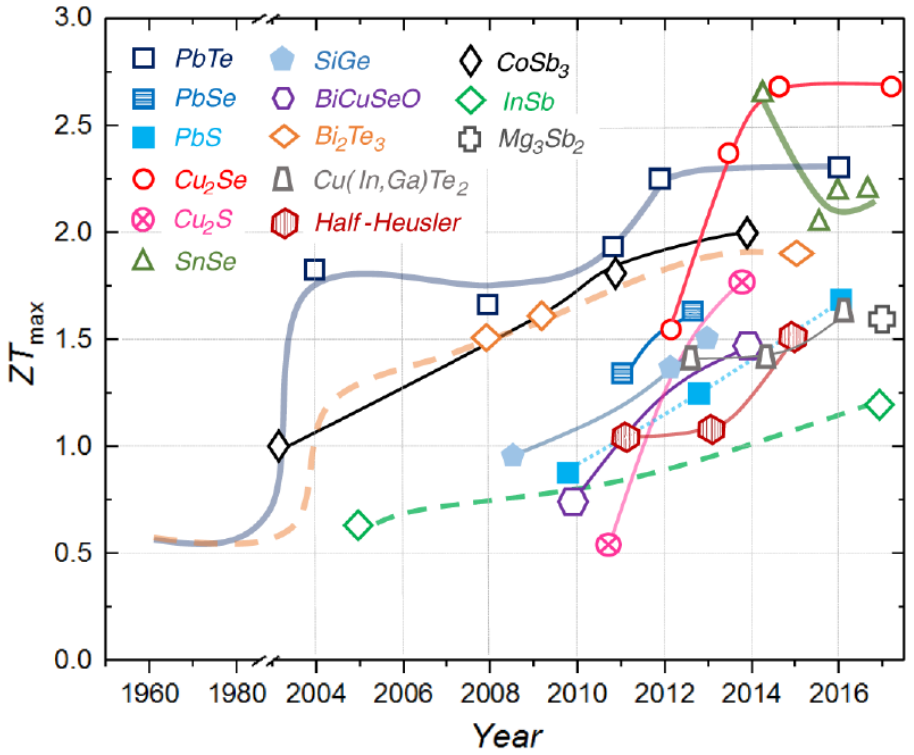
$$\boldsymbol{\sigma}(\mathscr{E}) = e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \tau_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) \otimes \mathbf{v}_n(\mathbf{k}) \delta(\mathscr{E} - \mathscr{E}_n(\mathbf{k}))$$

figure of merit zT

thermopower — conductivity

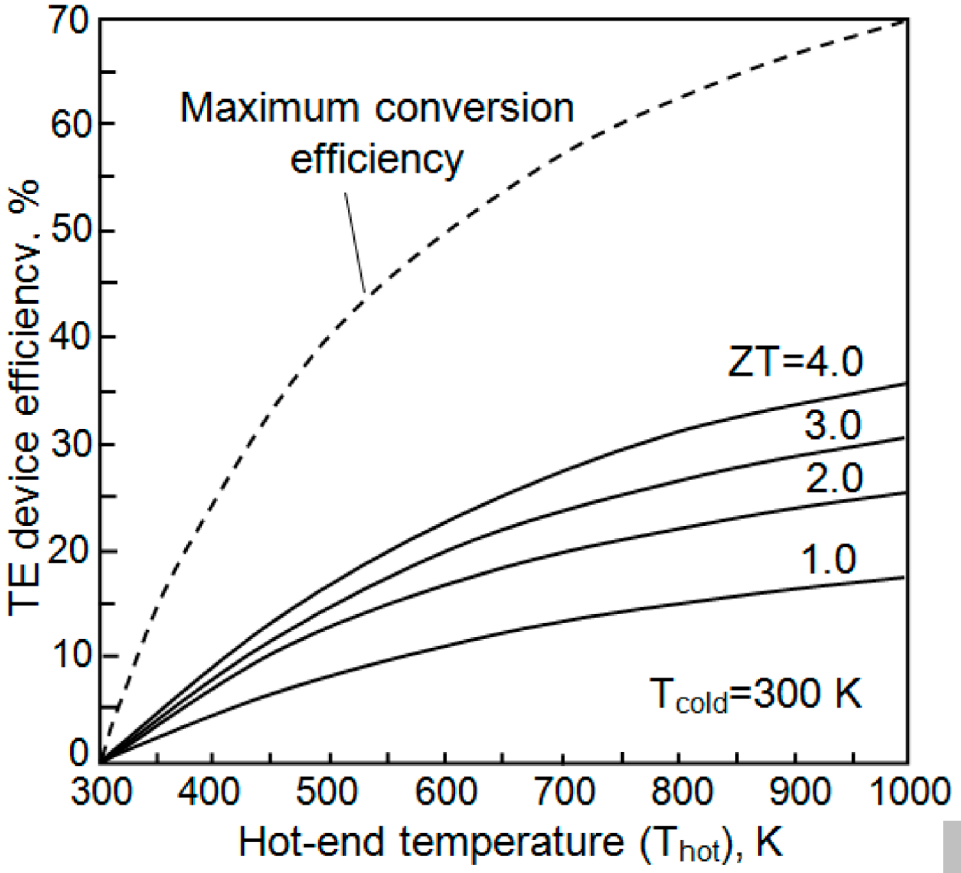
$$zT = \frac{S^2\sigma}{\kappa}T$$

thermal conductivity (lattice + electrons)



Introduction – thermoelectric materials

how is zT related to efficiency? any why optimization is difficult?



$$zT = \frac{S^2\sigma}{\kappa}T \qquad S = -\frac{1}{eT}\frac{L^{(1)}}{L^{(0)}} \qquad L^0 = \sigma$$

$$L^n = \int dE \left(-\frac{\partial f}{\partial E}\right)(E-\mu_c)^n \sigma(E)$$

related quantities:

large σ – small S: small Power Factor $S^2\sigma$

large σ – large κ: small zT

Possible ways of improving TE materials:

1) reduction of the thermal conductivity (e.g. nanostructuring)

2) "band engineering" to improve PF

Introduction – thermoelectric materials

best TE: doped semiconductors

standard strategy to optimize the TE properties:

tune the carrier concentration via doping

$$\sigma \propto \frac{ne^2\tau}{m^*} \qquad zT = \frac{S^2\sigma}{\kappa}T$$

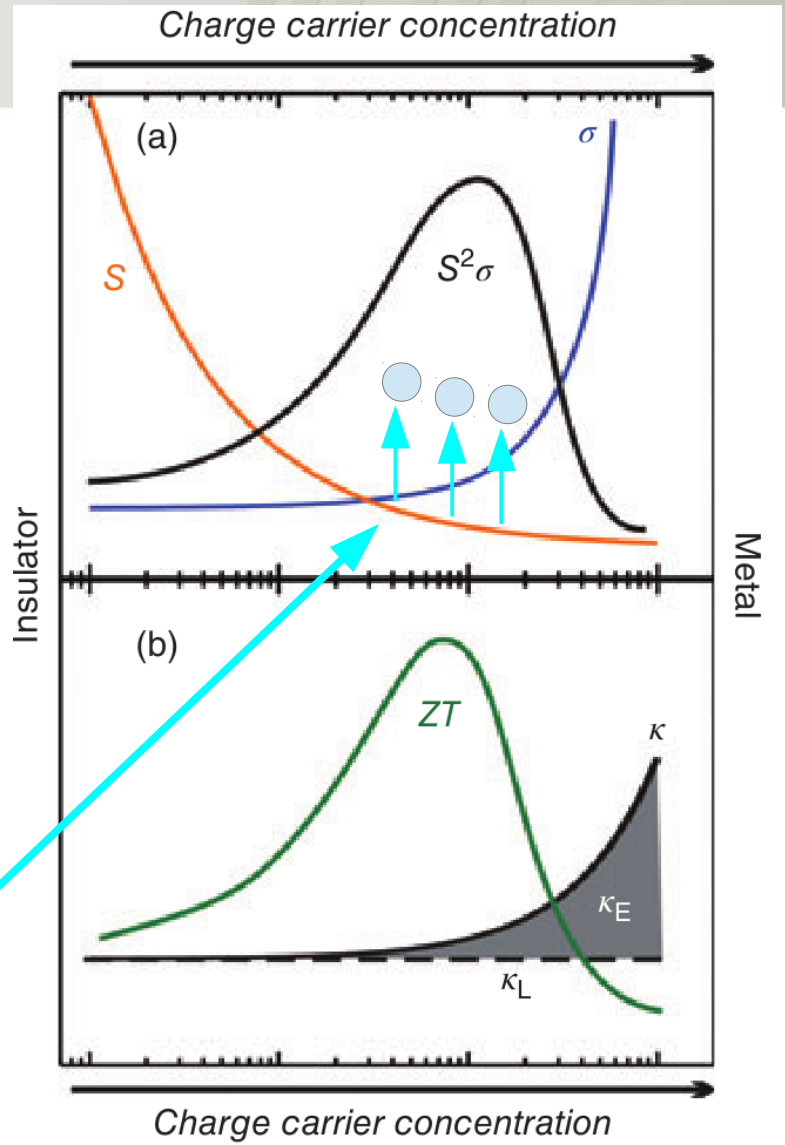
thermopower *S* bounded to carrier concentration

$$S = -\frac{1}{eT}\frac{L^{(1)}}{L^{(0)}} \qquad L^0 = \sigma$$

$$L^n = \int dE \left(-\frac{\partial f}{\partial E}\right)(E-\mu_c)^n \sigma(E)$$

metal S ~ 1-10 μV/K (300 K)

semiconductors: 50-300 μV/K (300 K)



Pisarenko curve: *S(n,p)*

Problem:

how to beat the Pisarenko relation ?!

Introduction – thermoelectric materials

TE generators: waste heat recovery

RTG in space applications

Mars Rover Curiosity 2011, PbTe

Cryogenic cooling of detectors

Power Pot

The Power Pot Portable Electric Generator
by Powerpractical
7 customer reviews

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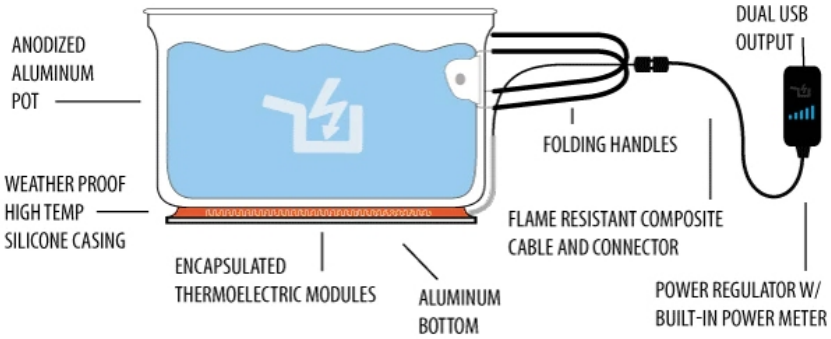
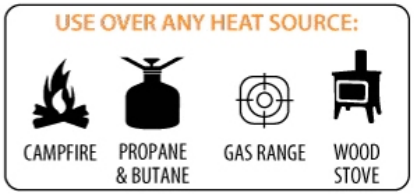
- Lightweight material makes it great to take on camping trips

THE POWERPOT X

10 Watt Thermoelectric Generator

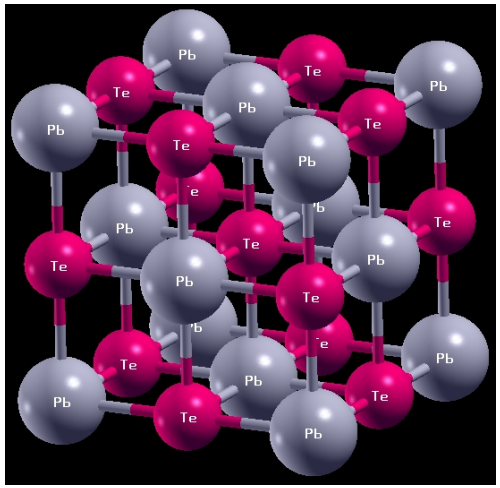




Motivation: PbTe:Tl

increase of thermopower after Tl doping

- **Thermoelectric community:**
  2% Tl doped PbTe
  J.P. Heremans et al. Science (2008)
  increase in thermopower and zT due to "resonant distortion of electronic DOS"

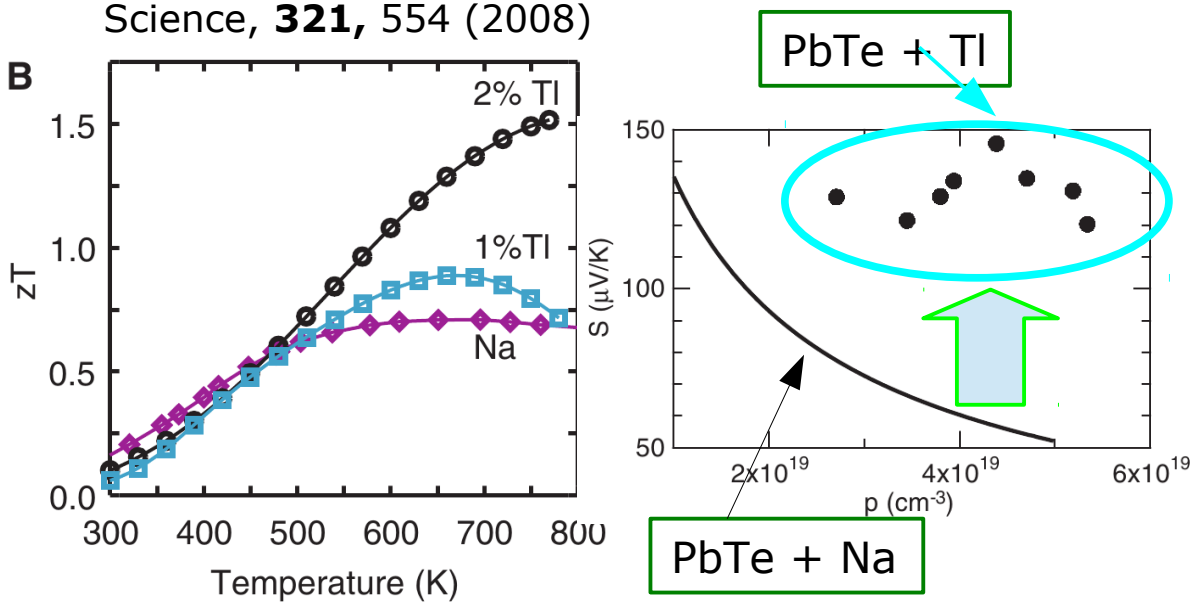


PbTe, *fcc* rock salt structure

Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States

Joseph P. Heremans,[1,2]* Vladimir Jovovic,[1] Eric S. Toberer,[3] Ali Saramat,[3] Ken Kurosaki,[4] Anek Charoenphakdee,[4] Shinsuke Yamanaka,[4] G. Jeffrey Snyder[3]*

Science, **321,** 554 (2008)



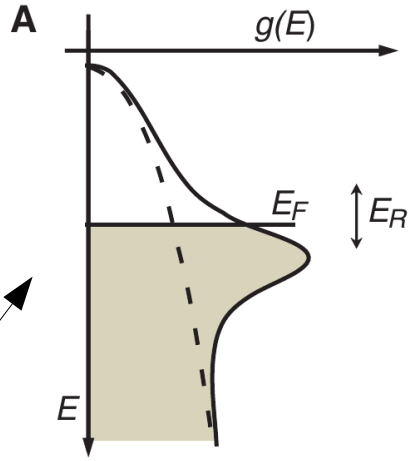
since 2011: my collaboration with JP Heremans' group
3x at OSU as a postdoctoral researcher

Motivation: PbTe:Tl

increase of thermopower after Tl doping

• Original explanation: “distortion” of DOS due to resonant state – increase in DOS at EF by DOS peak from resonant impurity

$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_BT\left\{\frac{d[\ln(\sigma(E))]}{dE}\right\}_{E=E_F} = \frac{\pi^2}{3}\frac{k_B}{q}k_BT\left\{\frac{1}{n}\frac{dn(E)}{dE}+\frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}_{E=E_F}$$



equivalent to increase in m* $S = \frac{8\pi^2 k_B^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3}$ m* ↗ S ↗

• **Questioning of RL mechanism of S enhancement:**

•Resonance = strong scattering, mobility reduction, bad for TE

•Peak in DOS – localized states, do not take part in transport, or form a narrow impurity band. Narrow band = small σ.

Two band system with 1 being narrow = no increase in S

$$S = \frac{\sigma_1 S_1 + \sigma_2 S_2}{\sigma_1 + \sigma_2}$$

Goal of my research

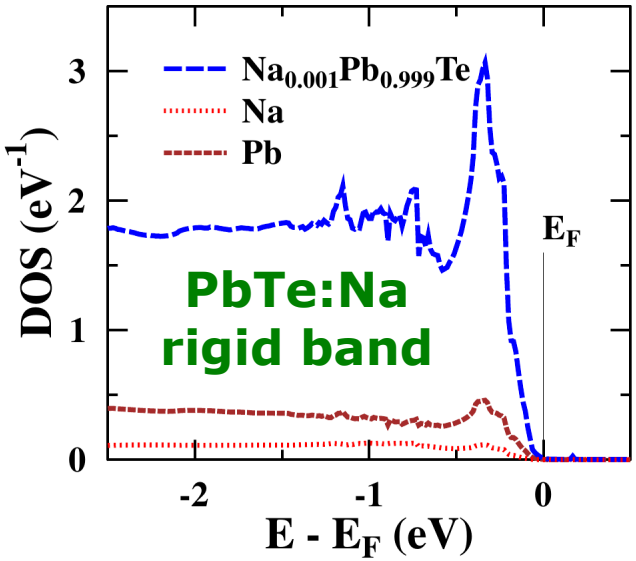
1) To investigate from first principle calculations, how RL modifies electronic structure of the studied material

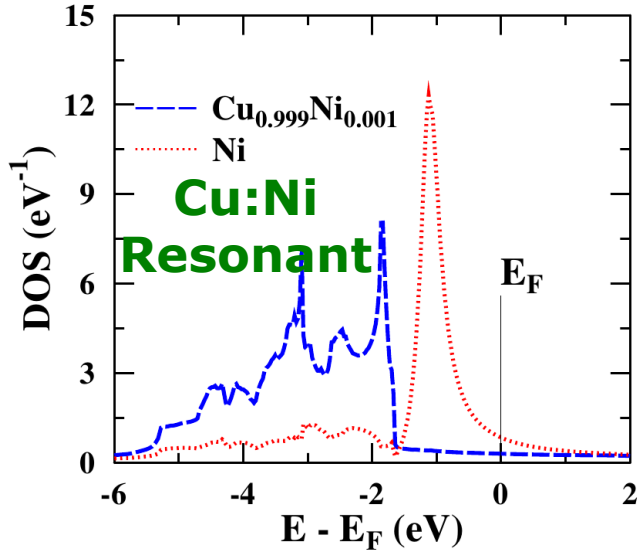
2) To verify whether RL may indeed increase the thermopower in semiconductor (counterarguments of localized states & narrow impurity band)

3) To search for new resonant impurities

"Classical" vs resonant impurity: DOS

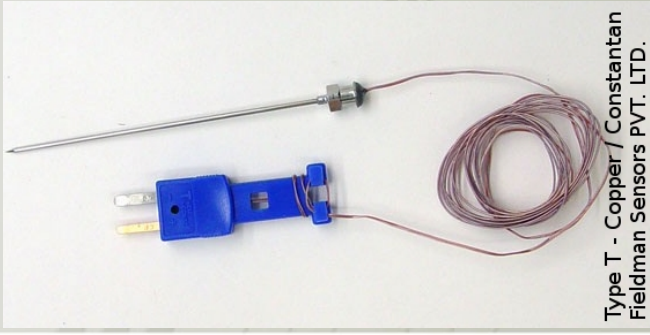
- **„Classical" impurity: (rigid-band-like)** does not change (much) the host band structure, adds carriers (e.g. Na:PbTe)
- **Resonant impurity:** resonant level (RL) or „virtual bound state" (Friedel, 1956), may lead to strong modifications of host bandstructure and resonant scattering (first works on diluted metallic alloys)
- **Fingerprint:** peak in DOS (diluted concentration ~0.1%)
- Very often in **(semi)magnetic semiconductors** HgSe:Fe, PbTe:Cr... **(PAS, Warsaw!)**
- **Possible effects:**
  - → strong (resonant) scattering (s-d in Cu-Ni)
  - → magnetism - (semi)magnetic semiconductors
  - → charge trap, EF in the gap (In in PbTe)
  - → increase of thermopower in low T (HgSe:Fe) or high T (PbTe:Tl, SnTe:In, Bi2Te3:Sn,...)
  - → superconductivity (?)





Example of Constantan (Cu-Ni)

Cu-Ni alloy, Ni concentrations 35-50%, one of the **best TE among metallic alloys**, thermocouples



- **Photoemission spectra of Cu-Ni alloy** - does not follow the rigid band model (expected shift in EF)

PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Photoemission and Optical Studies of Cu-Ni Alloys. I. Cu-Rich Alloys*

D. H. Seib† and W. E. Spicer
Stanford University, Stanford, California 94305

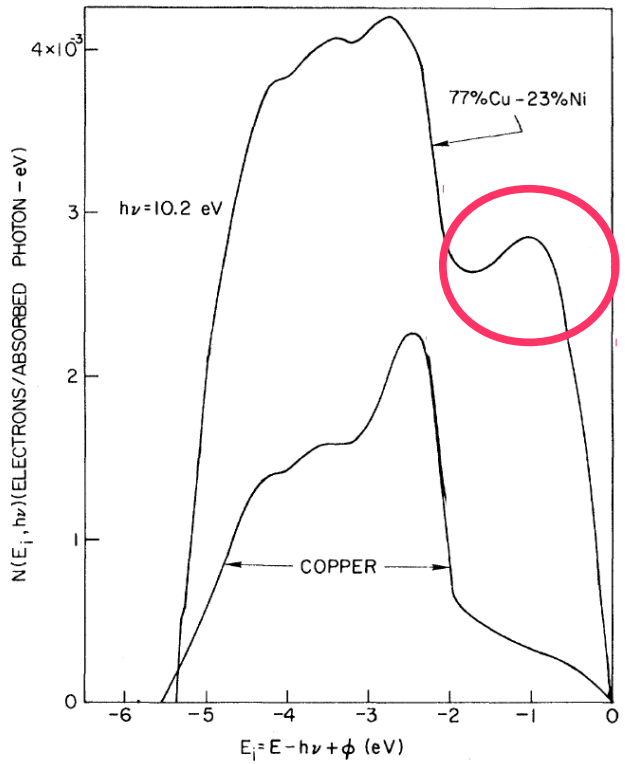
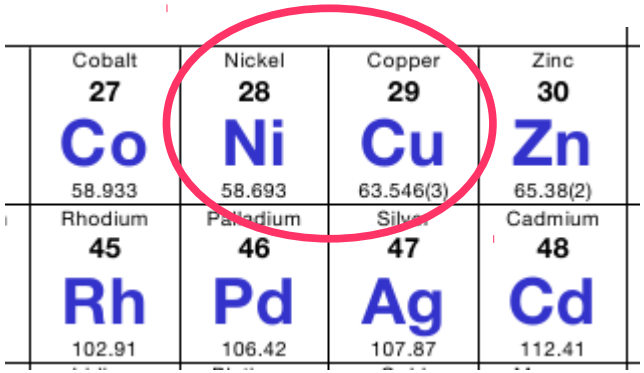


FIG. 10. Comparison of EDCs for Cu, 77% Cu. The curves are normalized to their respective yields. The energy position of structure from the Cu *d* states ($E_i < -2$ eV) remains constant; the buildup of structure at −1.0 eV is due to Ni *d* electrons in virtual-bound-type states.



described in ~.70 using KKR-CPA

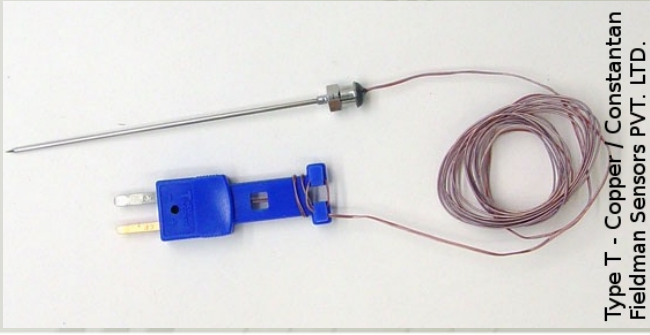
papers by Butler, Stocks, Gyorffy, Ehrenreich, Faulkner,...

– resonant state (virtual bound state) is formed

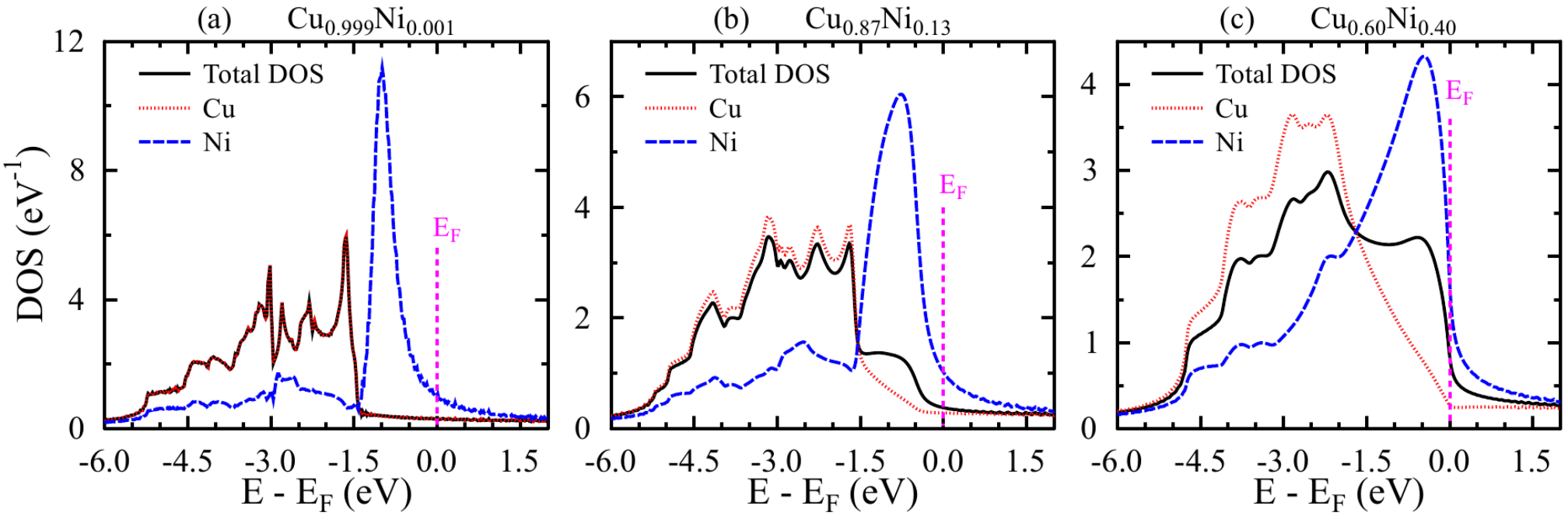
Peak from the rapid change of the phase shift

Example of Constantan (Cu-Ni)

Cu-Ni alloy, Ni concentrations 35-50%, one of the **best TE among metallic alloys**, thermocouples



- **Ni Resonant level** from KKR-CPA



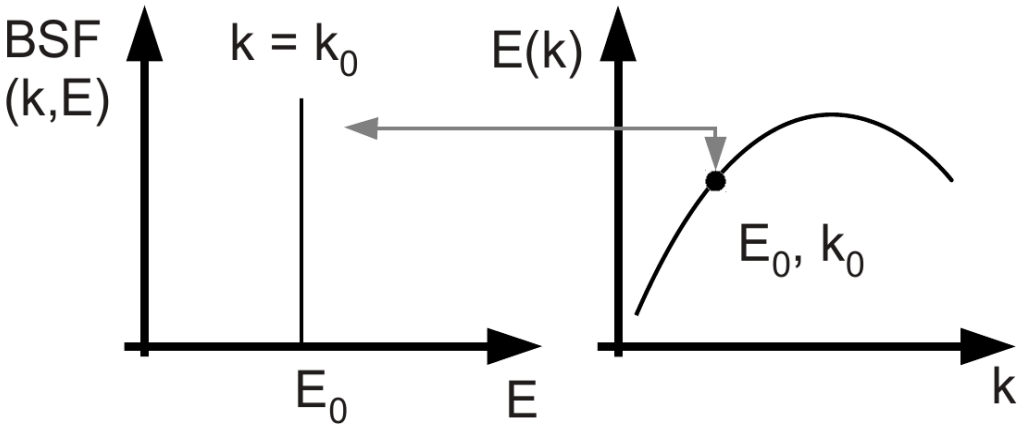
"Classical" vs resonant impurity: bands

Bands: disordered system - no Bloch states – E(k) not defined (in general)

Bloch spectral functions :

Crystal:

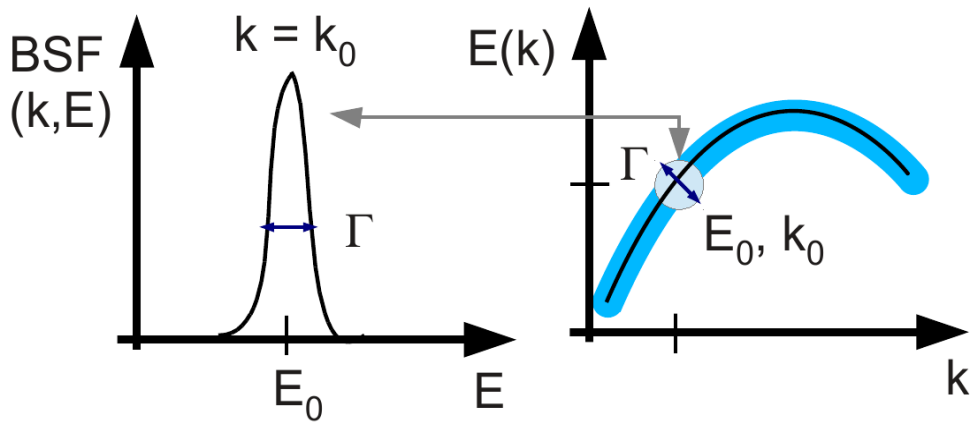
Dirac delta $A^B(\mathbf{k}, E) = \delta(E - E_{\nu,\mathbf{k}})$



- BSF shows band center
- sharp bands, life time:infinite

Alloy:

Lorentzian $A^B(\mathbf{k}, E) = \frac{1}{2\pi} \frac{\Gamma}{(E - E_{\nu,\mathbf{k}})^2 + (1/2\Gamma)^2}$



- BSF: Band center + band width
- "blurred" bands, finite life time

$$\tau = \frac{\hbar}{\Gamma}$$

k-resolved DOS: $n(E) = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\Omega_{\mathrm{BZ}}} d^3k A^B(\mathbf{k}, E)$

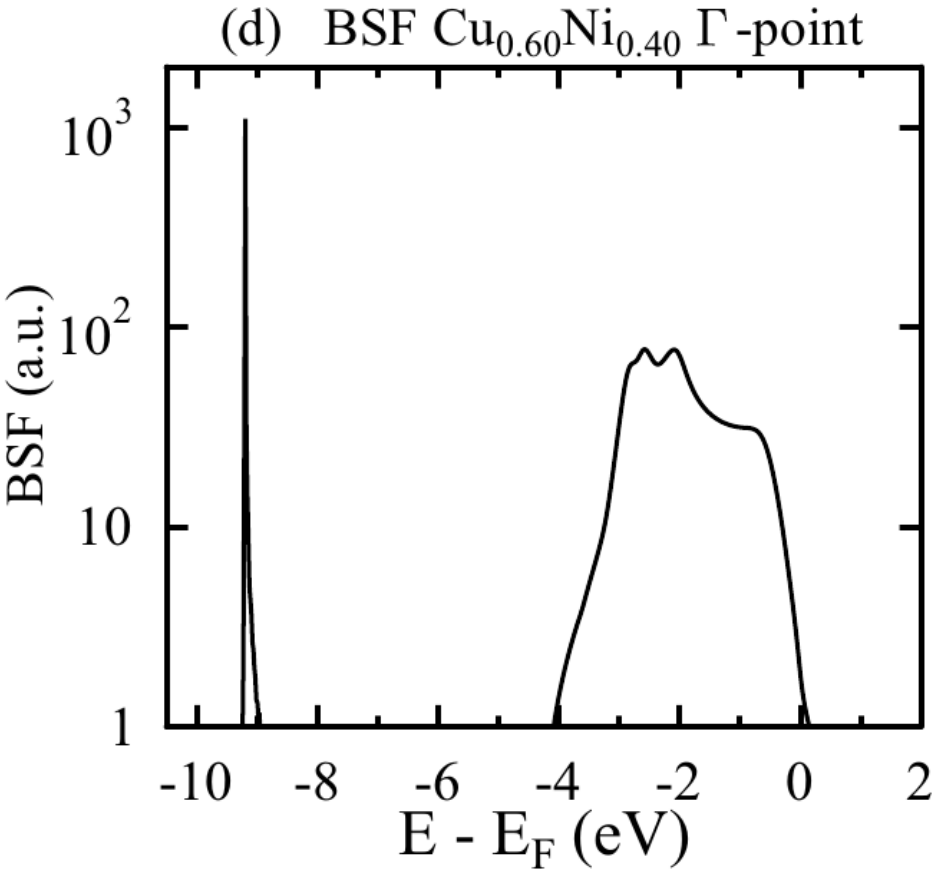
"Classical" vs resonant impurity: bands

Bands: disordered system - no Bloch states – E(k) not defined (in general)

Bloch spectral functions :

Crystal:

Dirac delta $A^B(\mathbf{k}, E) = \delta(E - E_{\nu,\mathbf{k}})$



Alloy:

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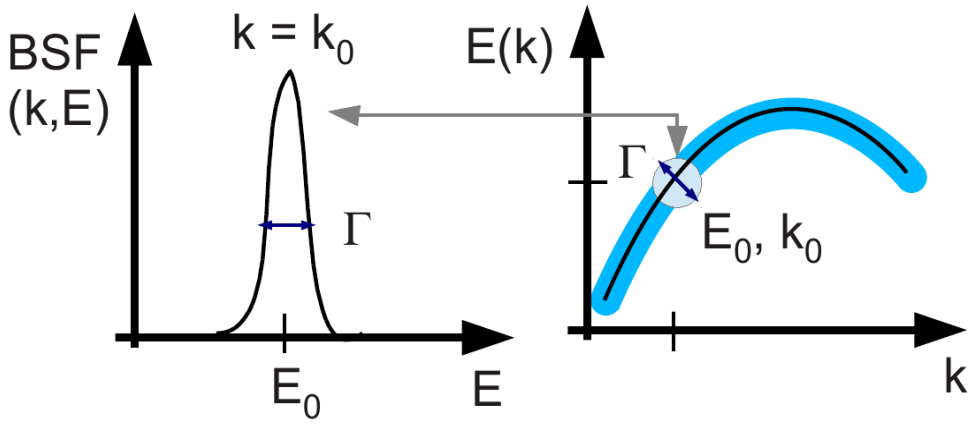


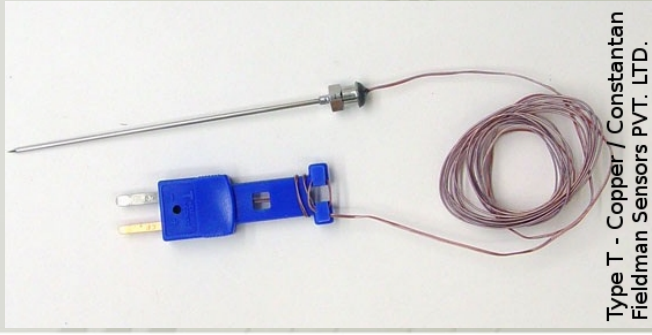
- BSF: Band center + band width
- "blurred" bands, finite life time

$\tau = \frac{\hbar}{\Gamma}$

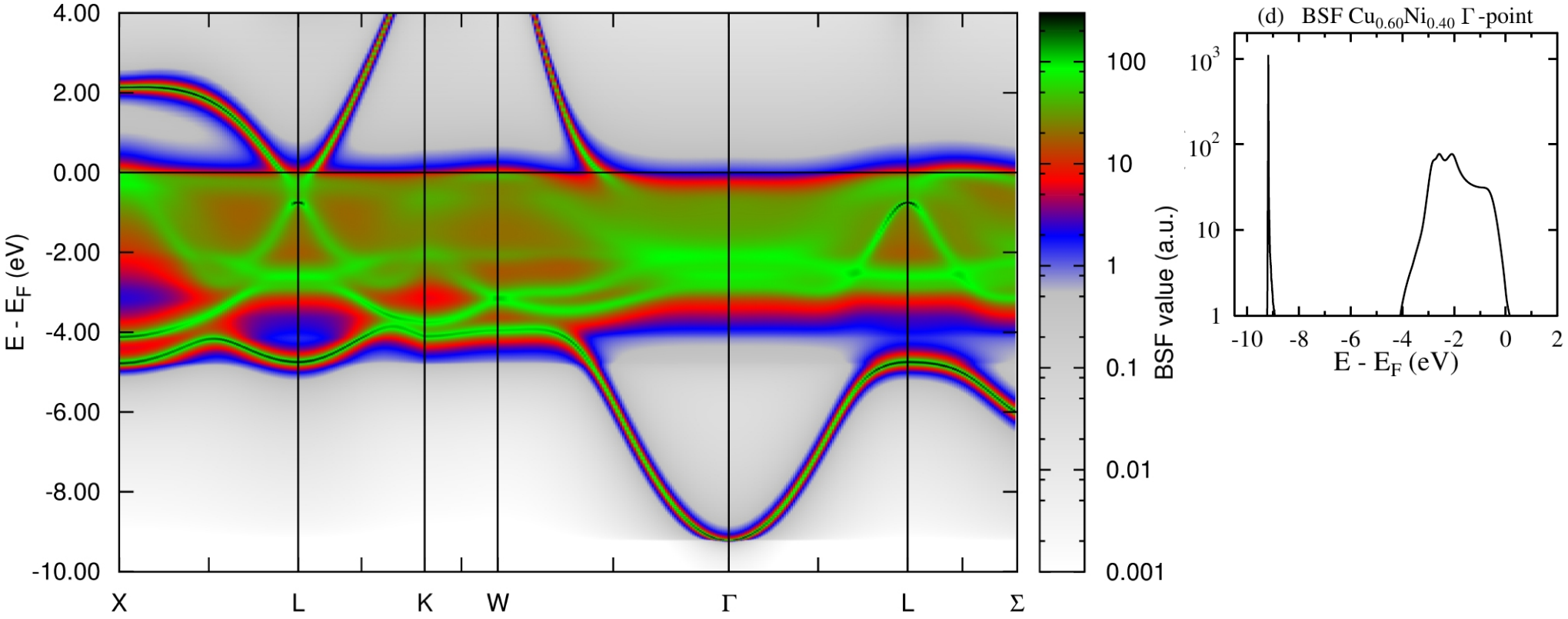
Resonant impurity: BSF very wide and non-Lorentzian (no well-defined bands)

Example of Constantan (Cu-Ni)

Cu-Ni alloy, Ni concentrations 35-50%, one of the **best TE among metallic alloys**, thermocouples



- **Ni Resonant level** from KKR-CPA



Bloch spectral function:
non-Lorentzian &
no sharp bands!

Example of Constantan (Cu-Ni)

how to deal with conductivity in such a disordered system?

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

no band center – how to calculate velocity (gradient of E(k))

In a case of a strongly scattering system (resonant levels):

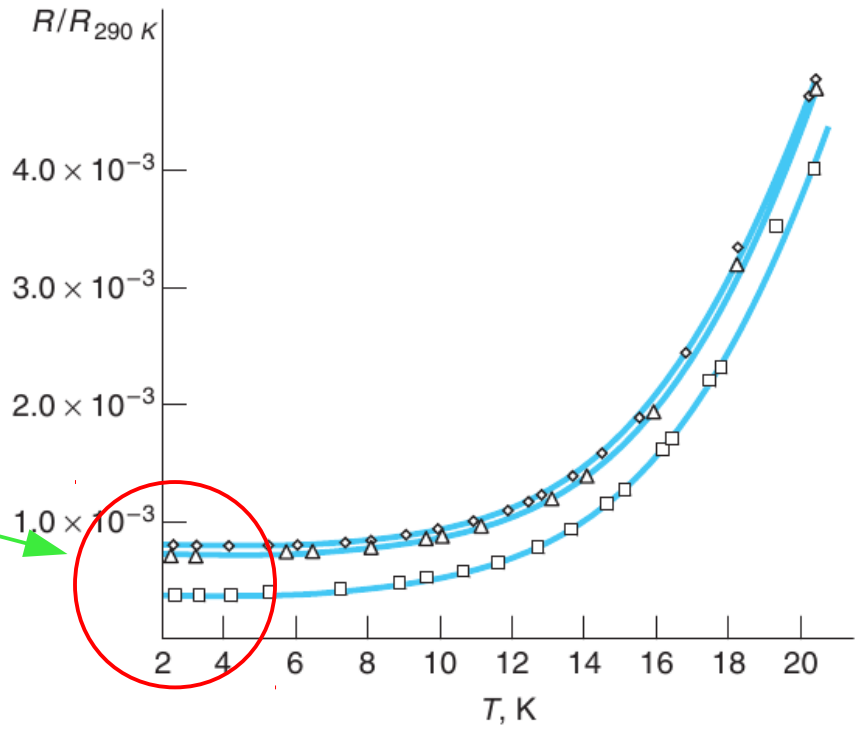
Kubo-Greenwood formalism in KKR-CPA

$$\sigma_{\mu\nu} = \frac{\hbar}{\pi N \Omega} \mathrm{Tr} \langle \hat{j}_\mu \Im G^+(E_\mathrm{F}) \hat{j}_\nu \Im G^+(E_\mathrm{F}) \rangle_c$$

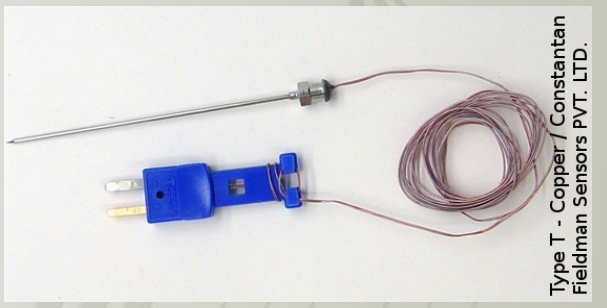
- This way you may compute σ(E) function at T = 0 K with no external parameters.
- $1/\sigma(E_F)$ is the residual resistivity
- Then we may compute the thermopower:

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

$$L^{(\alpha)} = \int dE \left(-\frac{\partial f}{\partial E} \right) (E - \mu_c)^\alpha \sigma(E)$$



Cu-Ni alloy & resonances

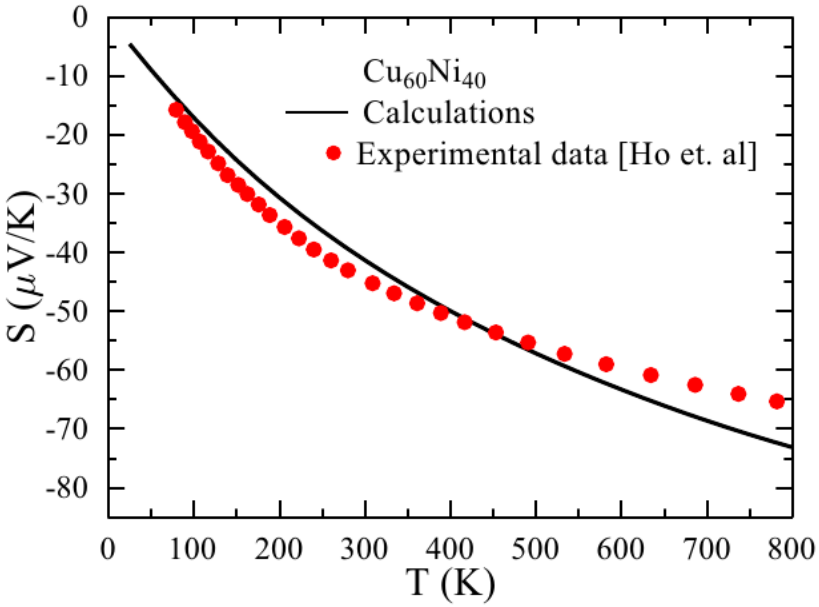


• transport properties dominated by the strong scattering on the resonance

$$\sigma(E) \propto 1/n(E) \qquad \sigma \propto \frac{ne^2\tau}{m^*}$$

• very good agreement of the computed thermopower with experiment, even though phonons are neglected ($\tau_{ph} >> \tau_e$)

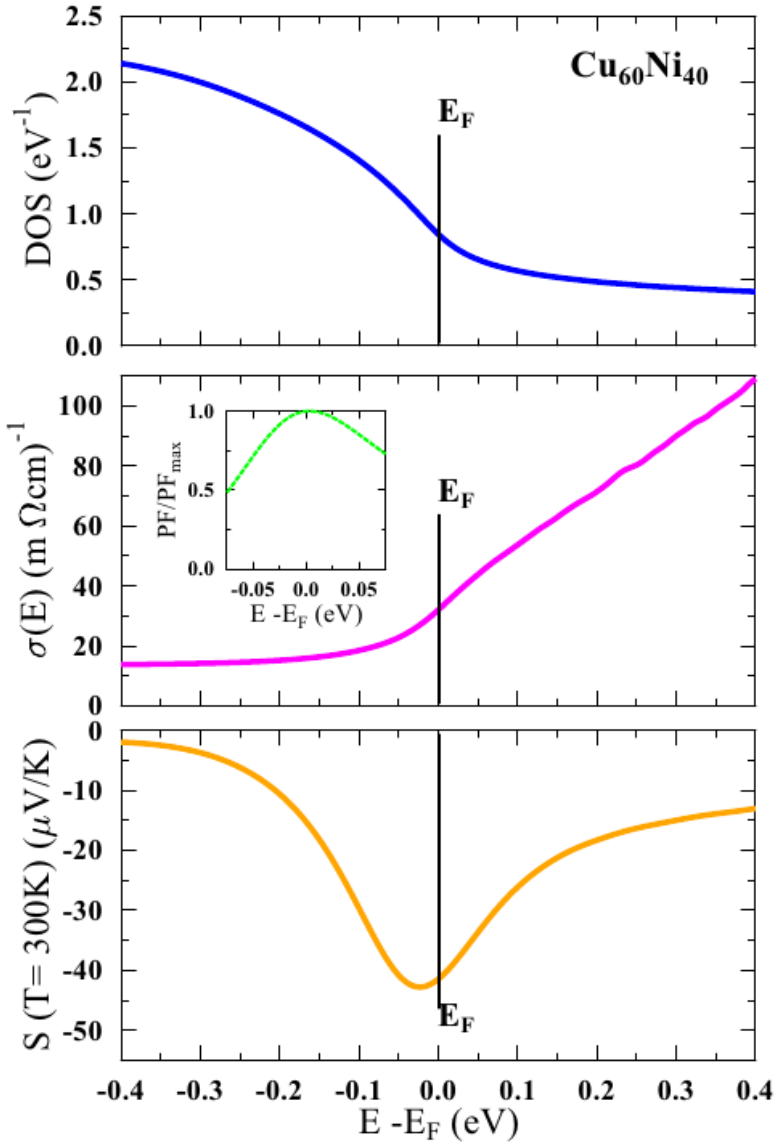
($1/\tau = 1/\tau_{ph} + 1/\tau_e = 1/\tau_e$)



300 K:

S_{calc} = -45 uV/K

S_{expt} = -42 uV/K



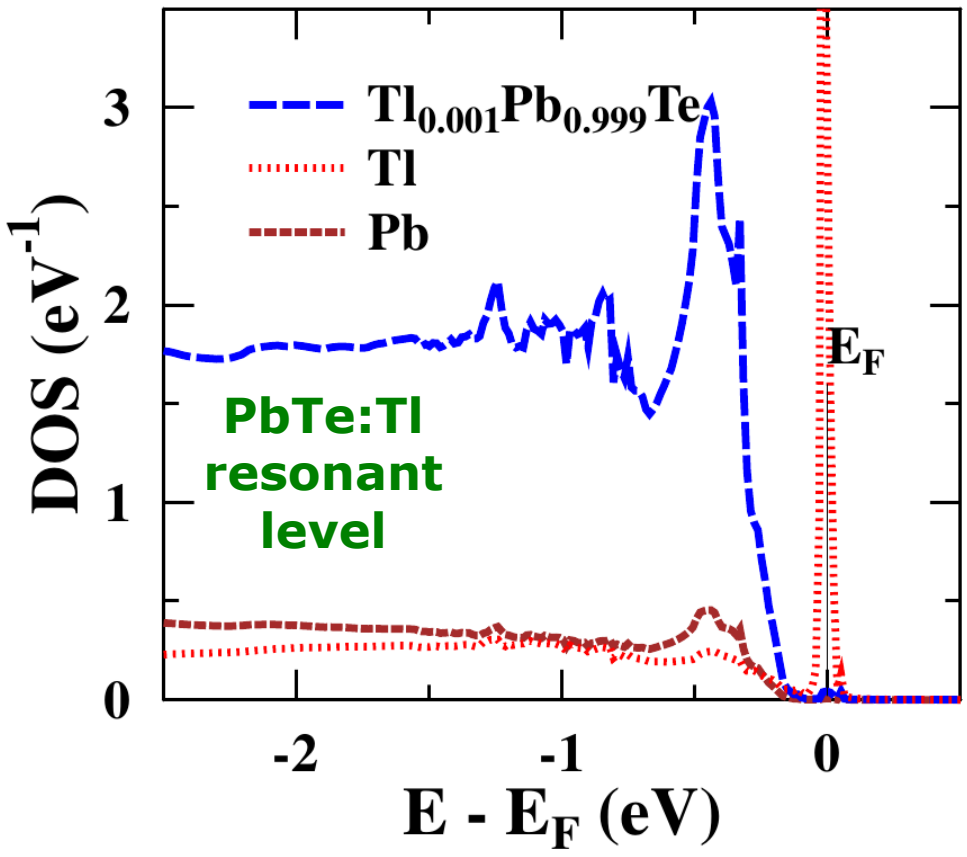
Lessons from the Cu-Ni example

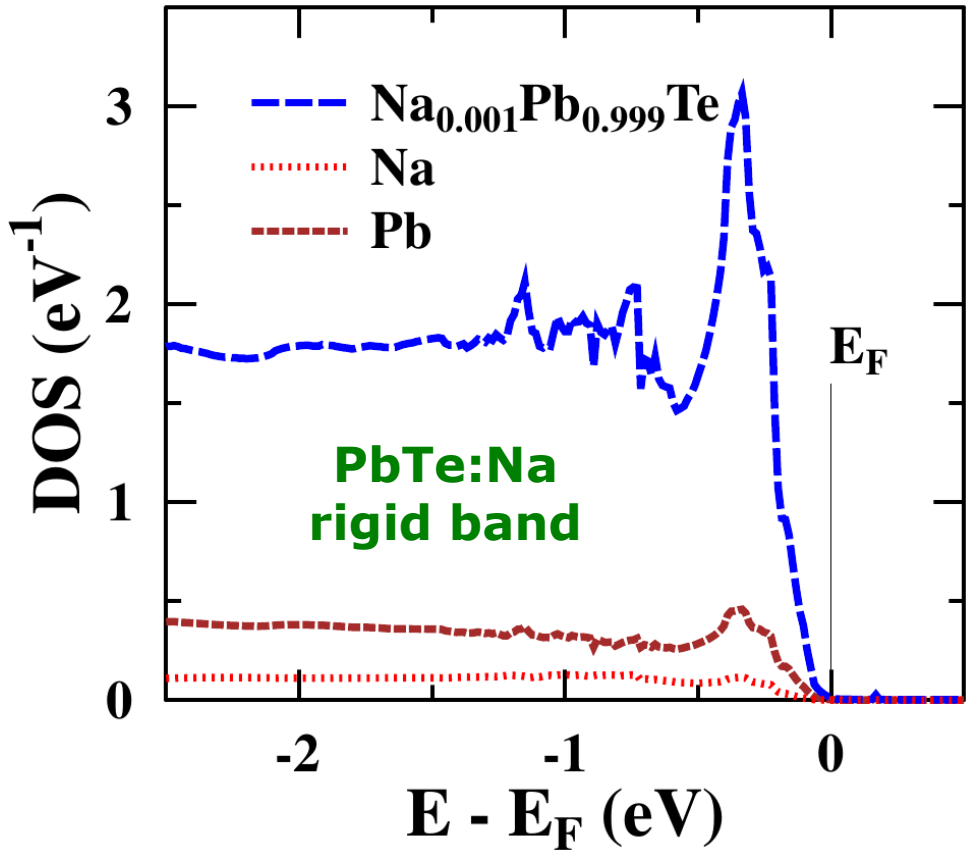
- Strongly smeared band structure due to presence of RL
- KKR-CPA + Kubo formalism works very well for metallic alloys with resonant states
- Large thermopower due to the strong dependence of the relaxation time on energy

=> But this is a concentrated alloy (30-50 % of “dopant”)

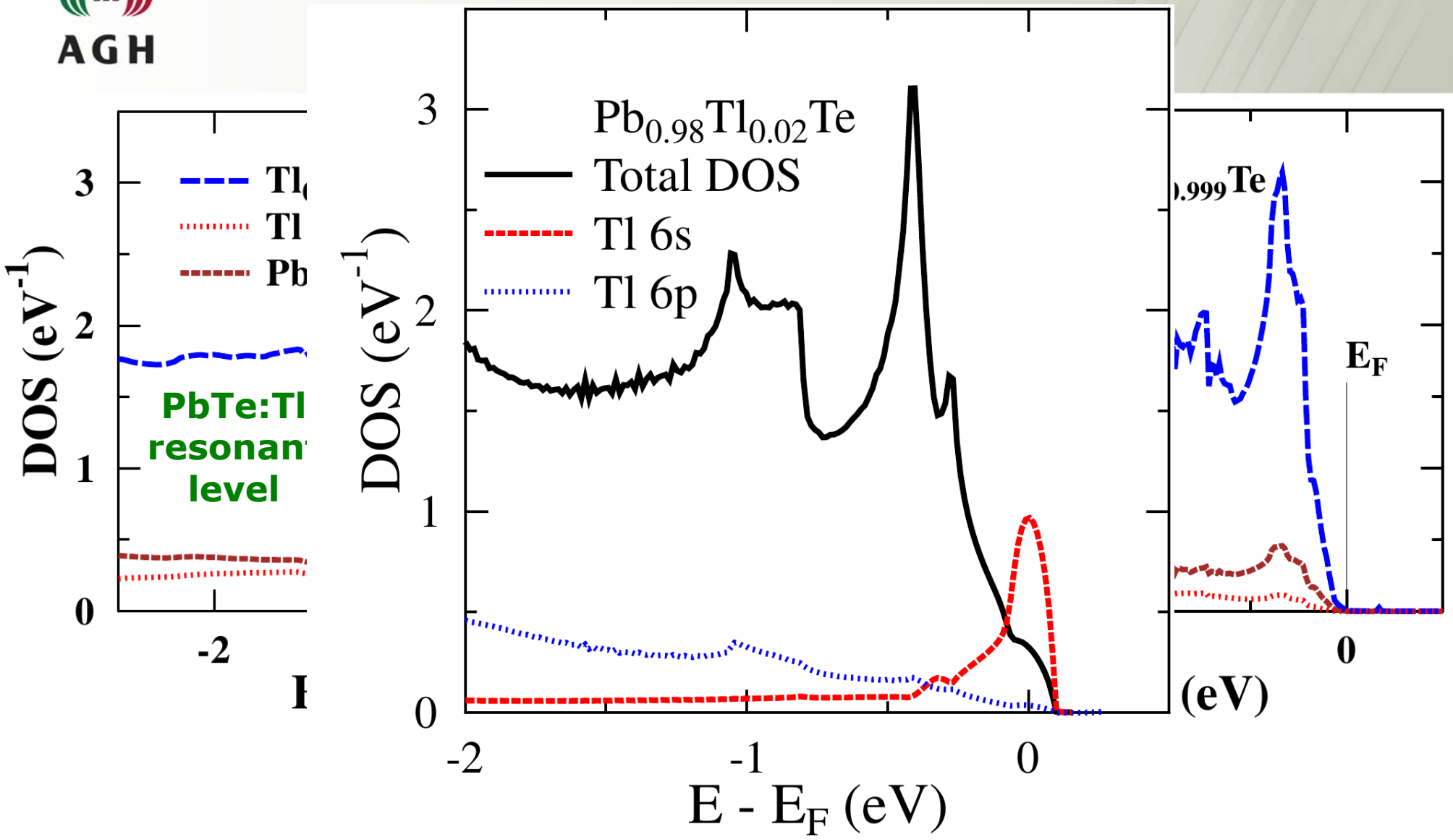
May we apply similar approach to semiconductors (with max. 1-2% of dopants?)

PbTe:Tl vs PbTe:Na – density of states



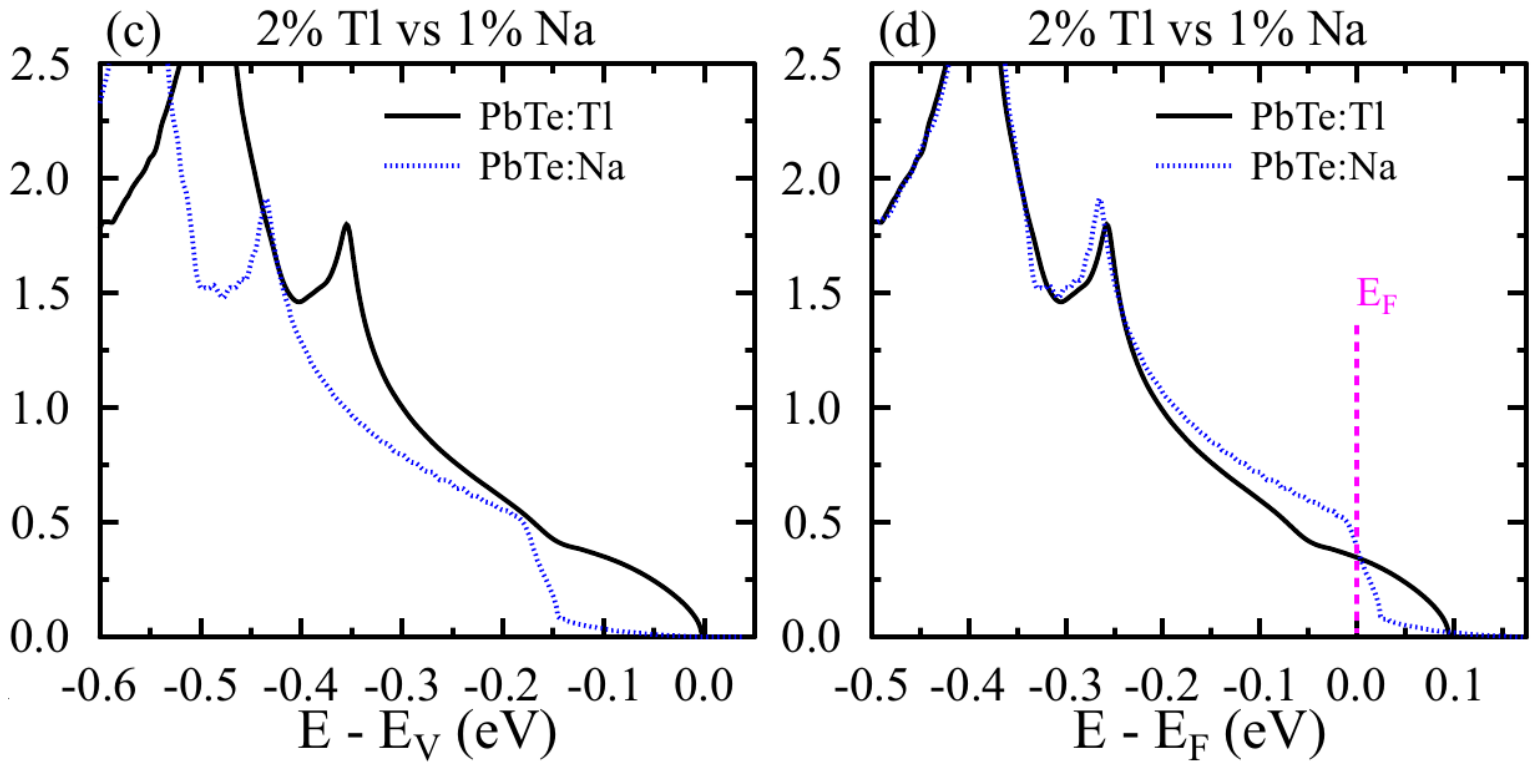


PbTe:Tl vs PbTe:Na – density of states



PbTe:Tl vs PbTe:Na – density of states

Larger dopant concentration – RL peak broadens & forms a "DOS hump"

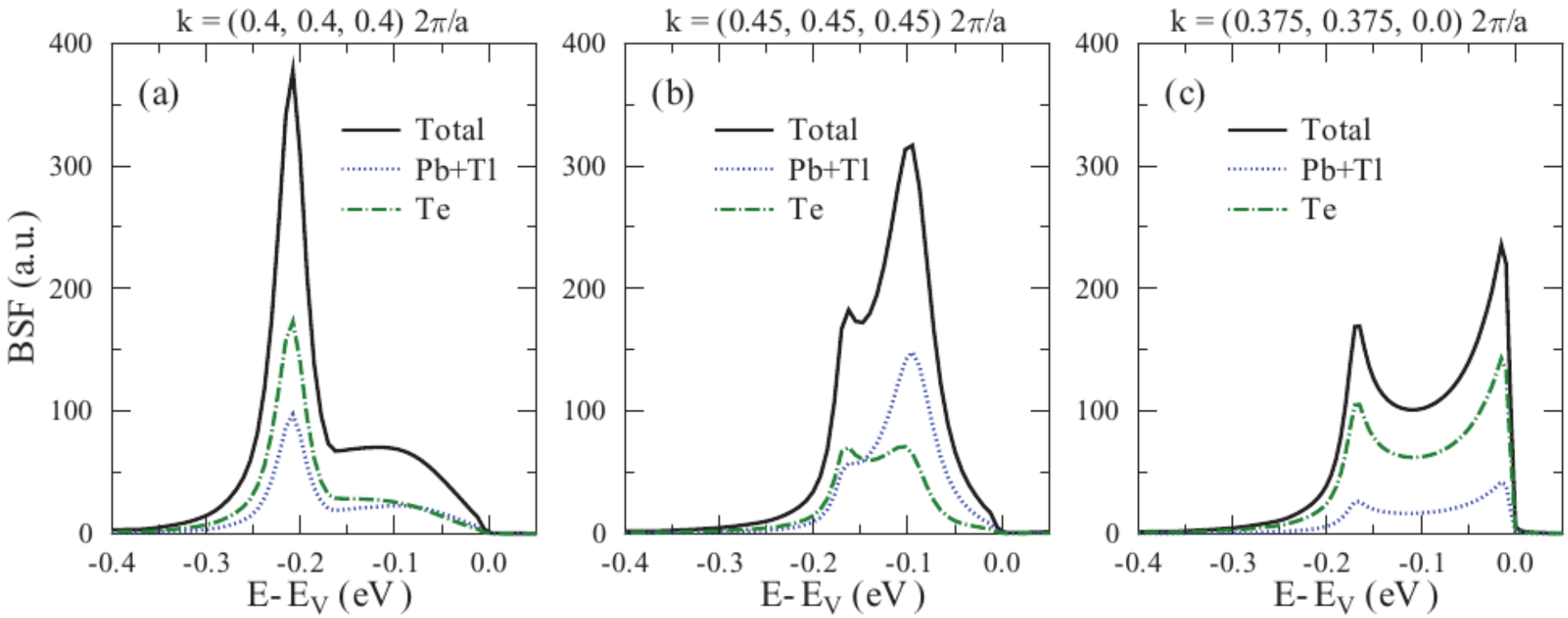


Effect of Tl = increase of DOS from redistribution of electronic states, transferred from lower-lying parts

Important: in 2% Tl-doped PbTe (most likely) carrier concentration is modified by Te vacancies, taken into account in our studies

PbTe:Tl

spectral functions

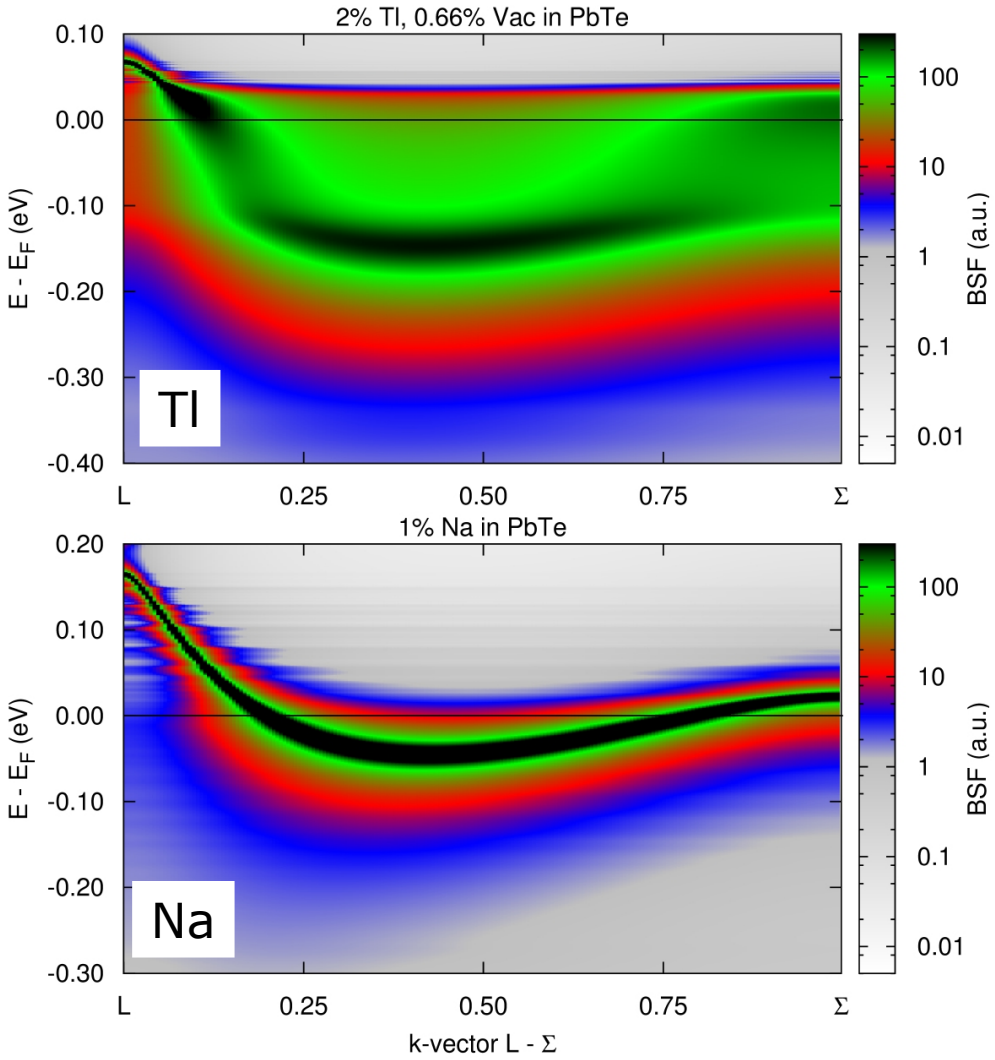


- Non-Lorentzian BSF with a shoulder
- Strong band blurring

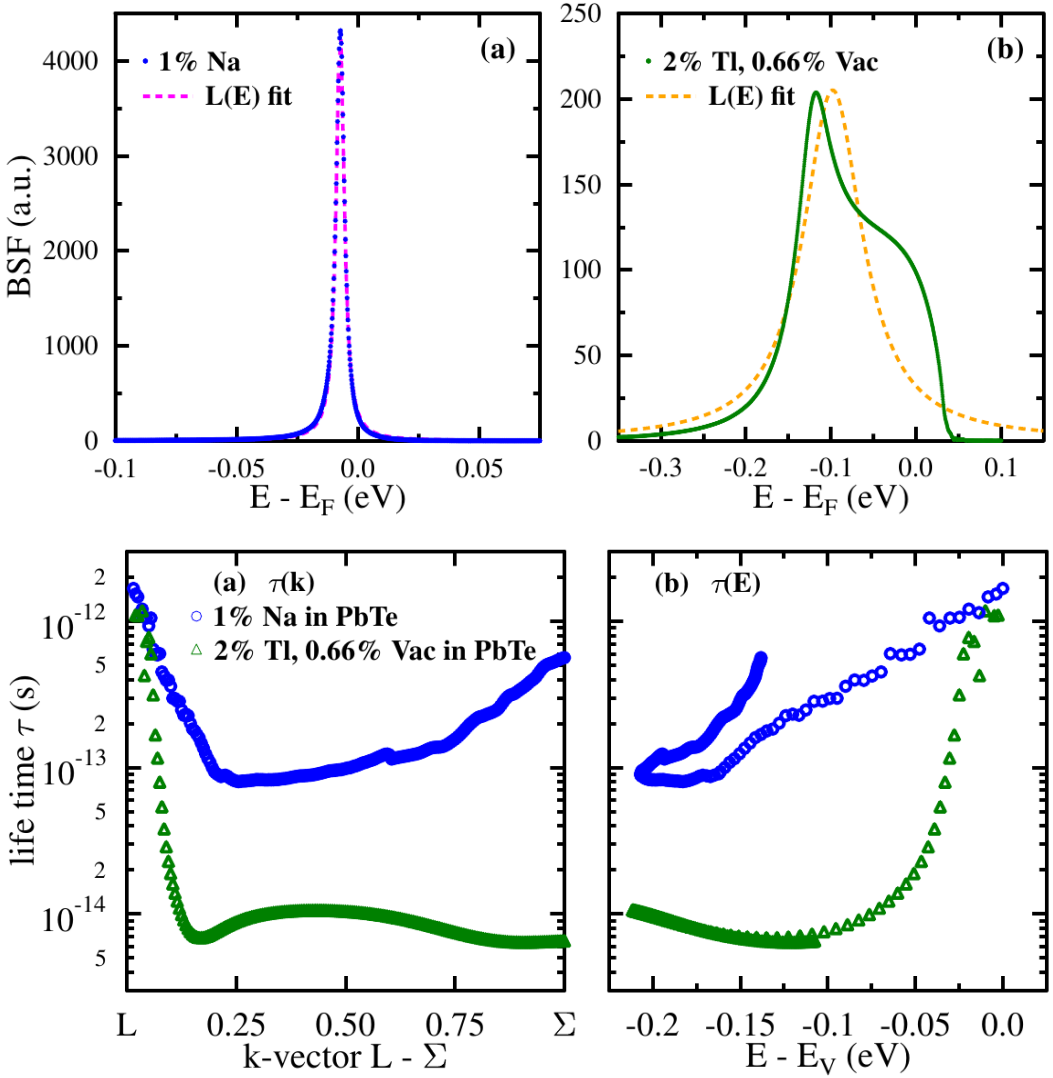
PbTe:Tl vs PbTe:Na

spectral functions & life time

$$L(E) = \frac{2}{\pi} \frac{\frac{1}{2}\Gamma}{(E - E_0)^2 + (\frac{1}{2}\Gamma)^2} \qquad \tau = \frac{\hbar}{\Gamma}$$



weak scattering from Na



strong reduction of the life time

PbTe:Tl – no impurity band

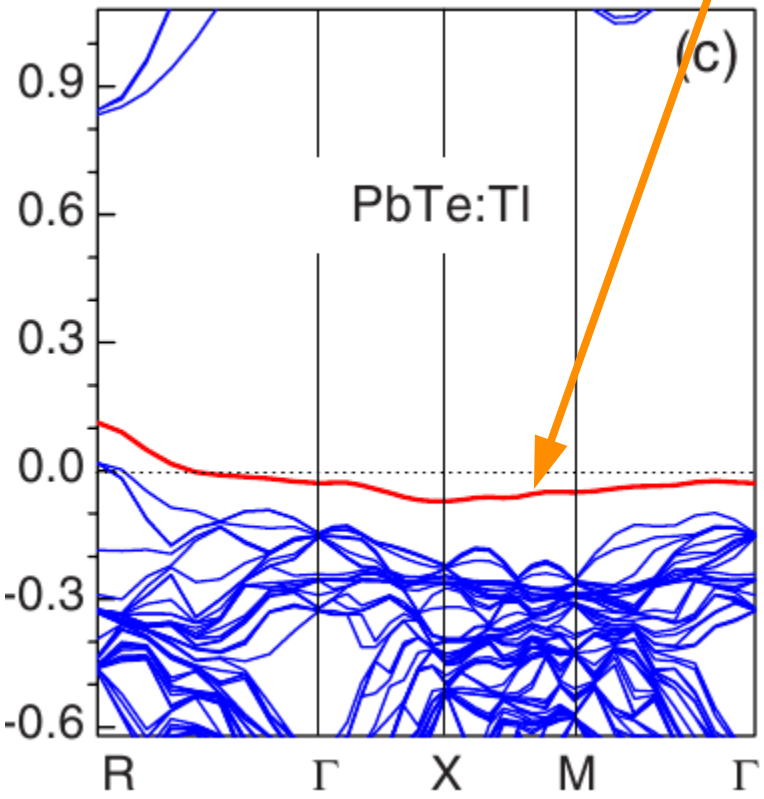
2-band system:

$$S = \frac{\sigma_1 S_1 + \sigma_2 S_2}{\sigma_1 + \sigma_2}$$

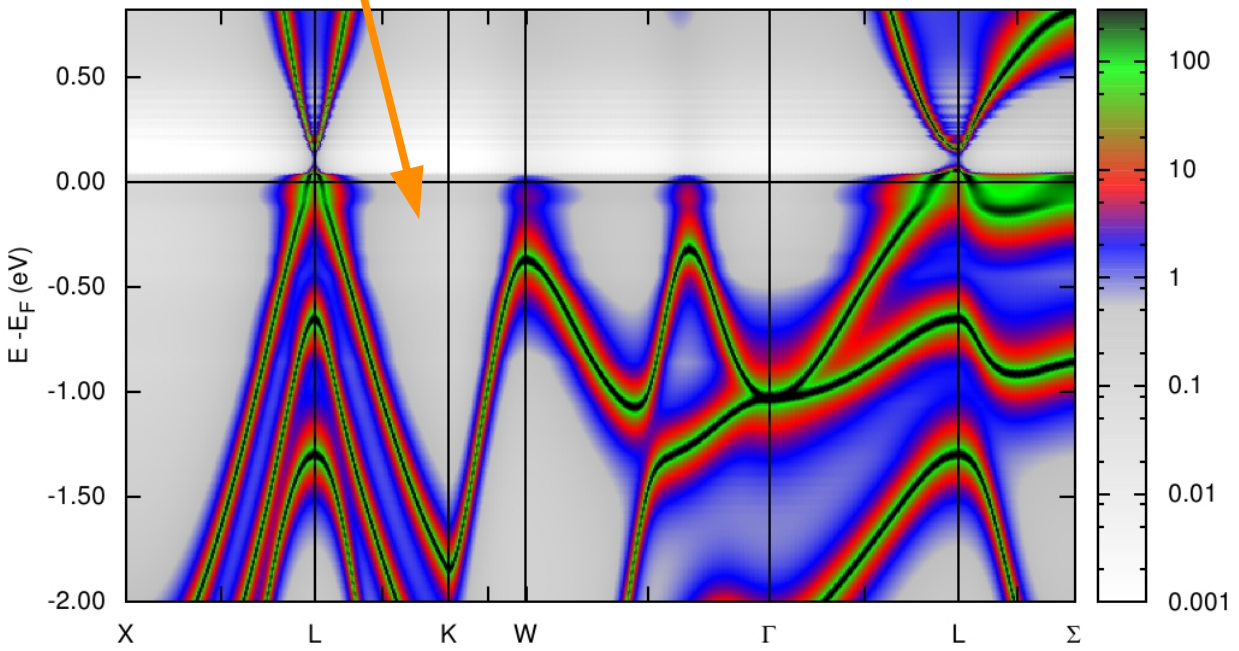
No enhancement in S if $\sigma_1 << \sigma_2$

Supercell calculations - narrow impurity band?

Hoang, Mahanti PRB 2008



no impurity band from spectral functions in KKR-CPA



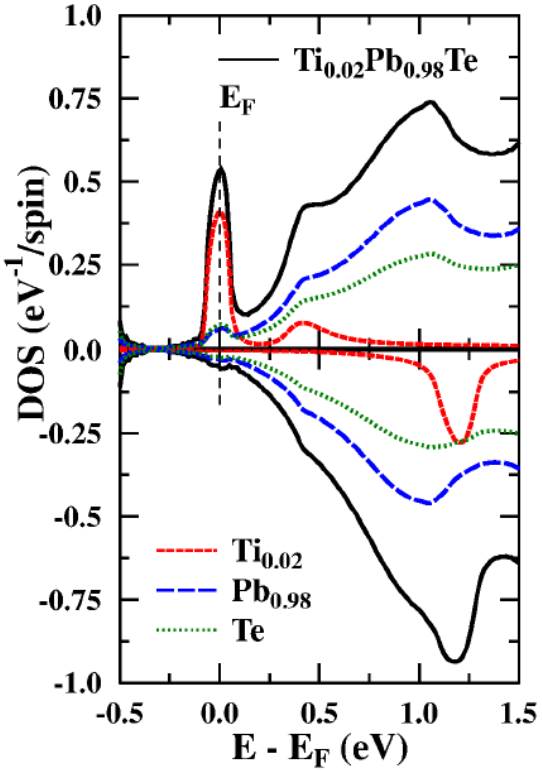
PbTe:Tl – no impurity band

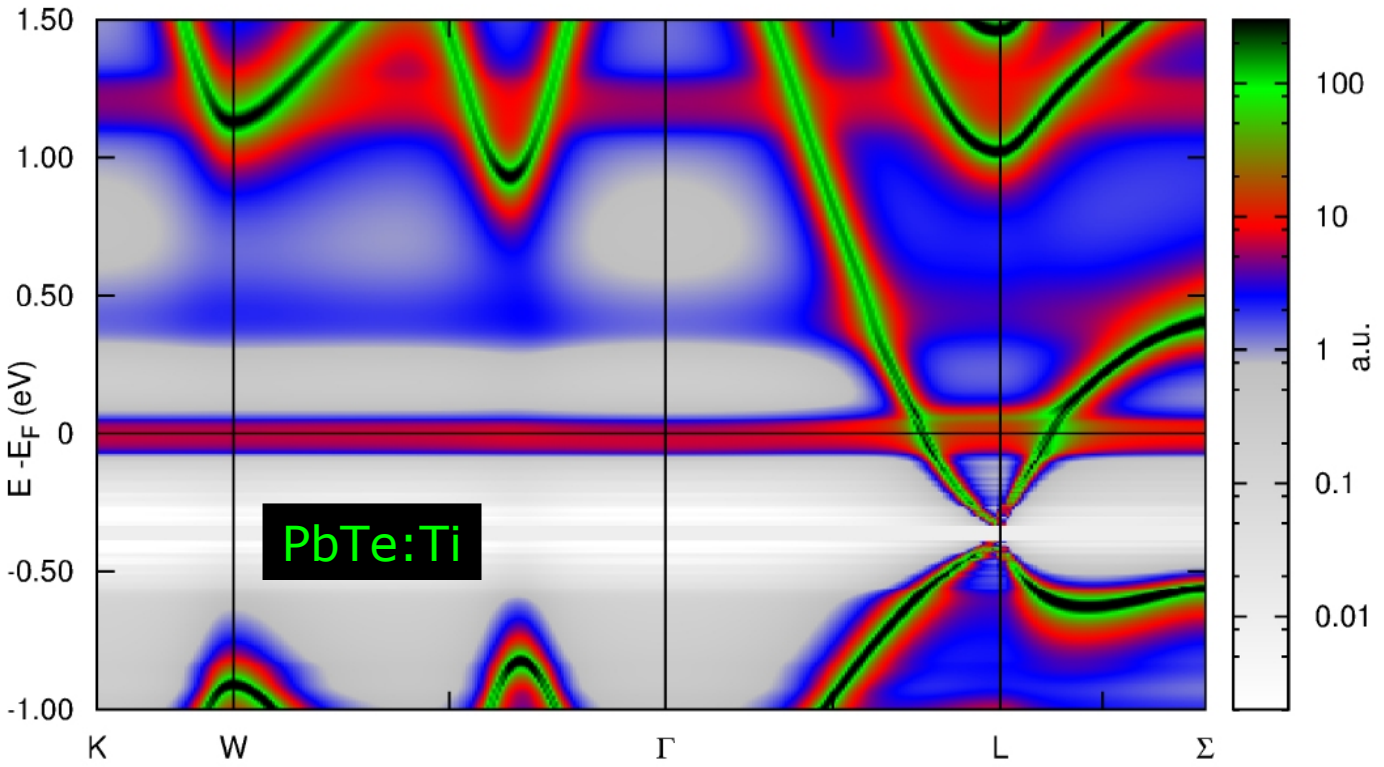
2-band system:

$$S = \frac{\sigma_1 S_1 + \sigma_2 S_2}{\sigma_1 + \sigma_2}$$

No enhancement in S if $\sigma_1 << \sigma_2$

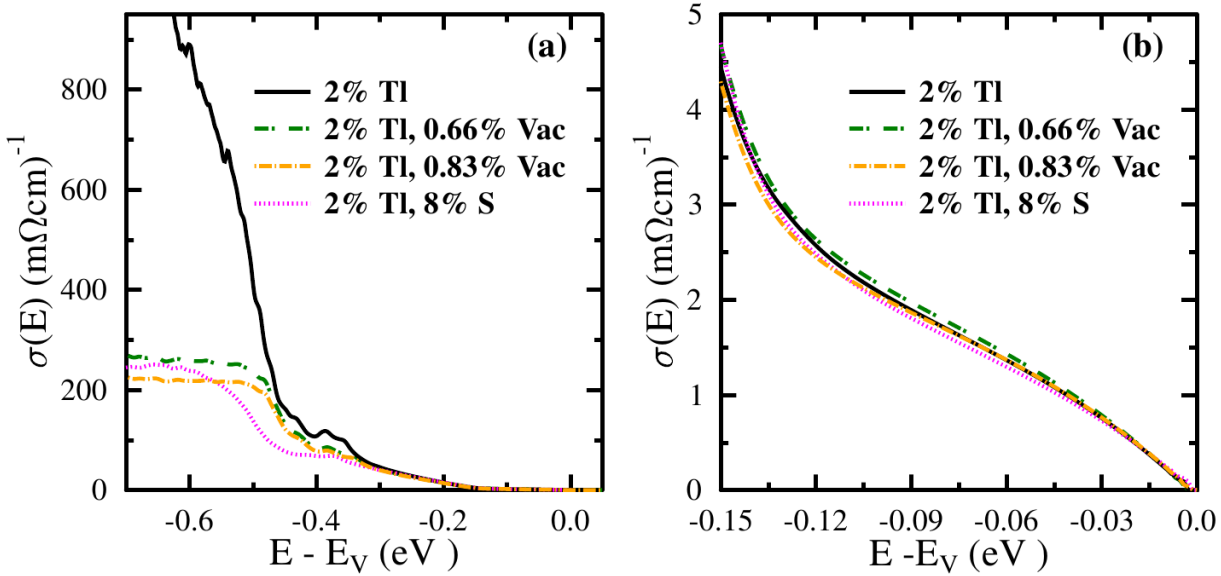
Spectral functions are able to investigate this problem: counter-example of PbTe:Titanium, where an impurity band is formed – see B. Wiendlocha, APL 2014

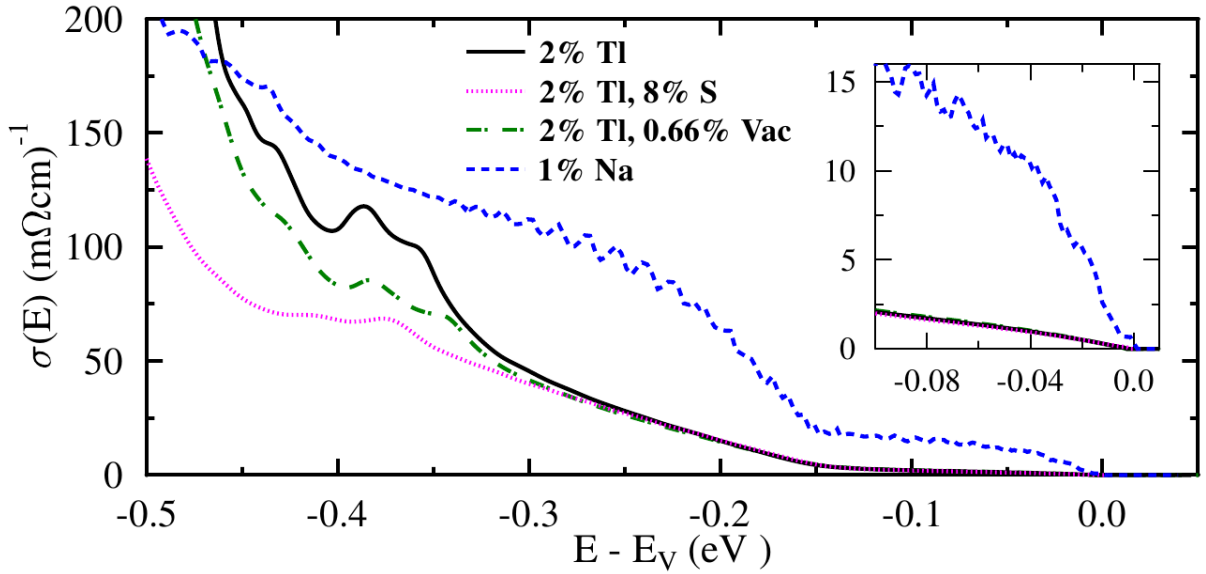




Transport function & residual resistivity PbTe:Tl vs Na

conductivity calculated at T = 0 K (Kubo formalism), takes into account scattering on impurities and RL





Calculations for PbTe with:
- 2% Tl
- 2% Tl + 0.66% Te Vac
- 2% Tl + 0.83% Te Vac
- 2% Tl + 8% S on Te
- 1% Na

Effect of Vac or S/Te seen in lower E
near VB edge RL dominates

Na-doped: much higher conductivity due to the longer life time τ
RL reduces σ

Transport function & residual resistivity PbTe:Tl vs Na

residual resistivity: comparison with experiment

independent proof of resonant level

x Tl (%)	y Vac (%)	p (cm^{-3})	ρ_0^{calc} (mΩcm)	ρ_0^{expt} (mΩcm)
2.0	0.00	$3.0 \cdot 10^{20}$	0.49	—
2.0	0.66	$1.0 \cdot 10^{20}$	0.85	~ 1 [11]
2.0	0.83	$5.0 \cdot 10^{19}$	1.37	—
1.6	0.49	$9.1 \cdot 10^{19}$	0.89	0.70 ± 0.10 [64]
1.4	0.35	$1.0 \cdot 10^{20}$	0.80	0.90 ± 0.10 [12, 71]
1.3	0.31	$1.0 \cdot 10^{20}$	0.81	0.80 ± 0.15 [71]
1.1	0.24	$9.2 \cdot 10^{19}$	0.83	$0.77 - 0.95$ [34, 71]
x Tl	y S			
2.0	8.0	$3.0 \cdot 10^{20}$	0.54	—
x Na	—			
1.0	—	$1.5 \cdot 10^{20}$	0.025	0.034 [72]

➔ relatively good agreement

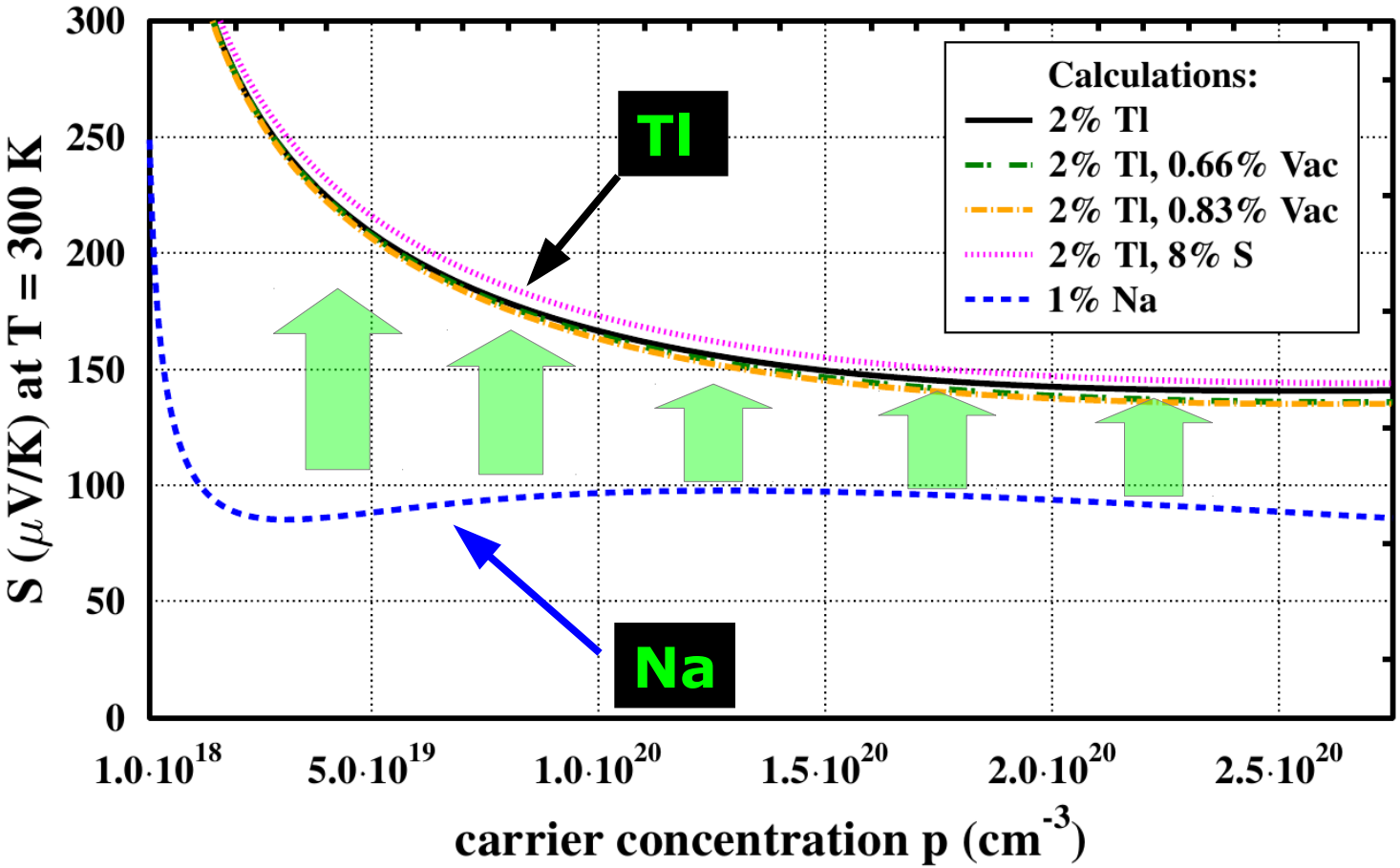
➔ independent proof for the existence of resonant state =

30x difference in ρ between Na and Tl doping

➔ support for the self-compensation model (ρ would be too small)

Thermopower calculations & comparison with experiment – PbTe:Tl vs Na

➔ **Confirmation** of the relative increase of *S* between Tl and Na doping

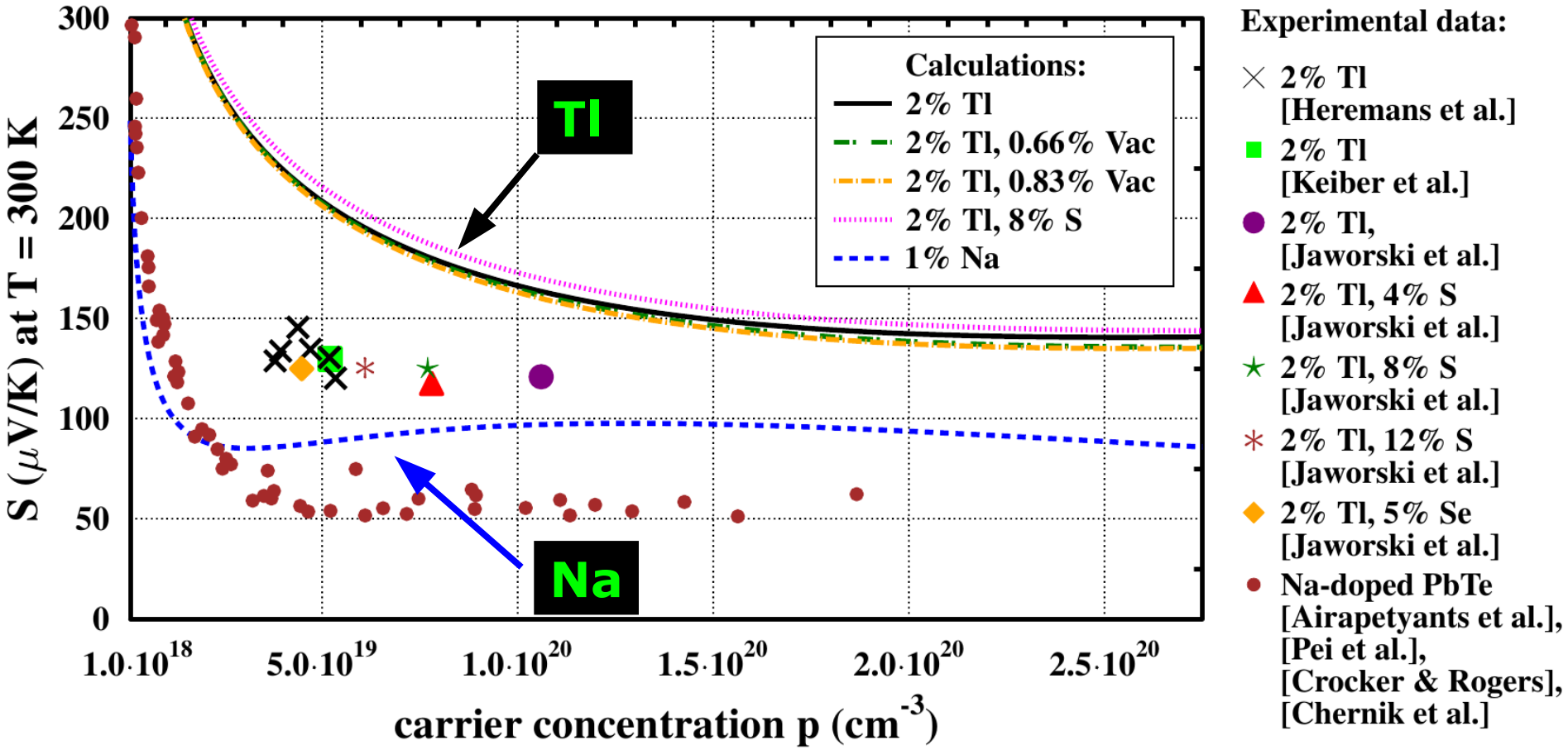


$$S = -\frac{1}{eT}\frac{L^{(1)}}{L^{(0)}}$$

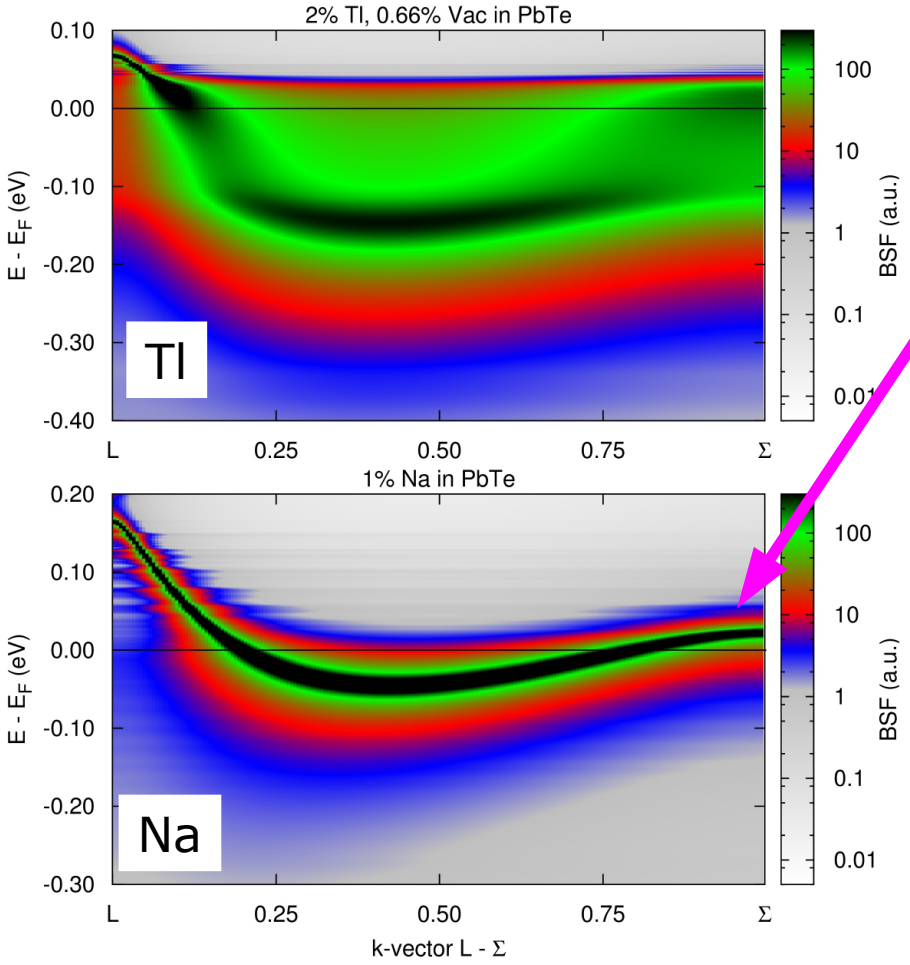
$$L^{(\alpha)} = \int dE \left(-\frac{\partial f}{\partial E}\right)(E-\mu_c)^{\alpha}\sigma(E)$$

Thermopower calculations & comparison with experiment – PbTe:Tl vs Na

➔ **Systematic overestimation** of *S* comparing to experiment



Source of the overestimation?



Possible source of overestimation:

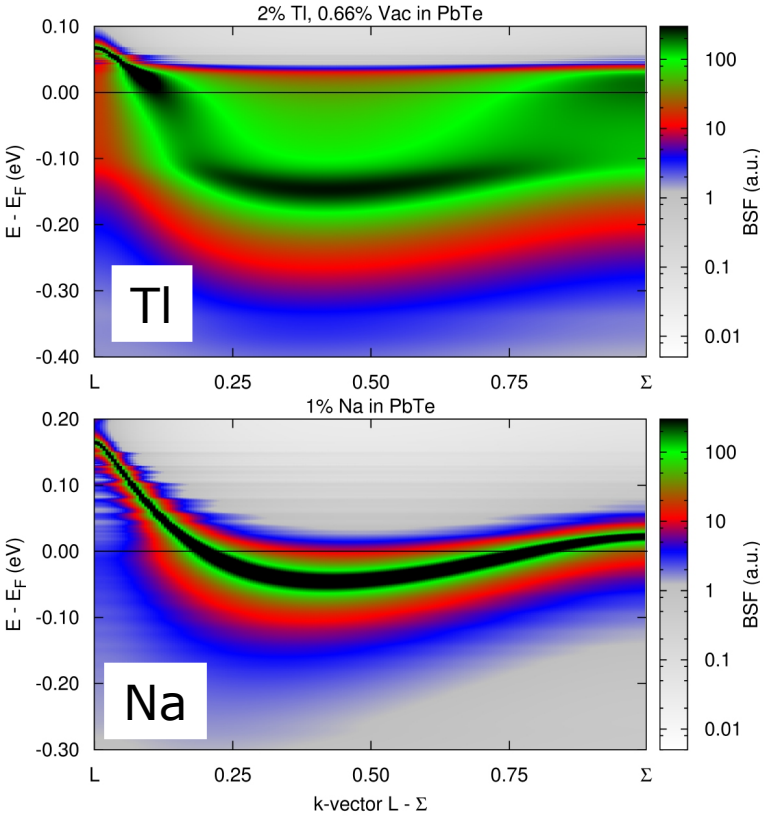
-> LDA exchange-correlation problem (Σ-band too high)

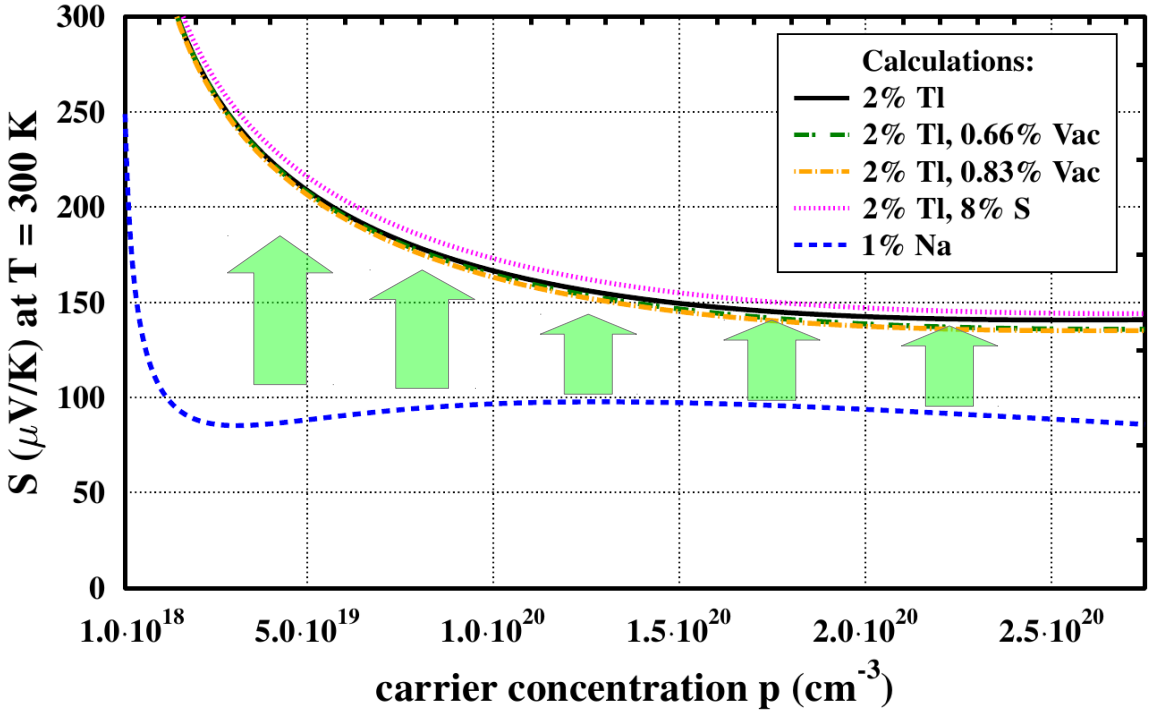
-> Neglect of the electron-phonon scattering

for more see: B. Wiendlocha, Phys Rev B 2018

Source of the overestimation?

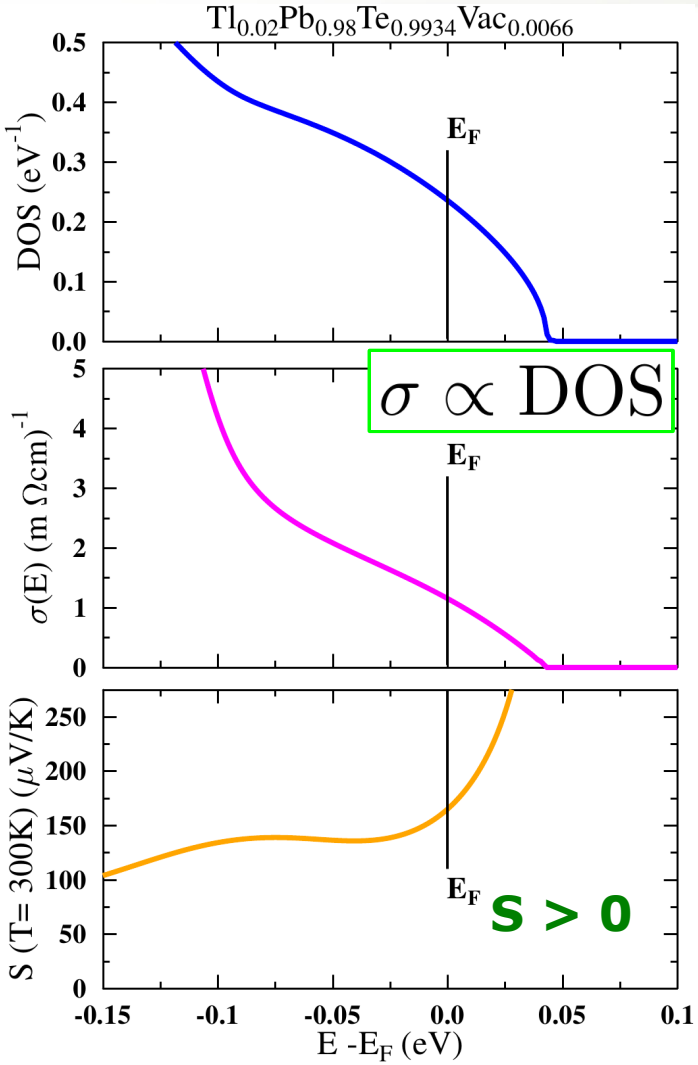
However, this is a systematic error, present in both cases, so it does not affect the conclusion on a relative increase of the thermopower due to resonant state





Comparison PbTe:Tl vs Cu-Ni

$$\sigma \propto \frac{ne^2\tau}{m^*}$$



PbTe:Tl

- σ controlled by *n*
- scattering on RL

(s states) not that strong

- Phonons more important,

$\tau_{ph} \sim \tau_{res}$

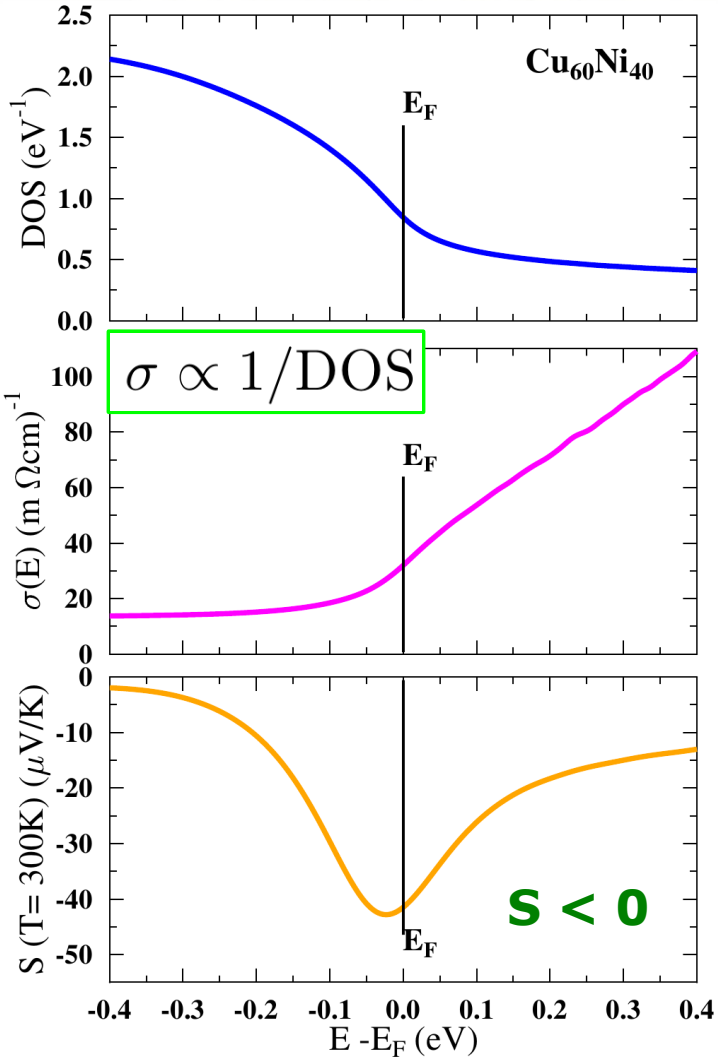
Cu-Ni

- σ controlled by τ
- scattering on RL

(d states) very strong

- Phonons not important,

$\tau_{ph} > \tau_{res}$



semiconductor: less-intuitive RL

metal: more-intuitive RL

#1 summary: PbTe:Tl

Resonant level may increase thermopower of semiconductors

- "Delocalized" resonant level does not form an impurity band (in PbTe:Tl) (important counter-example of PbTe:Titanium, where an impurity band is formed – see B. Wiendlocha, APL 2014)
- Transfer of electronic states towards the valence band edge – increase in the number of carriers – thermopower enhancement
- Comparison of PbTe:Tl with PbTe:Na - enhancement of *S* confirmed quantitatively, in spite of the stronger scattering on RL
- independent evidence of RL – analysis of the residual resistivity

#1 References

PHYSICAL REVIEW B **97**, 205203 (2018)

Thermopower of thermoelectric materials with resonant levels: PbTe:Tl versus PbTe:Na and $Cu_{1-x}Ni_x$

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Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Aleja Mickiewicza 30, 30-059 Krakow, Poland

(Received 16 February 2018; published 9 May 2018)

PHYSICAL REVIEW B **88**, 205205 (2013)

Fermi surface and electron dispersion of PbTe doped with resonant Tl impurity from KKR-CPA calculations

Bartlomiej Wiendlocha*
Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland
(Received 14 July 2013; revised manuscript received 24 September 2013; published 13 November 2013)

APPLIED PHYSICS LETTERS **105**, 133901 (2014)

Localization and magnetism of the resonant impurity states in Ti doped PbTe

Bartlomiej Wiendlocha[a)]
Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, Krakow 30-059, Poland and Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio 43210, USA

#2: RL as a novel doping mechanism – Bismuth + In, Ga, Sn

Different aspect of RL – novel doping mechanism (?) in Bi:In

Energy & Environmental Science

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Cite this: *Energy Environ. Sci.*, 2015, **8**, 2027

P-type doping of elemental bismuth with indium, gallium and tin: a novel doping mechanism in solids†

Hyungyu Jin,*[a] Bartlomiej Wiendlocha*[ab] and Joseph P. Heremans*[acd]

Hyungyu Jin[1], Bartlomiej Wiendlocha[1,3], Joseph P. Heremans[1,2]

1. Department of Mechanical Engineering
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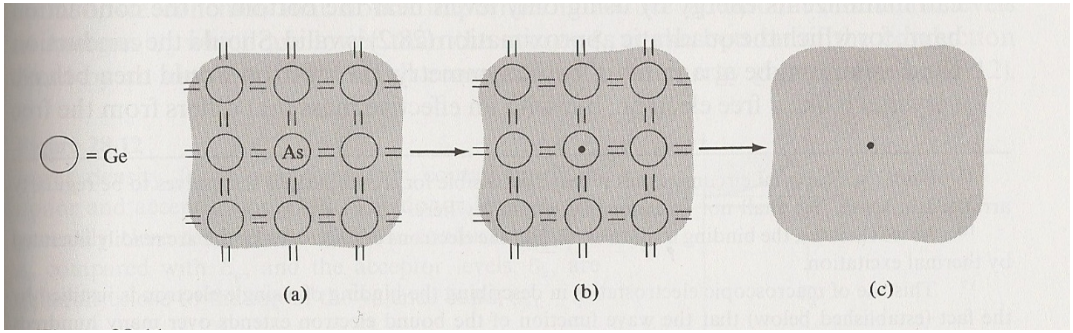
3. AGH University of Science and Technology, Krakow, Poland

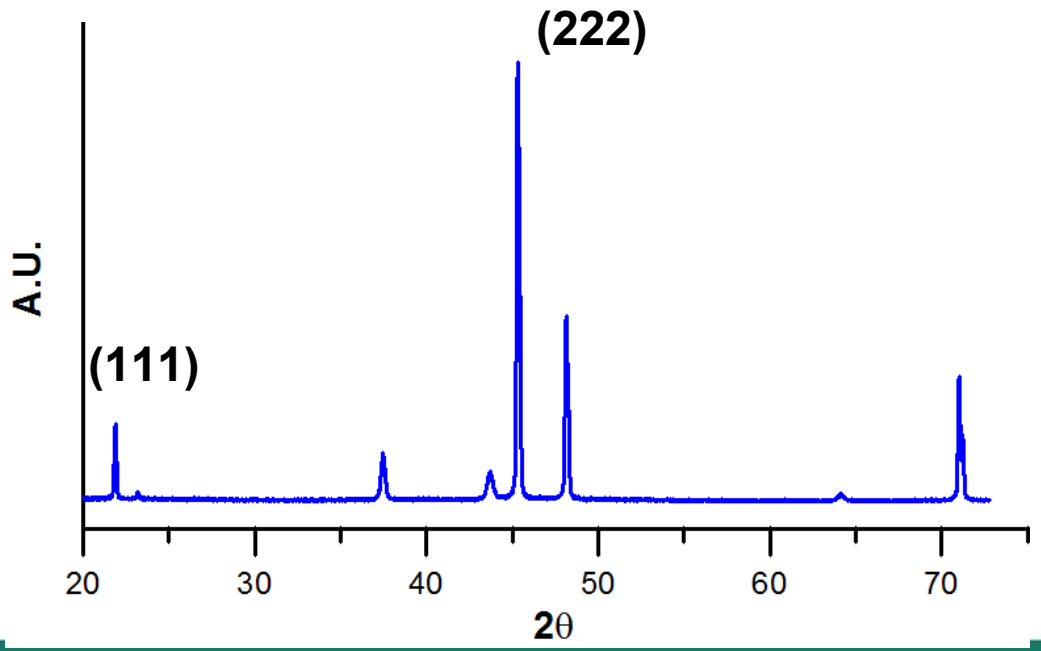


Ashcroft & Mermin, "Solid State Physics"

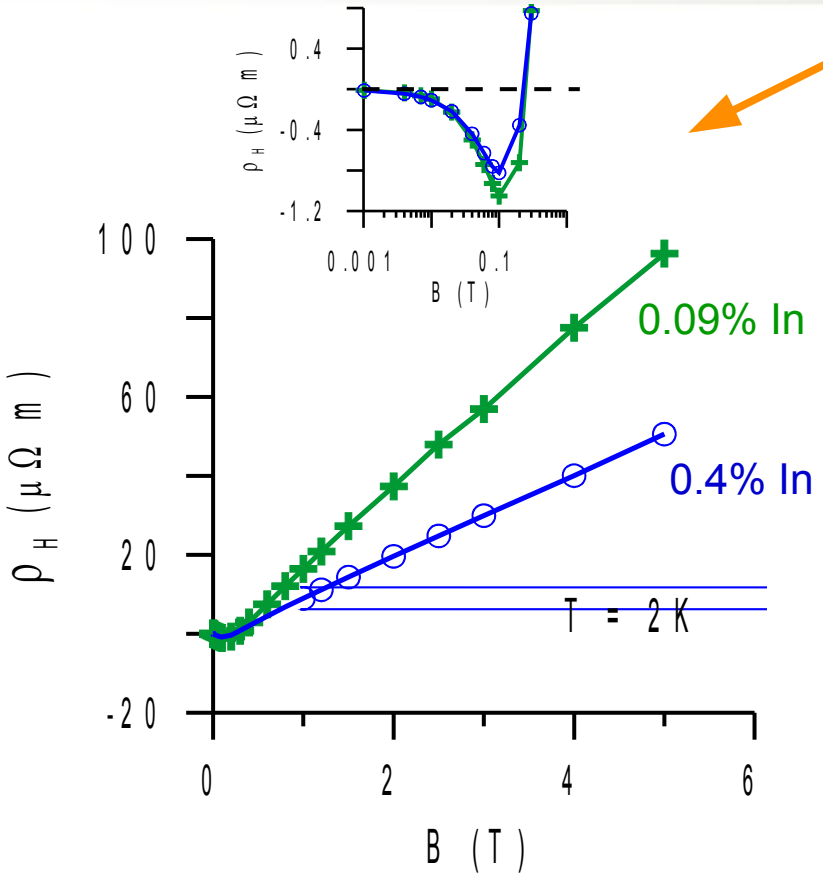
Single crystals of Bi:In - sample preparation

Bi as a starting point to optimize Bi-Sb alloy (best TE for cryogenic applications): Bi1-xSbx (zT ~ 0.5 @ T < 200K)

- Pure Bi (5N), and 0.09%, 0.4% indium doped single crystalline Bi
  - Grown by modified horizontal Bridgman method
- Samples were cleaved along trigonal plane
- XRD measurements to detect single crystal peaks

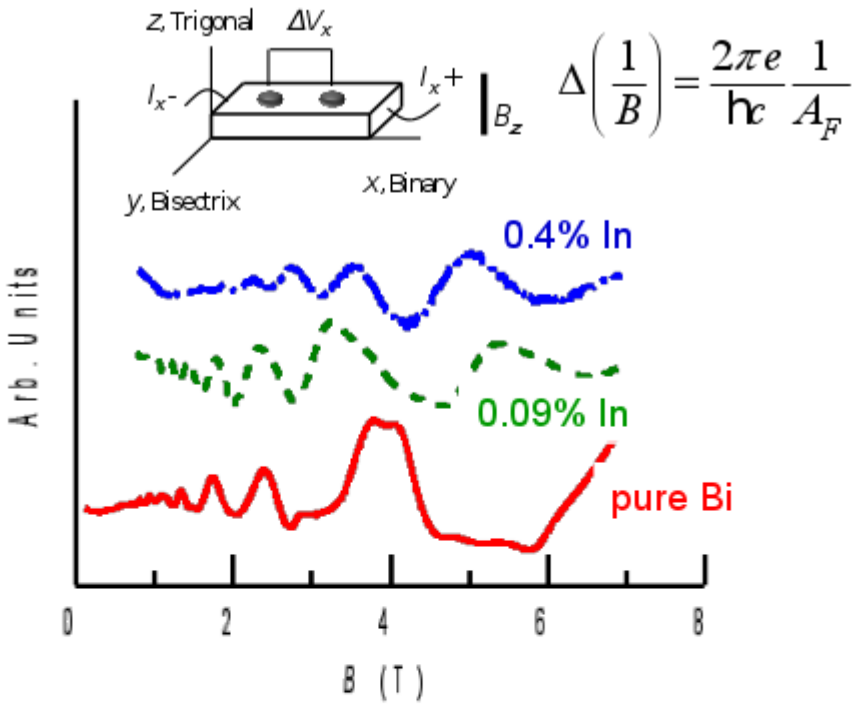


Indium is an acceptor in bismuth



Hall

SdH



Sample	N (10^{17}cm-3)	P - N (10^{17}cm-3)	P (10^{17}cm-3)
0.09% In	0.74	3.2	3.94
0.4% In	0.58	6.5	7.08

Sample	$[\Delta(1/B)]^{-1}$ (T)	AF (10^{16}m-2)	EF (meV)	P (10^{17}cm-3)
pure Bi	6.352	6.06	11.5	2.93
0.09% In	7.665	7.31	13.9	3.88
0.4% In	12.09	11.5	21.9	7.69

Assuming rigid band model

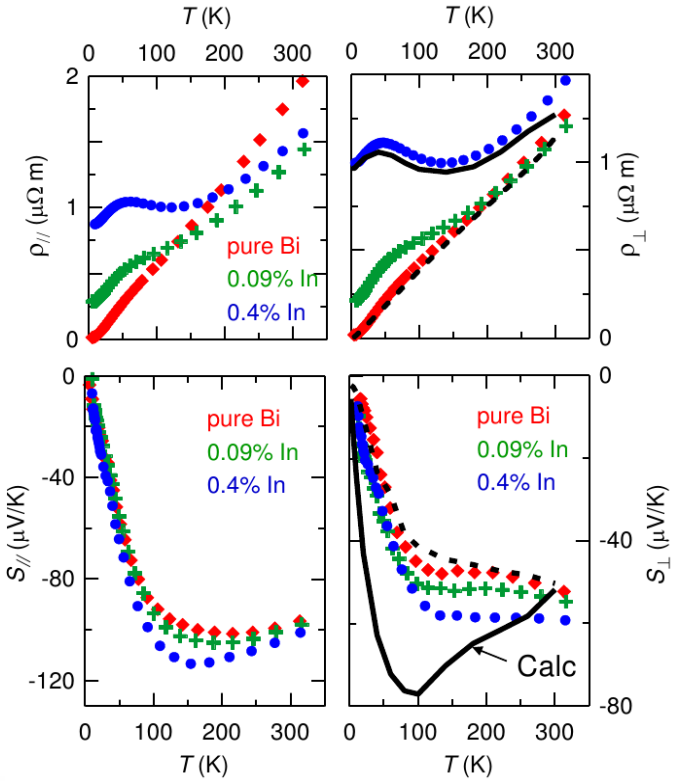
How come indium is an acceptor in bismuth?

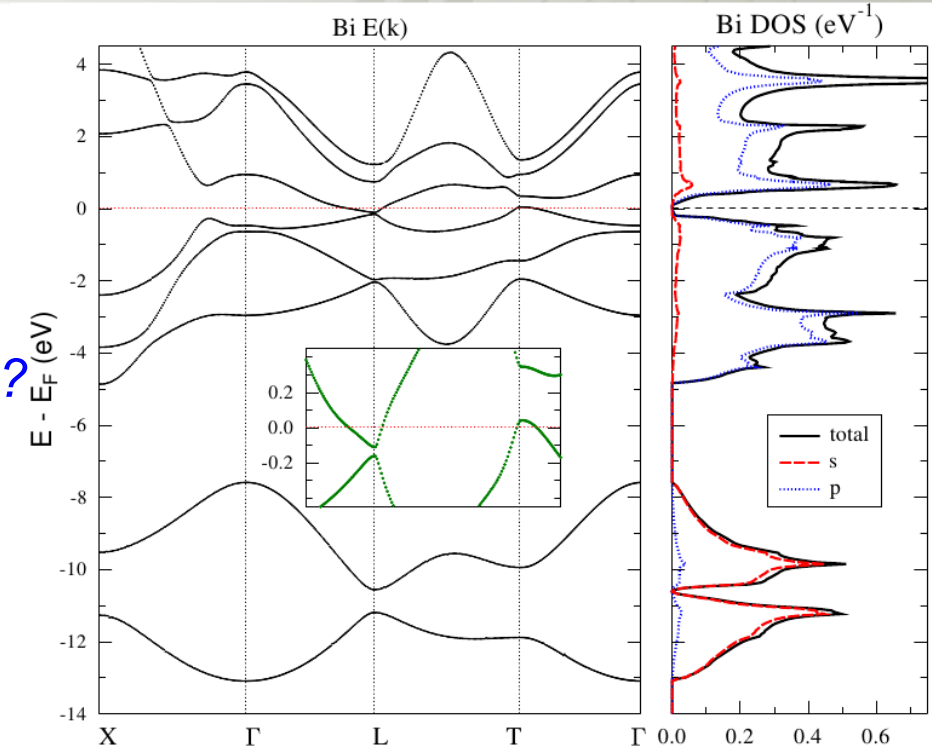
Indium and bismuth are both trivalent:

In: [Kr] 4d10 5s2 5p1

Bi: [Xe] 4f14 5d10 6s2 6p3

How can indium become an acceptor in bismuth?

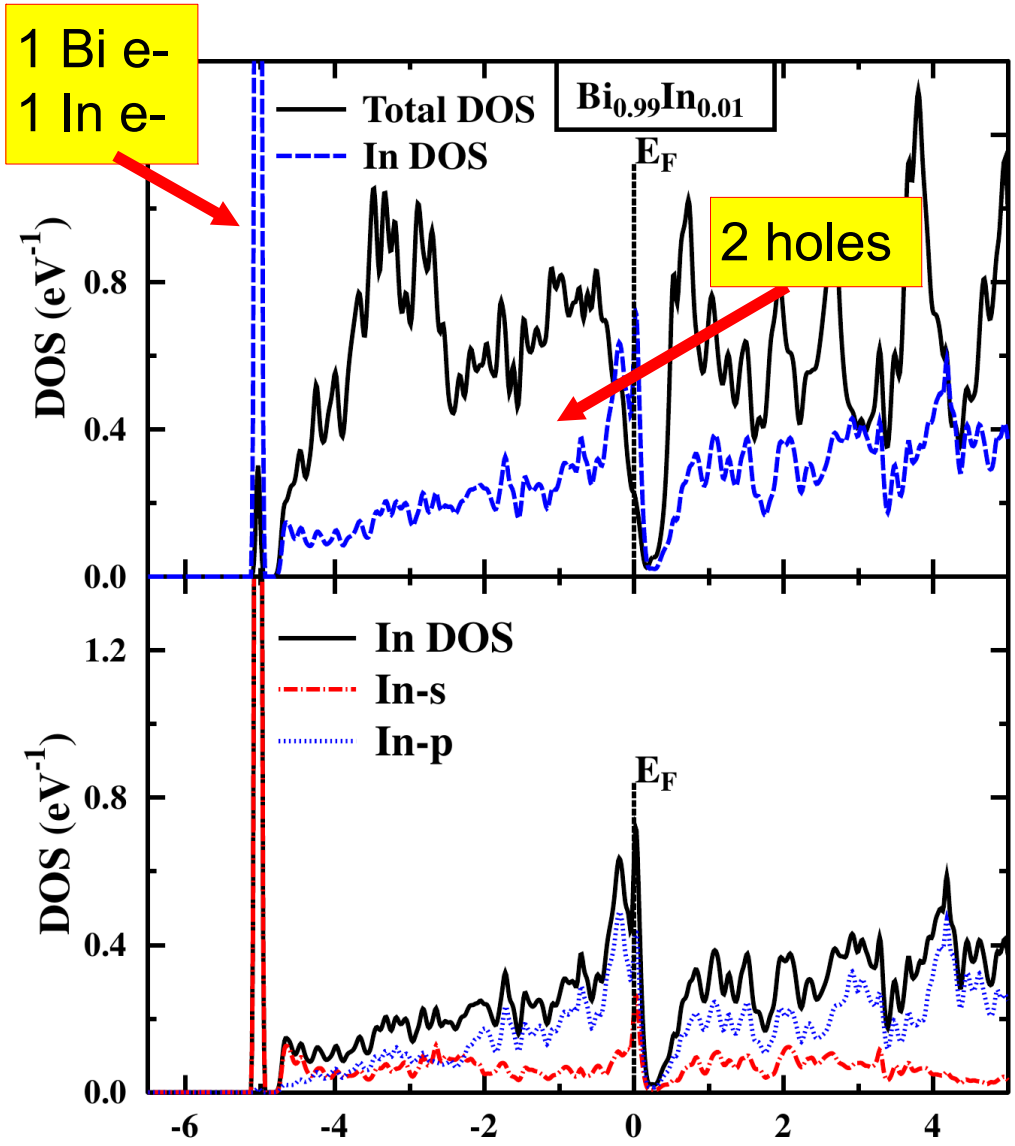


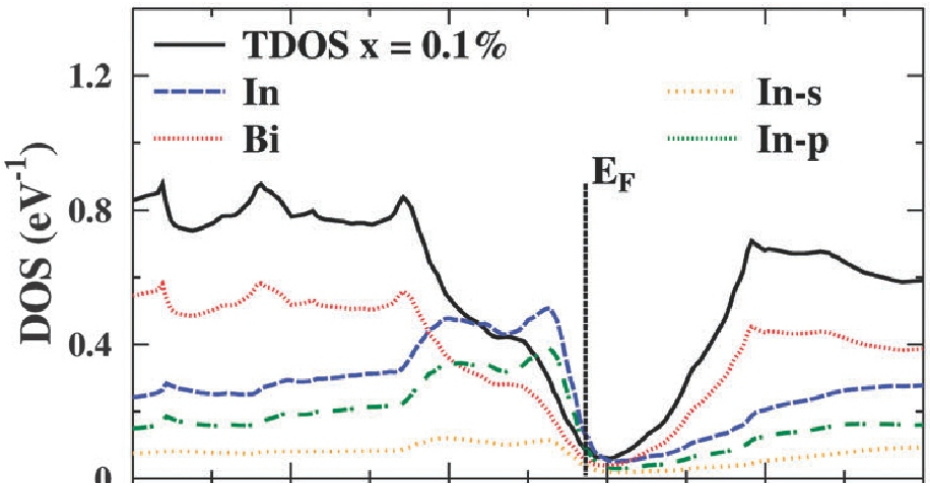


Moreover: transport properties suggest that neutral impurity scattering is observed

-> Indium is both neutral and acceptor?

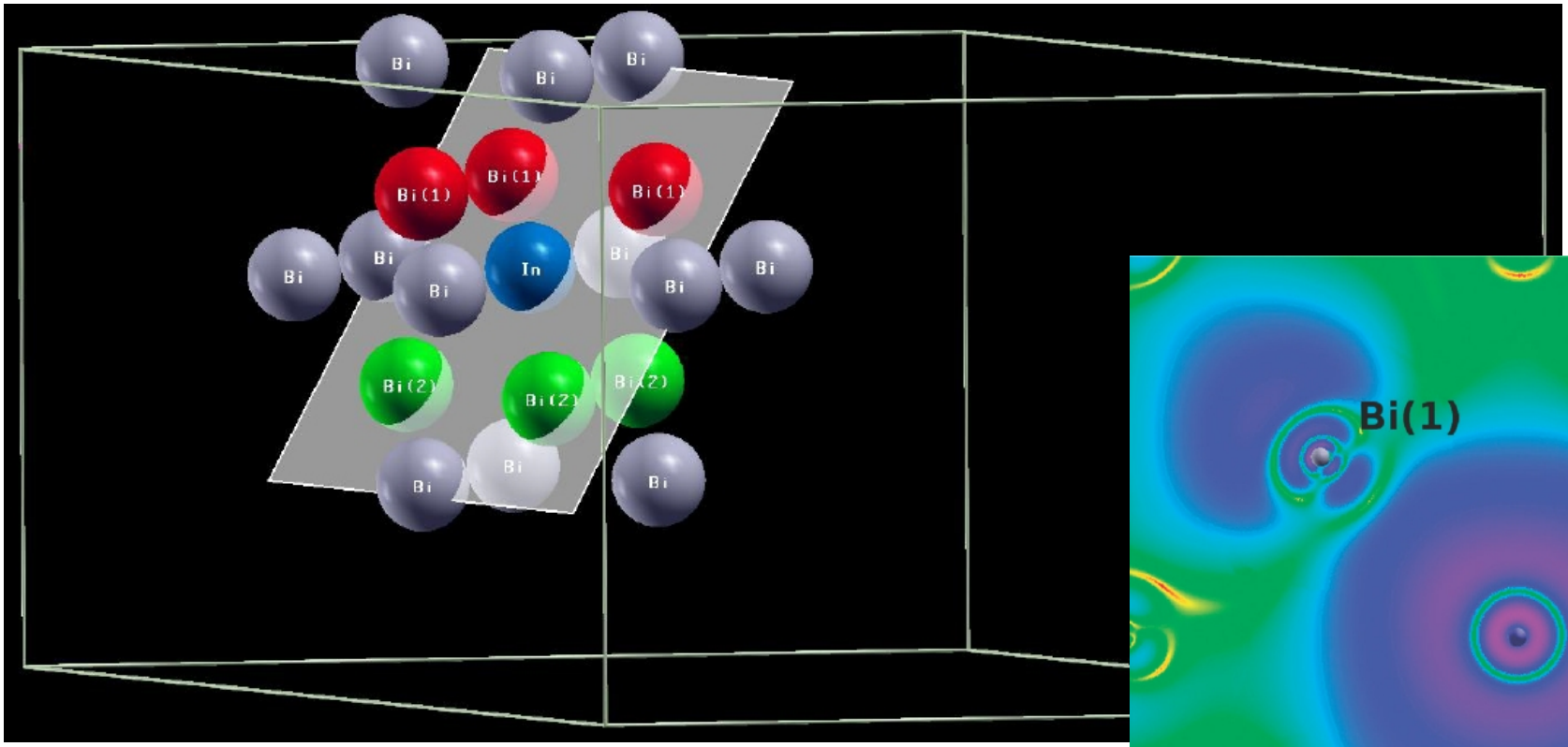
Doping via deep RL

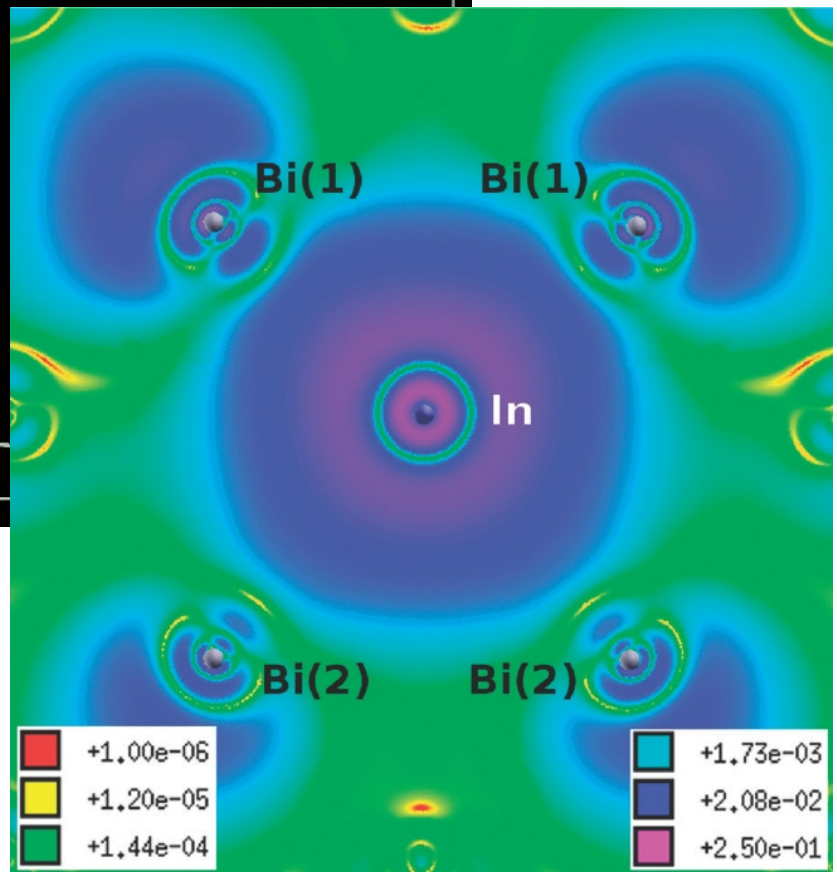




- Hyperdeep defect state (HDS) deprives of two electrons from the main valence block! (including 1 from Bi)
- Deep RL as a source of p-type doping
- Near EF - “local” rigid band

Charge density distribution





Indium is both an acceptor (via deep RL) and "neutral" impurity (3 valence electrons)

Revisit Bi:Sn

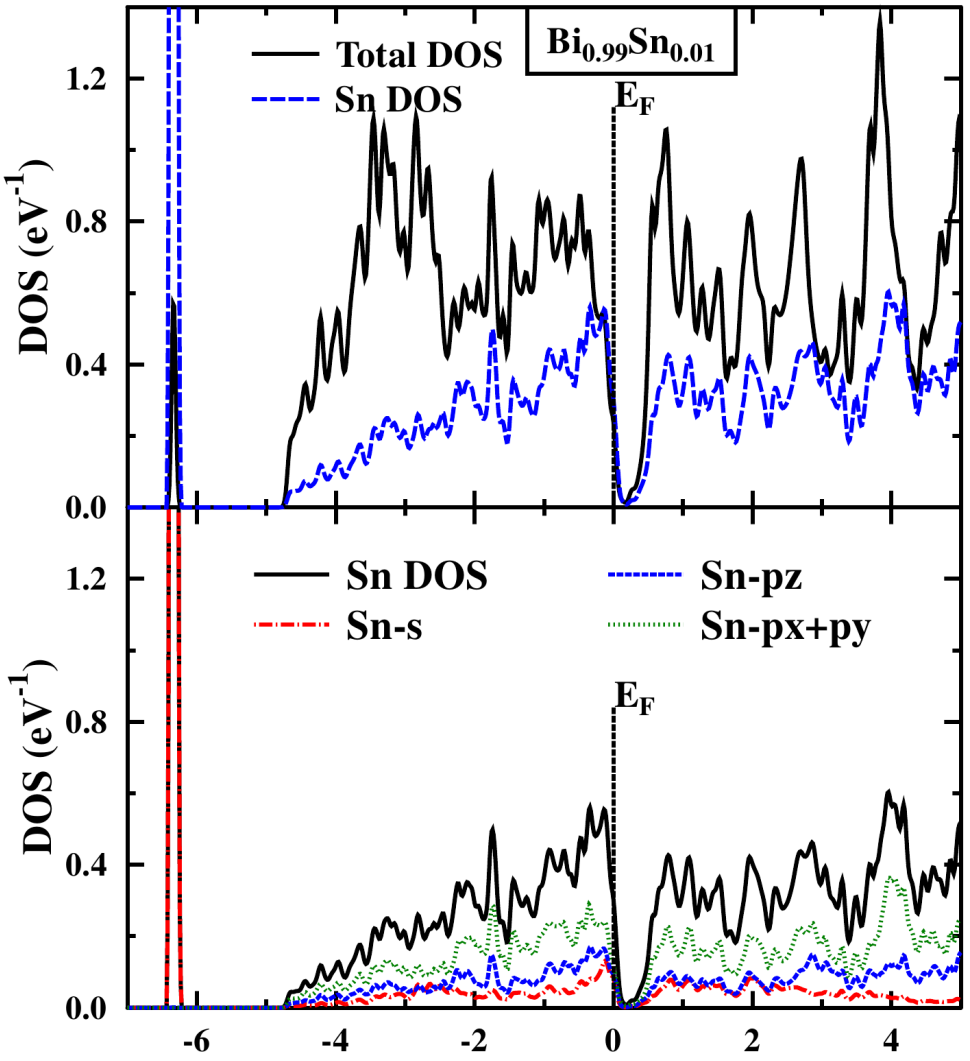
- Similar effect (theory and experiment) for Bi:Ga (isoelectronic)

- Sn has been known as a classical monovalent acceptor in Bi since 1960.

- Here, we show that Sn is not a simple acceptor impurity!

- Similar behavior with In and Ga in Bi

- Doping through HDS, but here Sn is not neutral (4 valence e)



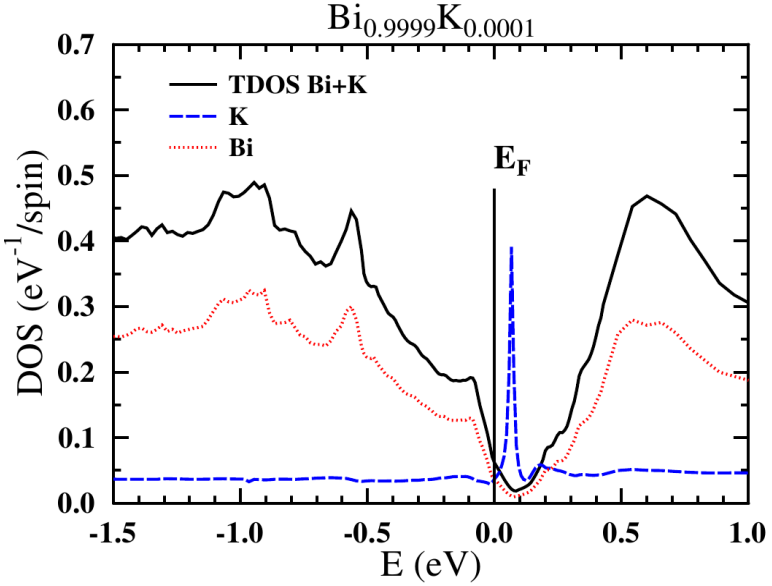
#2 summary: Bi:In

- Indium is an **isovalent acceptor** in bismuth
  - More Indium, higher hole concentration
- We suggest doping through formation of a hyperdeep RL as a new doping mechanism
- Allows to avoid an ionized impurity scattering
- Mechanism more general – similar for Sn and Ga in Bi
- Indium introduces neutral impurity scattering over wide temperature range
  - Enhanced $S \rightarrow zT \uparrow$

#3: search for new resonant impurities in thermoelectrics

Theoretical predictions – Bi & BiSb

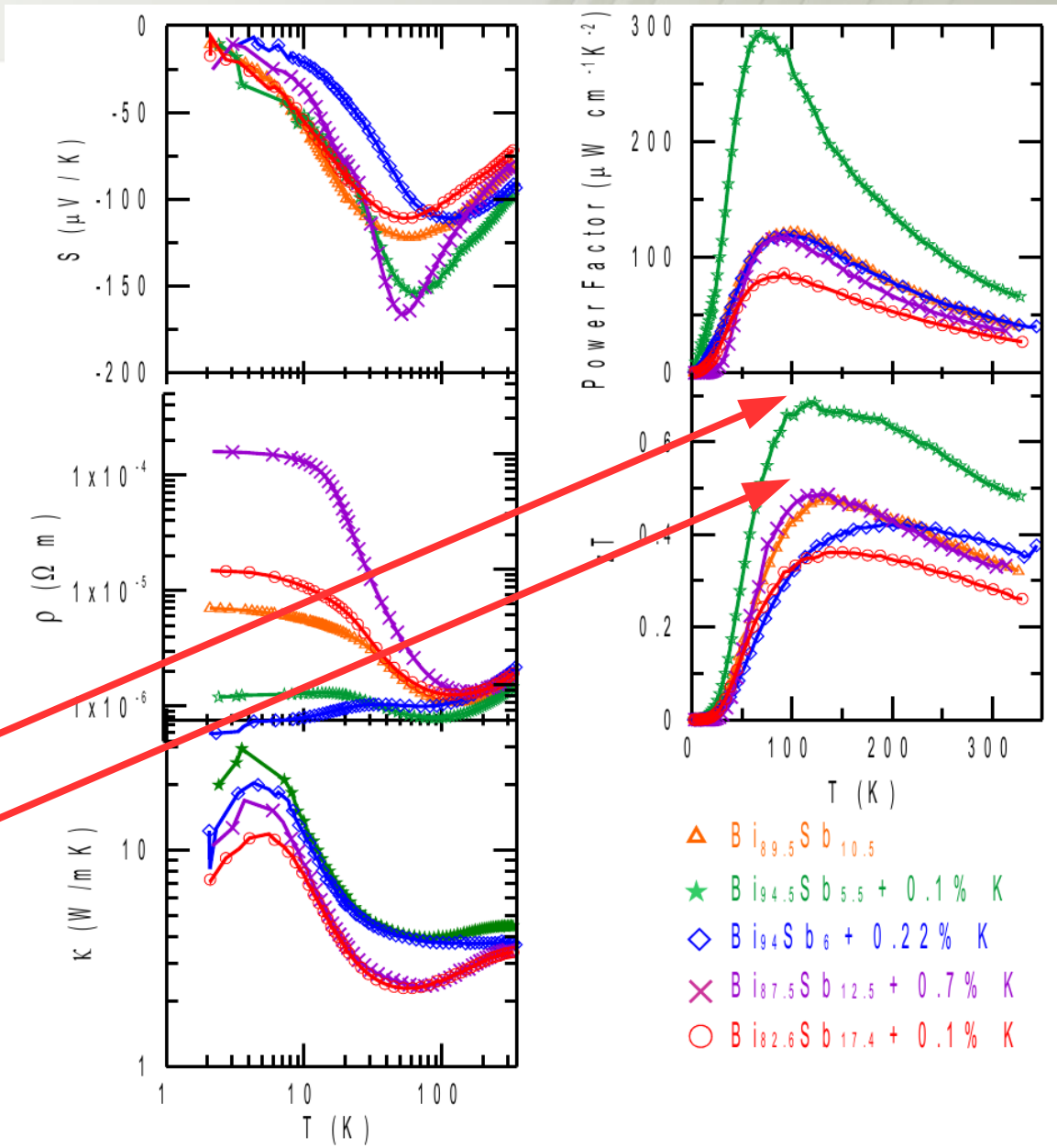
- RL on potassium!



- **experiment: zT +50% !!**

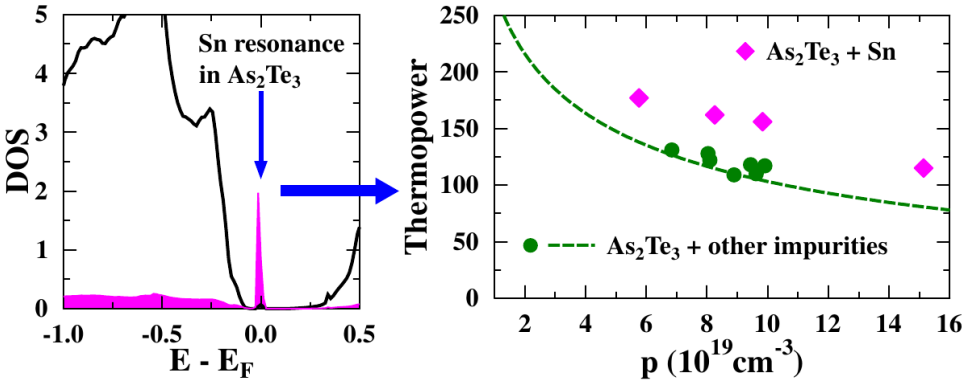
- but: problem with samples

(no second sample)



Theoretical predictions – Tetradymites (Bi_2Te_3 - related)

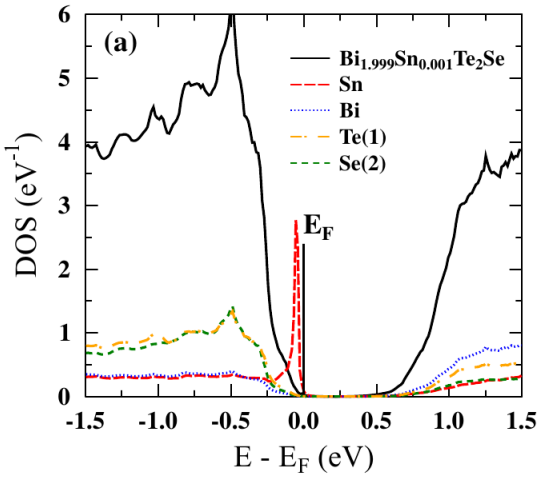
➔ Identification of RL on Sn in As_2Te_3



An Sn-induced resonant level in β-As_2Te_3

Bartlomiej Wiendlocha, *[a] Jean-Baptiste Vaney,[b] Christophe Candolfi,[b] Anne Dauscher,[b] Bertrand Lenoir[b] and Janusz Tobola[a]

➔ theoretical predictions of RLs (Sn, Al, Ga) for Bi_2Se_3, Bi_2Te_2Se and Bi_2Te_3



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Resonant Levels, Vacancies, and Doping in Bi_2Te_3, Bi_2Te_2Se, and Bi_2Se_3 Tetradymites

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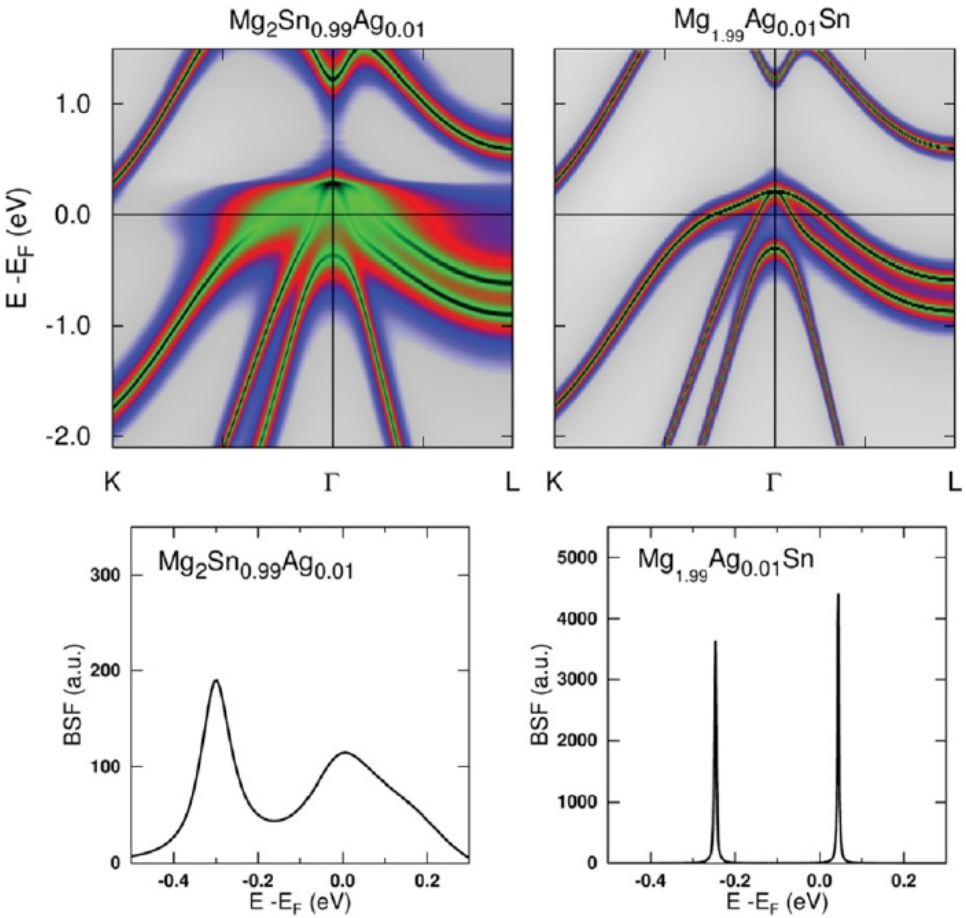
Theoretical predictions – Mg_2Sn

➔ Ambiguous behavior of Ag in Mg_2Sn

(RL on Sn site, rigid-band on Mg site)



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Electronic structure and thermoelectric properties of p-type Ag-doped Mg_2Sn and $Mg_2Sn_{1-x}Si_x$ ($x = 0.05, 0.1$)

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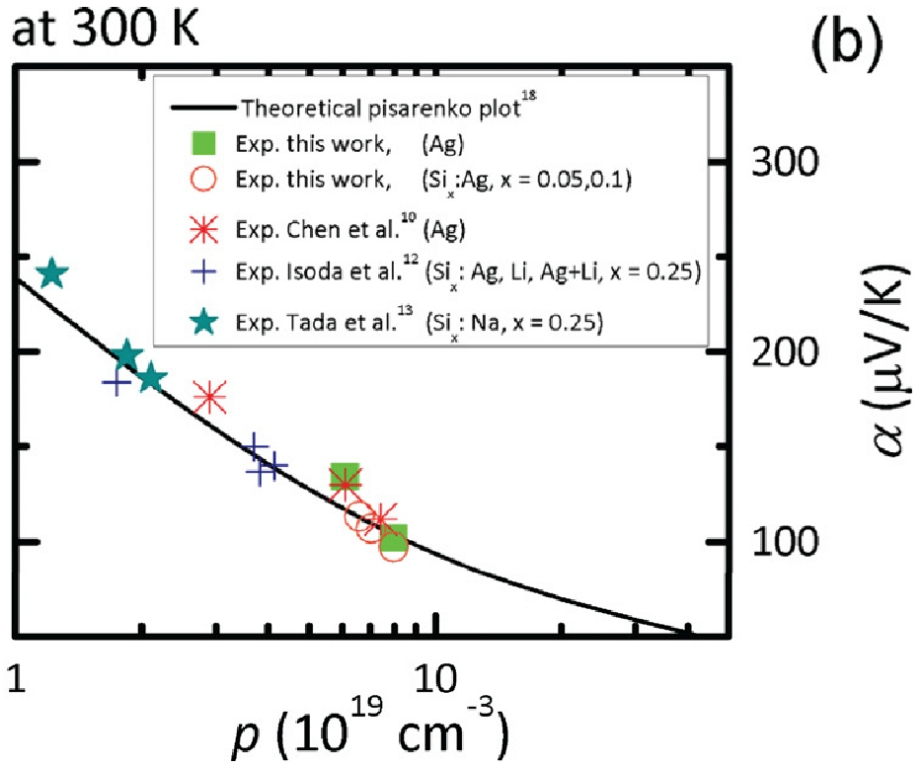

Summary

Resonant levels are interesting!

- *Delocalized* resonant level may increase thermopower
- Deep resonant level may lead to isovalent doping mechanism
- Calculations are able to predict existence of new RLs

Thank you for your attention!