Resonant Level Enhancement of the Thermoelectric Power of Bi_2Te_3 with Tin

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Outline

The physics of resonant levels: mechanisms by which they enhance ZT

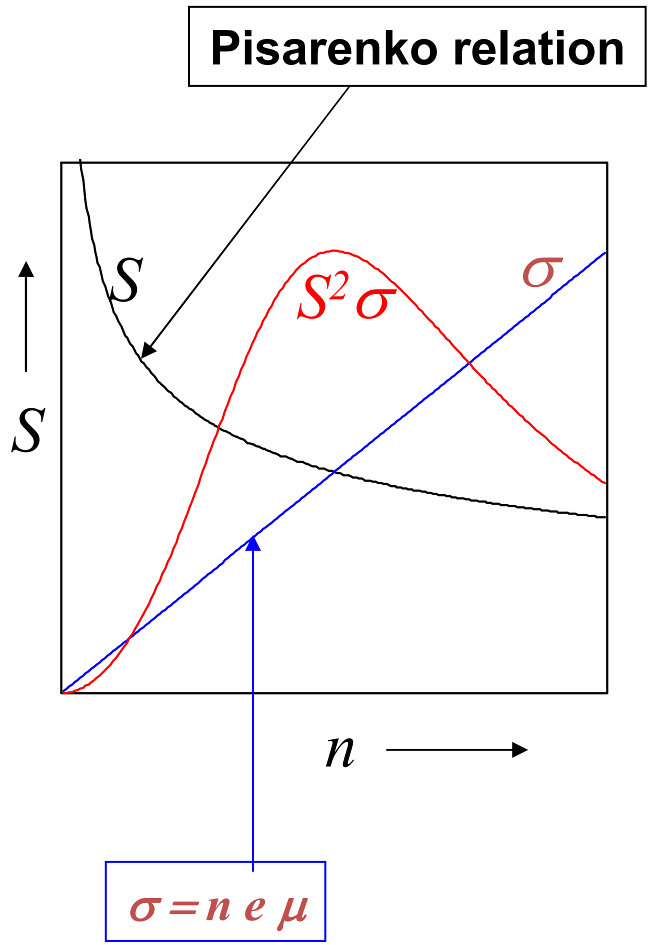
The Pisarenko (thermopower versus carrier density) relation in Bi_2Te_3

Tin is a resonant level in the valence band of Bi_2Te_3

1. Band structure
2. Resistivity, Seebeck, Hall and Nernst effects

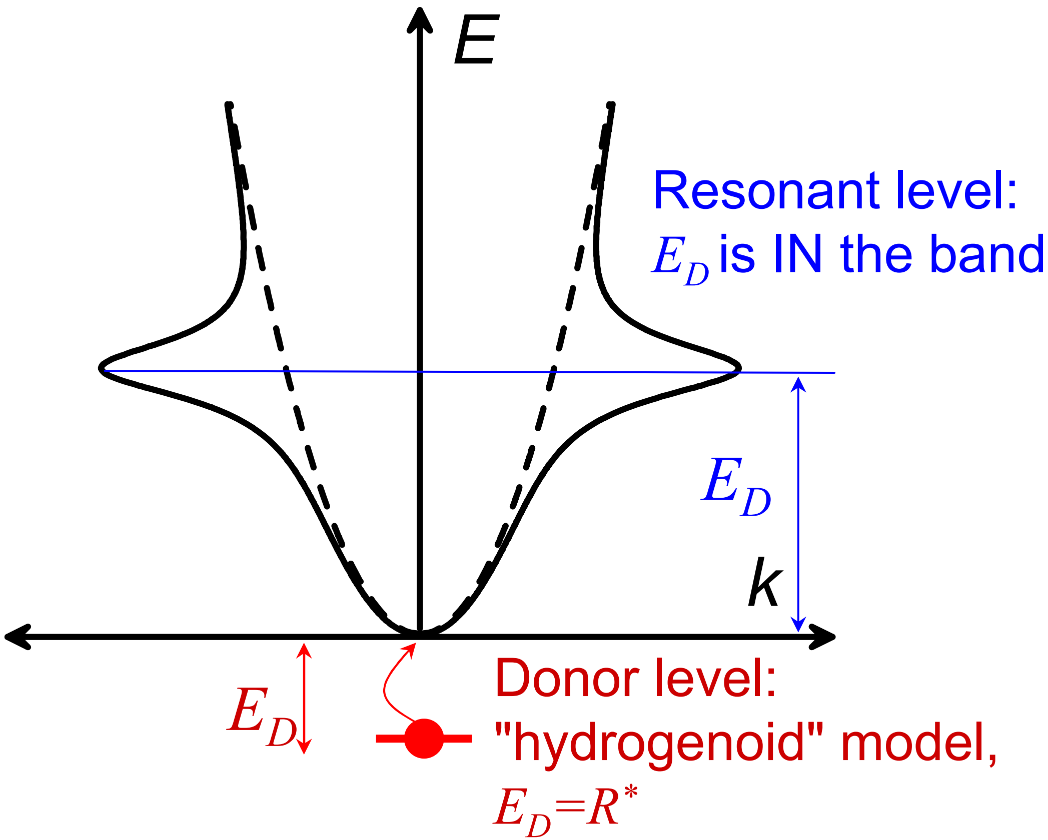
Enhancement in thermopower in single-crystal Bi2Te3

Application to practical p-type thermoelectric $(Bi_{30}Sb_{70})_2Te_3$ alloys for heat pumps

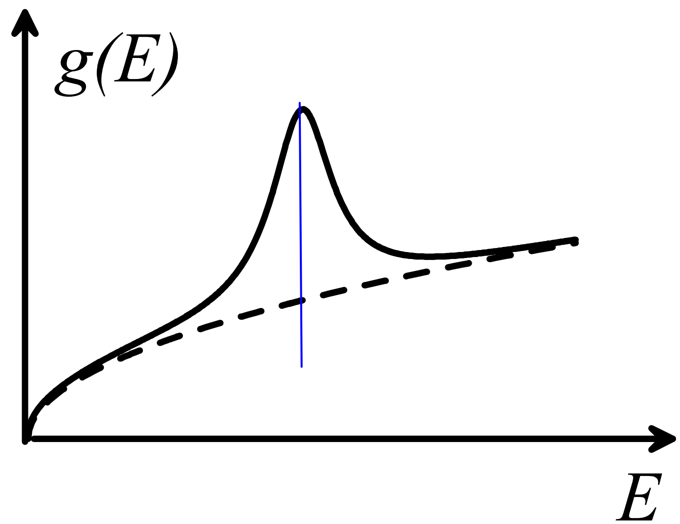


Resonant energy levels: definition

Dispersion



Density of states

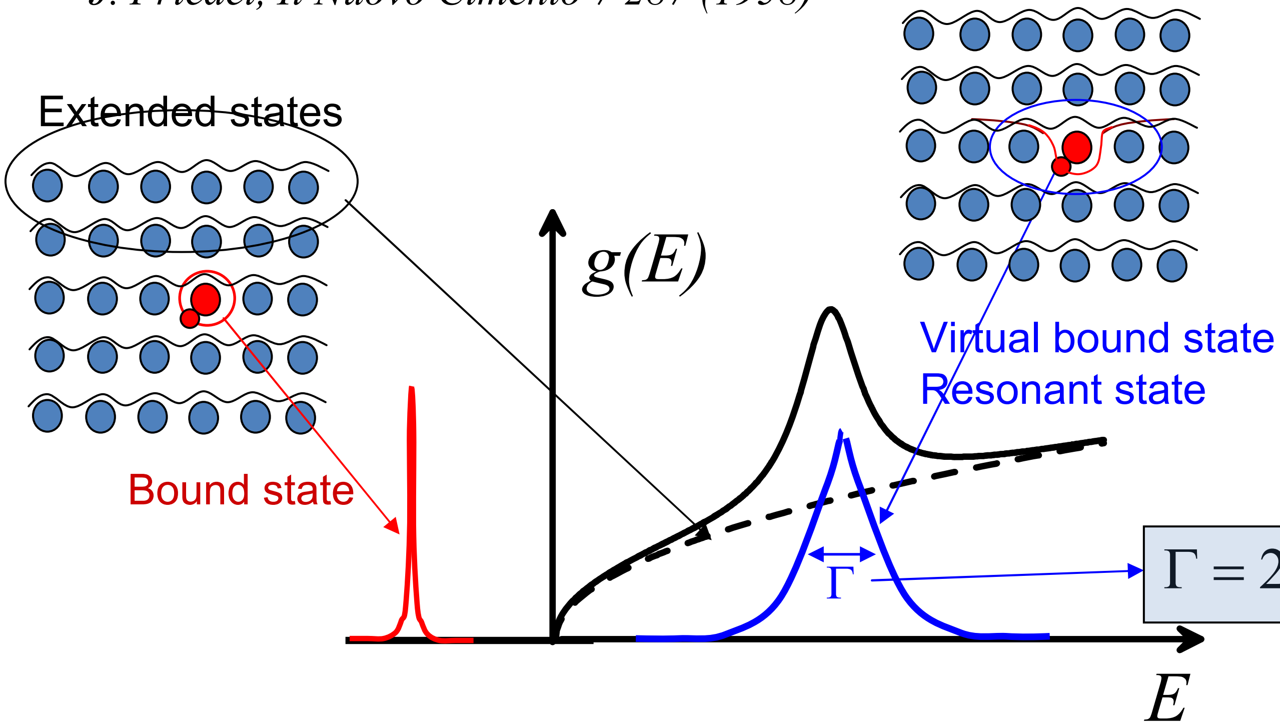


Resonant levels in metals and semiconductors

- Concept comes from atomic physics
- First in metals: "Friedel States" or "Virtual bound states"

  *J. Friedel, Can. J. Physics **34** 1190 (1956)*

  J. Friedel, Il Nuovo Cimento 7 287 (1958)



L = atomic level of impurity

V = potential

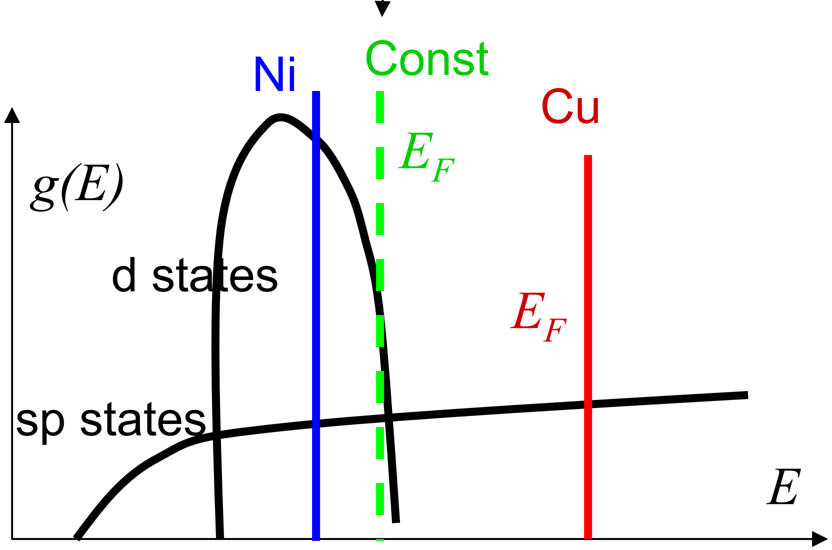
$g(E)$ = density of extended states - - - - - - - - - line

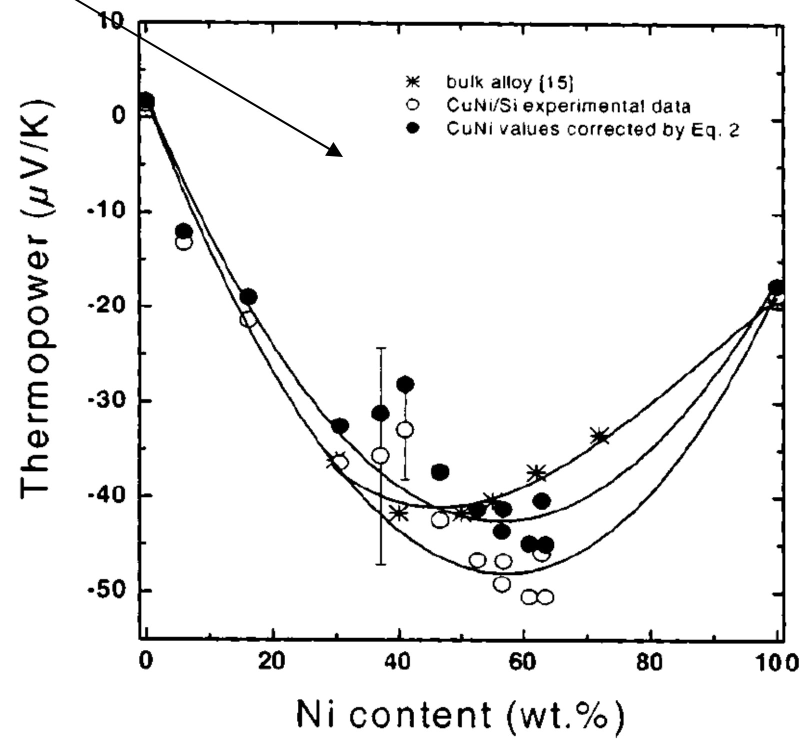
$$\Gamma = 2\pi \,|< L \,|\, V \,|\, k >|^2 \; g(E)$$

Friedel: "It is useful to think of the bound state as still existing, with a positive energy. But as it has now the same energy as an extended state, it will resonate with the l^{th} spherical component, to build up two extended states of slightly different energies; these in turn will have the same energies as the extended states with whom they will resonate, etc..."

Similar to Kondo and thermocouple alloys

1. Isolated atoms, Friedel state, dilute limit
1 bis. with magnetic moment: Kondo effect (Au+0.02% Fe) *Prog. Theo. Phys.* ***34*** *372, 1965*
2. Resonant levels ($Pb_{98}Tl_2Te$): semi-dilute alloys: states can intereact
3. Concentrated alloys (Constantan)



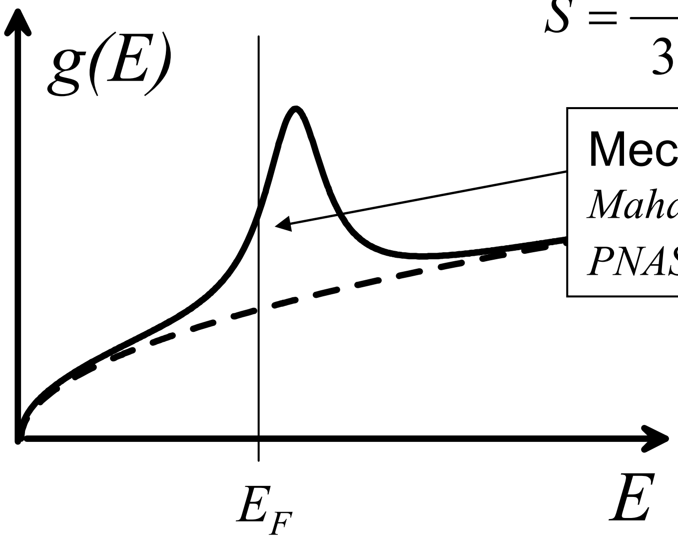


Constantan: main effect from *g(E)*
Thermocouple material up to 750^0C

Resonant levels increase thermopower

Mott relation for degenerate statistics

$$S = \frac{\pi^2}{3}\cdot\frac{k_B}{e}\cdot k_B T\cdot\left[\frac{1}{g(E)}\cdot\frac{\partial g(E)}{\partial E}+\frac{1}{\mu(E)}\cdot\frac{\partial \mu(E)}{\partial E}\right]_{E=E_F}$$



Mechanism 1
Mahan and Sofo, PNAS ***93*** *7436, 1996*

Mechanism 2: Resonant scattering

A. Blandin & J. Friedel, Le Journal de Physique et le Radium ***20*** *160, 1959*

In PbTe: *Yu. Ravich, CRC Handbook on Thermoelectrics, D. M. Rowe, Ed. 1995*

In Bi_2Te_3: *M. K. Zhitinskaya, S. A. Nemov and T. E. Svechnikova, Phys. Solid State* ***40*** *1297, 1998*

- Works great at cryogenic temperatures
- Will NOT give high *zT* at operating temperatures where acoustic/optic phonon scattering dominates

Which dominates? Can be proven experimentally by measuring Nernst effect

Nernst coefficient can determine mechanism

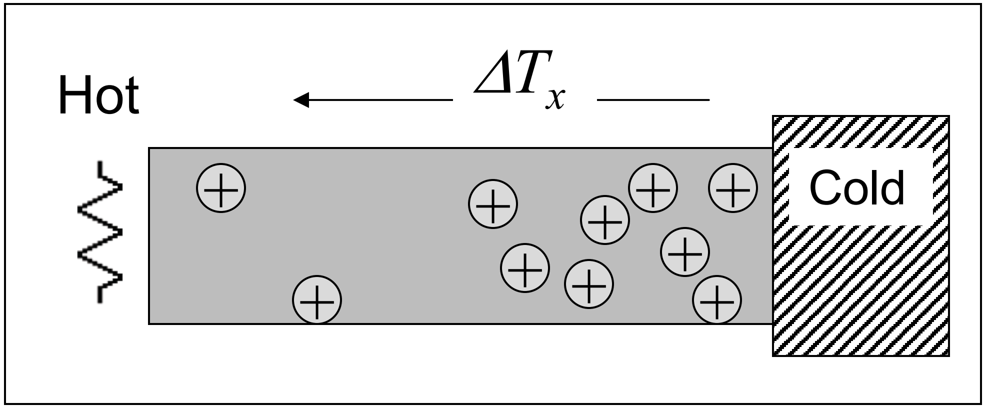
Seebeck coefficient:
Charge carriers diffuse under ΔT_x => Condense on cold side

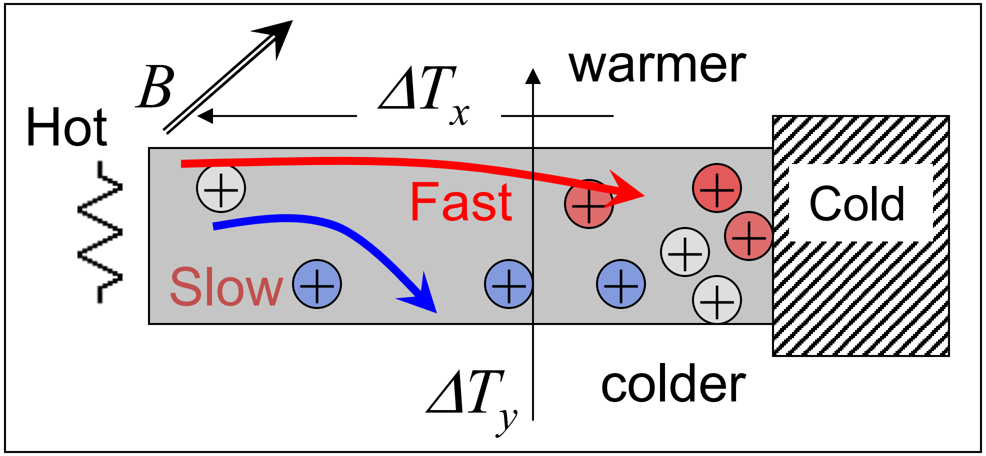
Nernst:
Slow-diffusing carriers are more deflected by magnetic field than fast-diffusing carriers

=> Lower energy carriers condense on one side

=> cools down => ΔT_y

Seebeck coefficient x ΔT_y => Nernst coefficient
Nernst gives energy-dependence of scattering mechanism



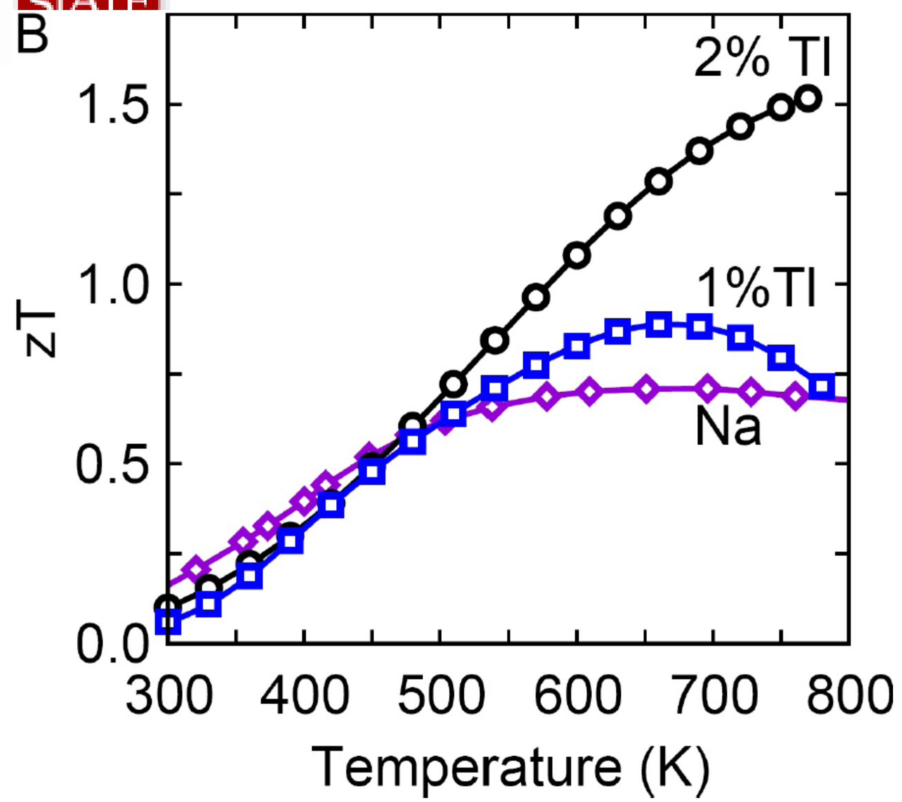


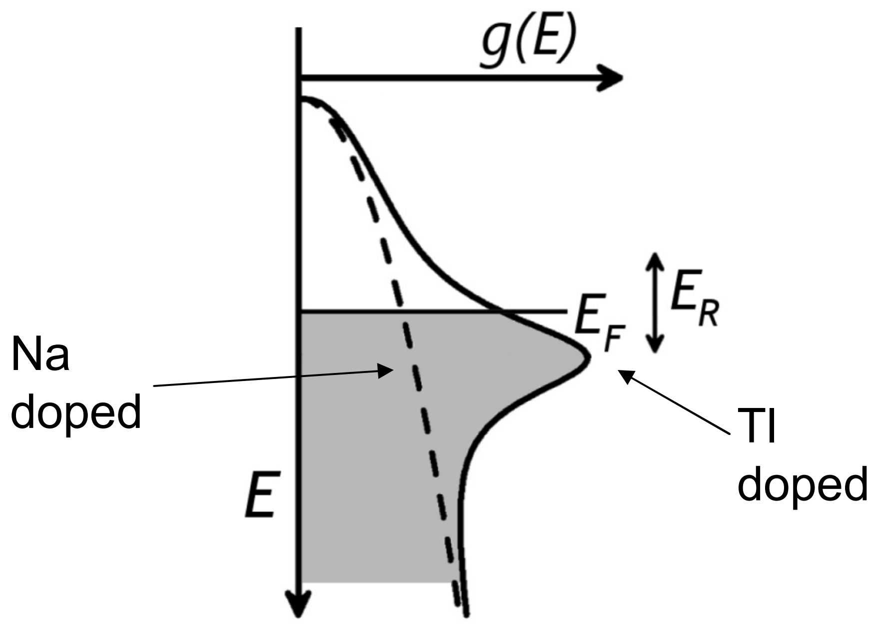
Very schematically for non-degenerate system:

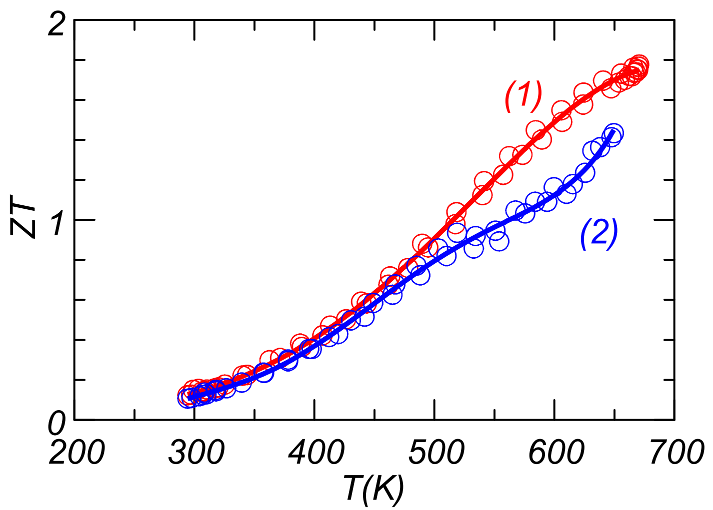
$$\text{Define}: \tau = \tau_o E^{\Lambda} \quad => N \approx \Lambda \mu \left(\frac{k_B}{|q|} \right)$$

If resonant scattering => Large Λ => Large N
If ac. phonon scattering => $\Lambda=-1/2$ => $-N/(88\mu V/K) \sim \mu/2$

PbTe:Tl doubles zT







Heremans et al, Science 321 554 2008

Bi_2Te_3:Sn

- Kulbachinskii identifies Sn as resonant level in Bi_2Te_3
  V. Kulbachinskii, N. B. Brandt et al., Phys. Stat. Sol. ***150*** *237 (1988)*

- Zhitinskaya suggests resonant SCATTERING boosts thermopower at 120 K (will NOT work when phonon scattering dominates, at 300K)
  M.K. Zhitinskaya, ***S.A.*** *Nemov, T.E. Svechnikova, p 72, 16th International Conference on Thermoelectrics (1997)*

- We use Kulbachinskii's Bridgeman $Bi_{2-x}Sn_xTe_3$ single crystals with x=0.0025, 0.0075, 0.015 (0.05, 0.15, 0.30 at% Sn)

- Measure four transport properties– S,N,R_H,ρ (2-400K) and use method of 4 coefficients

- Calculate Pisarenko relation (Thermopower vs. carrier concentration) for Bi_2Te_3

- Measure Shubnikov-de Haas to determine area of the Fermi surface
  B ⊥ <001> axis, current // <100> axis for all measurements

Bi_2Te_3:Sn Proposed Valence Structure

- Upper valence band with small mass

  *A. von Middendorff, G.Landwehr: Solid State Communications, **11** 203 (1972)*

- Lower valence band (LVB) position: Kohler - 20.5 meV

  *H. Kohler, Physica Status Solidi (b), **74**. 591 (1976)*

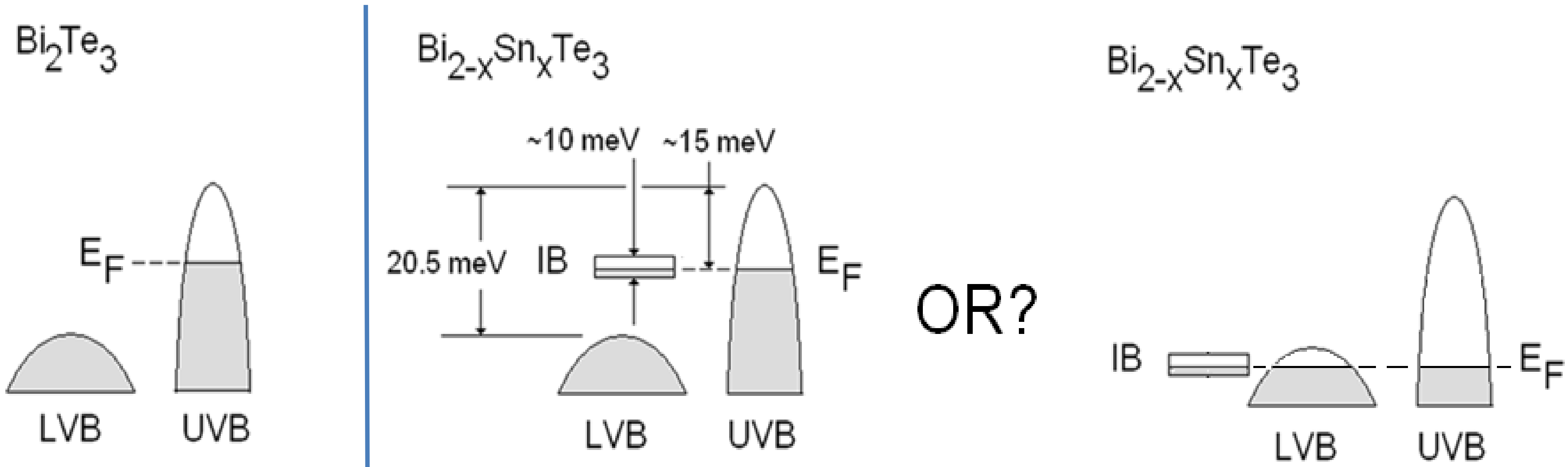
  In *k* space: LVB |ΓA| UVB: |ΓX|

- Kulbachinski: Sn resonant impurity band 15meV below UVB

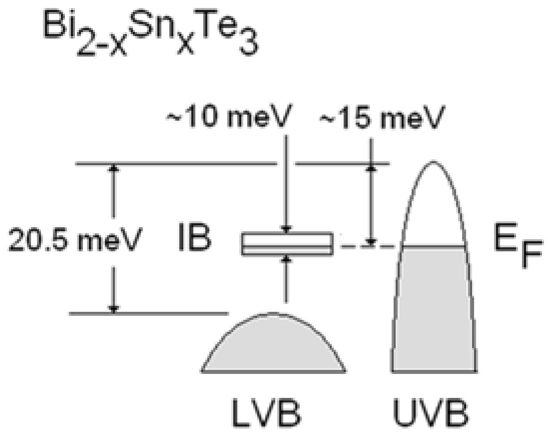
  *V.A.. Kulbachinskii, Physica Status Solidi (b), **199** (1997)*

- Zhitinskaya: Impurity Band (IB) is 10 meV wide

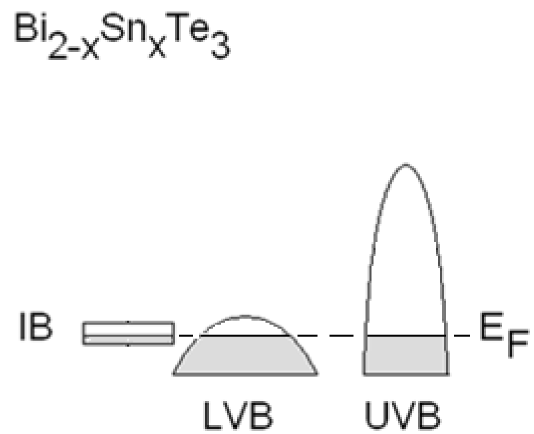
  M. K. *Zhitinskaya, Fizika Tverdogo Tela,**45**, No. 7, (2003); Fizika i Tekhnika Poluprovodnikov **34** No 12 (2000)*

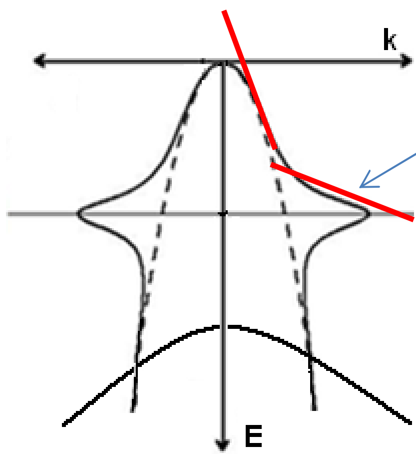


Bi_2Te_3:Sn Proposed Valence Structure

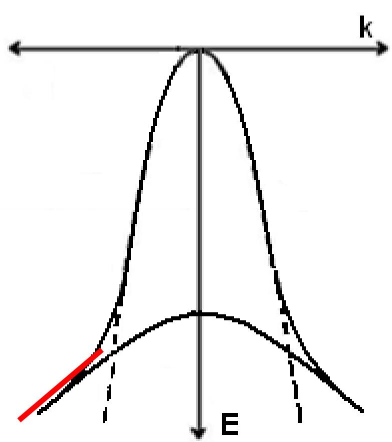


OR?





Higher mass

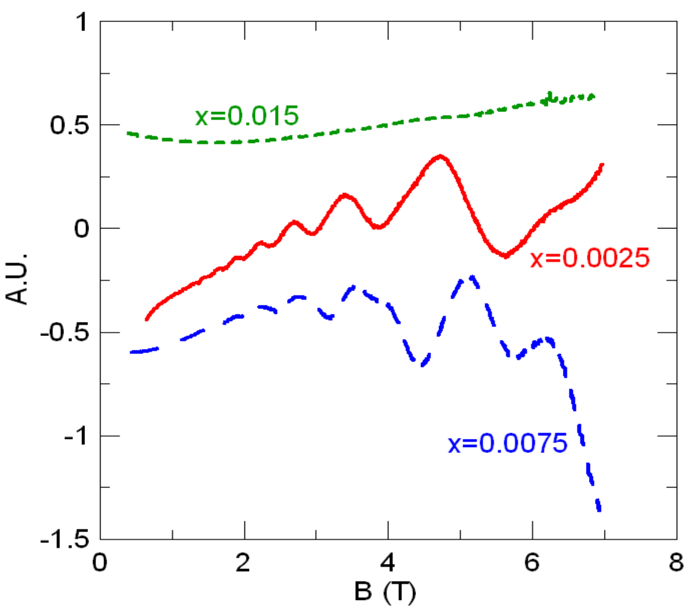


$$\frac{1}{\hbar^2}\left(\frac{\partial^2 E(k)}{\partial k^2}\right) = \frac{1}{m^*}$$

Shubnikov-de Haas (SdH)

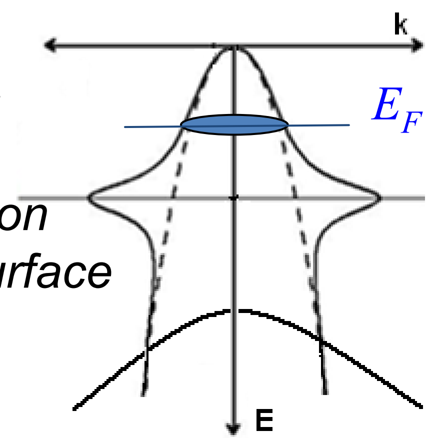
Oscillations in resistance periodic in 1/magnetic field

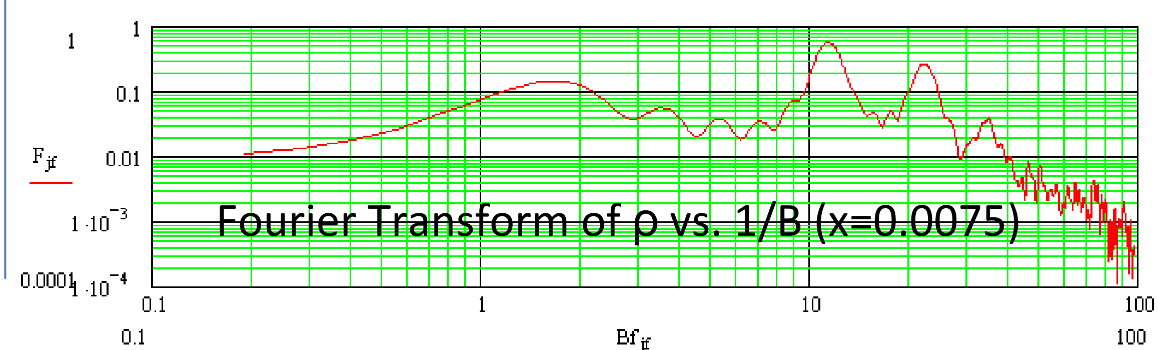
- Magnetic field quantizes allowable energy levels $E_n = n\hbar\omega_C = n\hbar\frac{2B}{m_C^*}$
- Area of Fermi surface given by: $\Delta\frac{1}{B} = \frac{2\pi\cdot q}{\hbar A_F}$
- Need mean free path longer than one cyclotron orbit: $\omega_C\tau = \mu B >> 1$



SdH oscillations in resistivity

Period of Oscillations Measures Cross-section Of Fermi surface



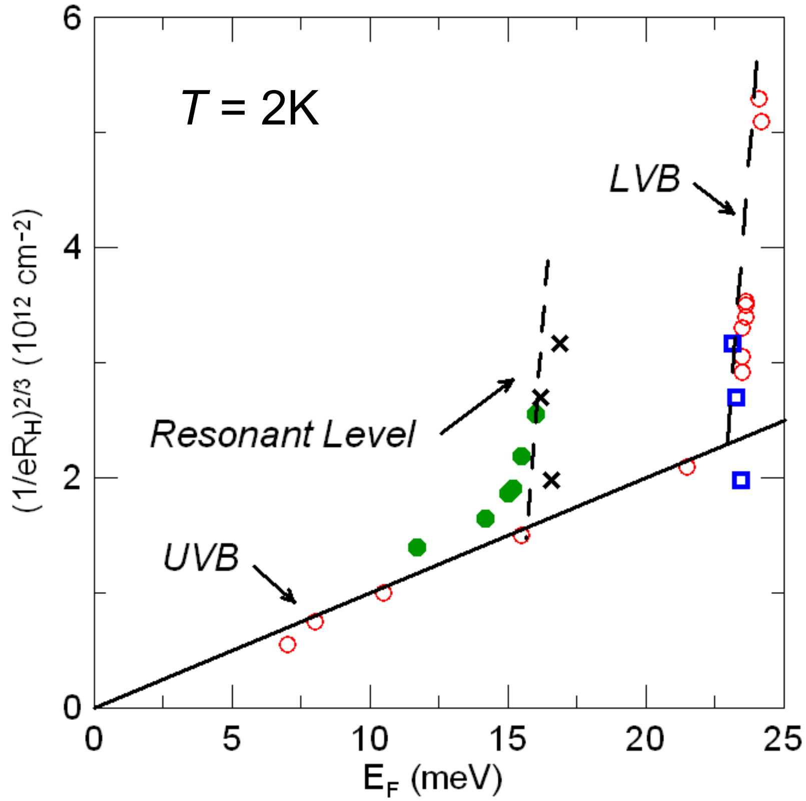


Fourier Transform of ρ vs. 1/B (x=0.0075)

Analysis of SdH oscillations

Evidence for resonant level from SdH alone is ambiguous: 2 harmonics or 2 periods?

Tin Content	Oscillation Frequency	Fermi Surface Area
$Bi_{2-x}Sn_xTe_3$	$[\Delta(1/B)]^{-1}$ T	(m^{-2})
x=0.0025	12.7	1.21E+17
	23.5	2.24E+17
x=0.0075	11.4	1.09E+17
	22.3	2.13E+17
x=0.015	13.5	1.29E+17
	22.1	2.11E+17



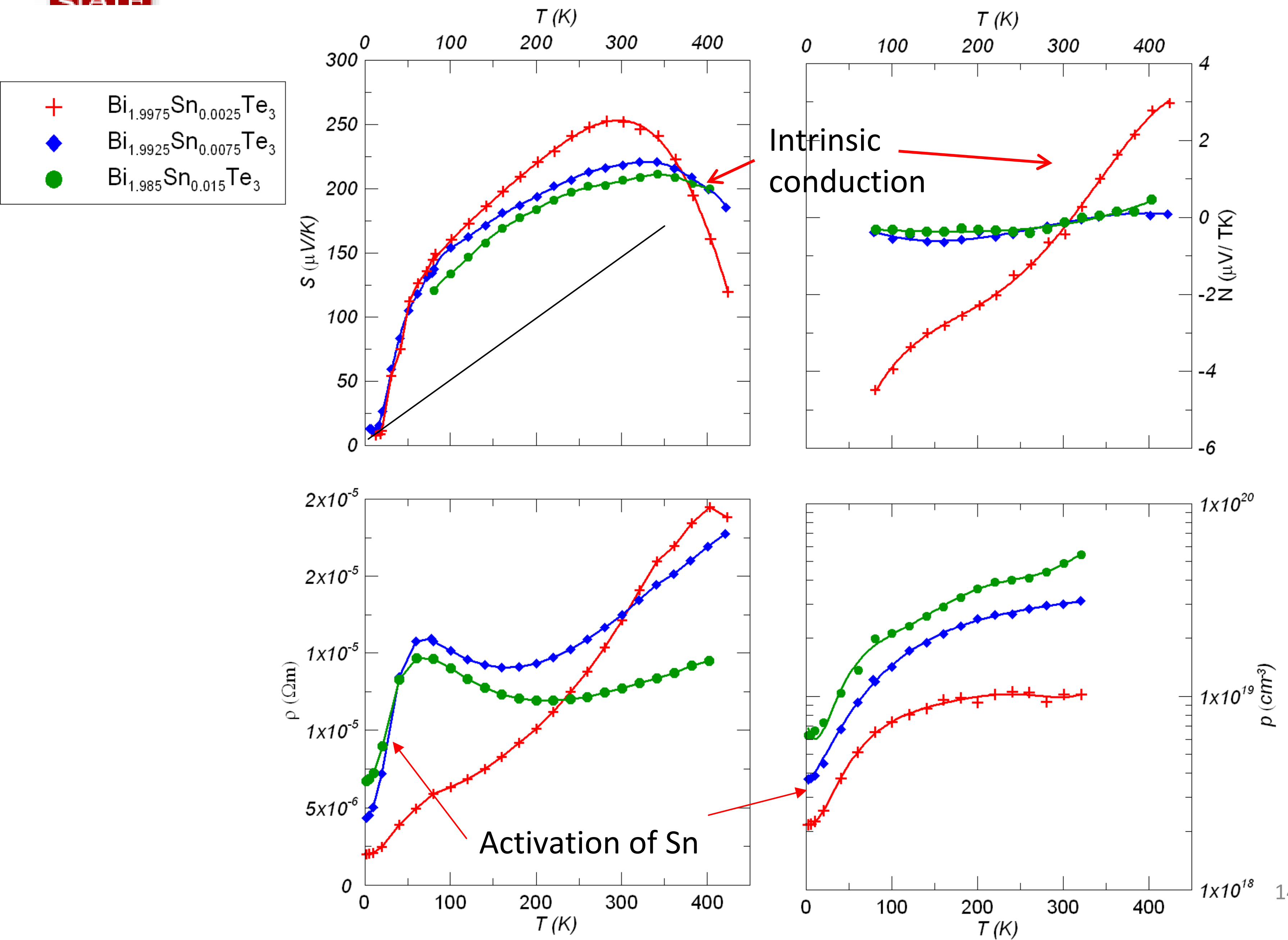
Tin Content	Hall 2K carrier density	Cyclotron mass	Fermi Level	m_D^* UVB	Carriers in 1st band	Carriers in 2nd band	m_D^* LVB
$Bi_{2-x}Sn_xTe_3$	p (cm^{-3}) 10^{18}	m_c^*/m_e	meV	m_D^*/m_e	p (cm^{-3}) 10^{18}	p (cm^{-3}) 10^{18}	m_D^*/m_e
x=0.0025	2.78	0.118	23.44	0.156	.966	1.814	1.89
x=0.0075	4.44	0.115	23.26	0.152	.917	3.523	3.29
x=0.015	5.63	0.113	23.14	0.149	.882	4.748	4.19

(●) $Bi_{2-x}Sn_xTe_3$ from (1),
(○) Bi_2Te_3 from (2),
(□ and ▷)$Bi_{2-x}Sn_xTe_3$ from this work using the method of 1(▷) and 2(□)
The solid line is calculated from (2)

Assuming that LVB starts at 20.5 meV

*Analysis after V. A. Kulbachinskii, Phys. Rev. B **50** 16921 (1994); H. Kohler: Phys Stat Solidi (b) **74** (1976).*

Transport Measurement Results



Method of the four parameters

Hypotheses:

- Single-carrier system – not rigorously the case here
- Parabolic (Bi_2Te_3) or non-parabolic bands
- Degenerate or non-degenerate statistics

Four unknown parameters

1. Density of carriers n
2. Mobility of carriers μ
3. Effective mass m^*_{DOS}
   - $(n) + (m^*_{DOS}) \Rightarrow (E_F)$
4. Energy dependence of scattering $\tau = \tau_0 E^{\lambda}$

λ = scattering exponent

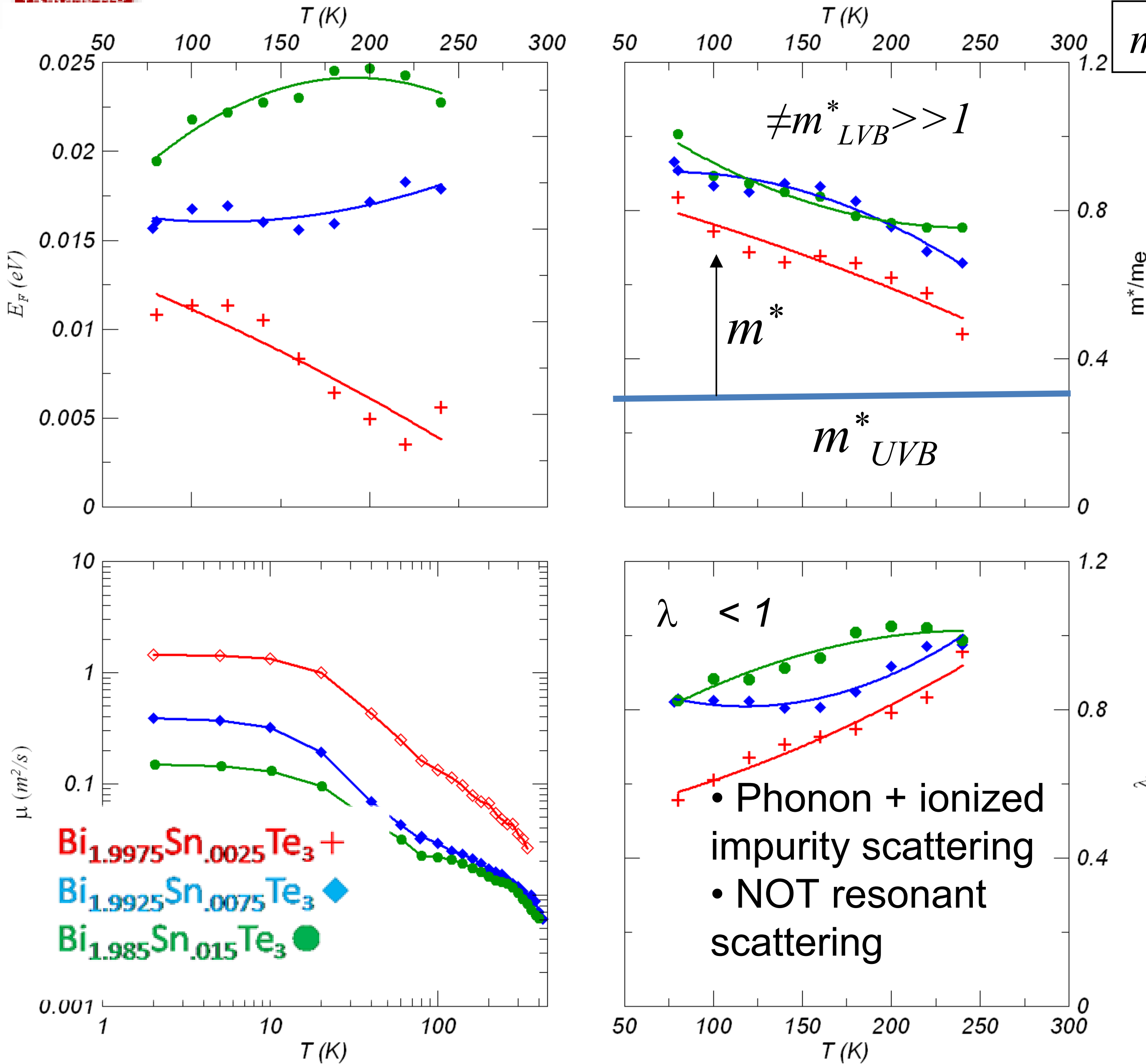
Use four independent measurements at each temperature T

1. Resistivity $\rho(T)$
2. Hall coefficient $R_H(T)$
3. Thermopower $S(T)$
4. Transverse isothermal Nernst-Ettingshausen coefficient $N(T)$

J. P. Heremans, C. M. Thrush and D. T. Morelli, Phys. Rev. B ***70*** *115334 (2004)*

Results of 4-Parameter Fit

$m^*_{UVB} < m^* < m^*_{LVB}$



Increase in m^* for higher tin concentrations

Scattering exponent increases with Sn: Sn acts as an ionized impurity

Calculation of Pisarenko Relation

Qualitative (here for non-degenerate statistics, for didactic purposes only): S depends on scattering mechanism λ, carrier concentrations, effective masses, and mobility

$$S \approx \frac{k}{q}\left(A(\Lambda) + \ln \frac{2(2\pi \cdot m_1^* k_b T)^{3/2}}{h^3 p_1} \right)$$

Quantitative: use Fermi integrals, assume parabolic model, multi-carrier conduction

$$p_{UVB} = \frac{6}{3\pi^2 \hbar^3}\left(2m_{UVB}{}^* k_B T\right)^{3/2} \int_0^\infty \left[\frac{x^{3/2} e^{x-x_F}}{\left(1+e^{x-x_F}\right)^2} \right] dx \quad p_{LVB} = \frac{6}{3\pi^2 \hbar^3}\left(2m_{LVB}{}^* k_B T\right)^{3/2} \int_0^\infty \left[\frac{x^{3/2} e^{x-(x_F-\Delta E_{UL})}}{\left(1+e^{x-(x_F-\Delta E_{UL})}\right)^2} \right] dx$$

$$\Delta E_{UL} = 20 meV$$

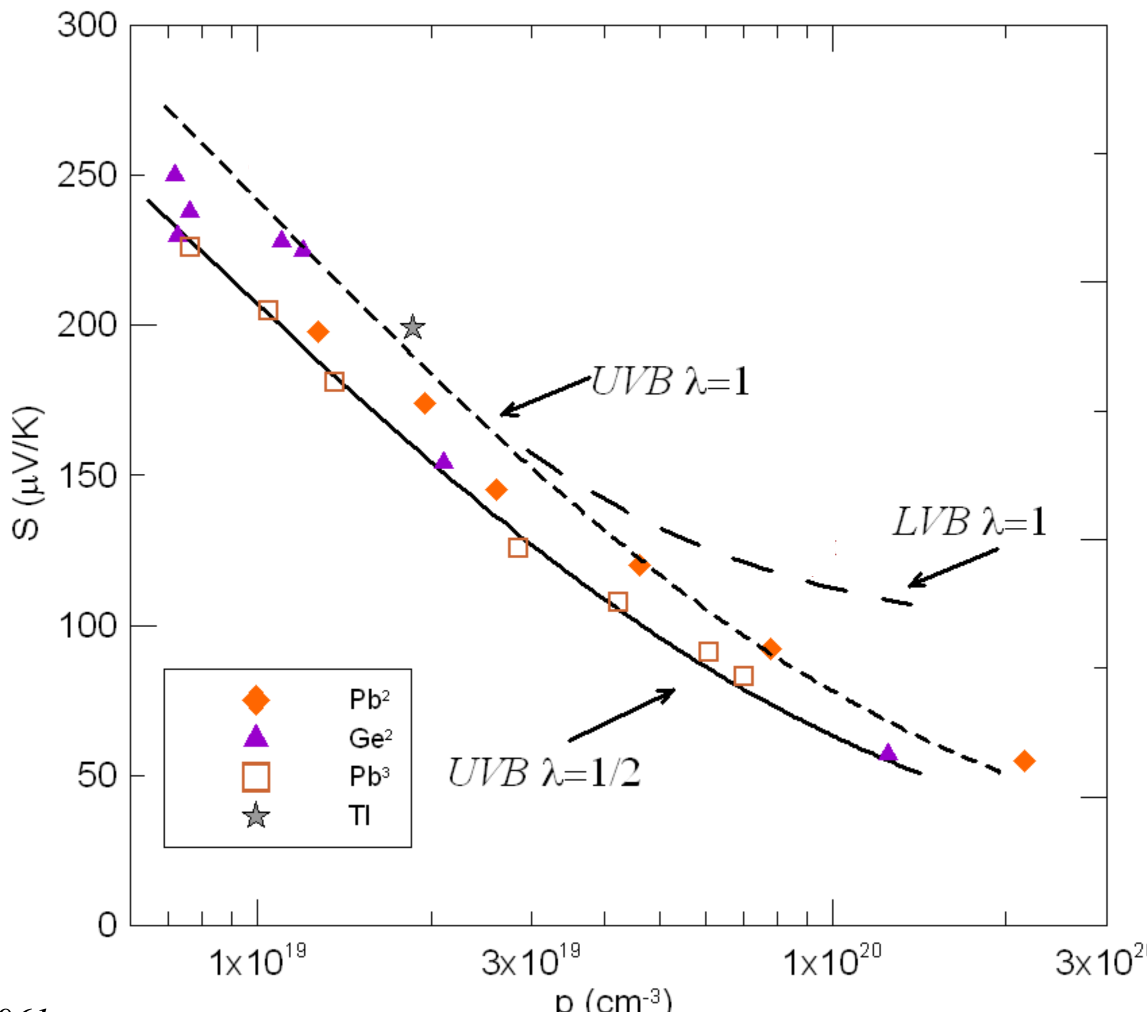
$$S_{LVB,UVB} = \frac{k_B}{q} \frac{\int_0^\infty \left[\frac{x^{5/2+\lambda} e^{x-x_F}}{\left(1+e^{x-x_F}\right)^2} \right] dx}{\int_0^\infty \left[\frac{x^{3/2+\lambda} e^{x-x_F}}{\left(1+e^{x-x_F}\right)^2} \right] dx} - x_F \qquad \sigma_{ratio} = \frac{\int_0^\infty \left[\frac{x^{3/2+\lambda} e^{x-x_F}}{\left(1+e^{x-x_F}\right)^2} \right] dx}{\int_0^\infty \left[\frac{x^{3/2+\lambda} e^{x-(x_F-\Delta E_{UL})}}{\left(1+e^{x-(x_F-\Delta E_{UL})}\right)^2} \right] dx} \left(\frac{m_{UVB}^*}{m_{LVB}^*} \right)^{1/2}$$

$$S = \frac{S_{UVB}\sigma_{UVB} + S_{LVB}\sigma_{LVB}}{\sigma_{UVB} + \sigma_{LVB}} = \frac{S_{UVB} \cdot \sigma_{ratio} + S_{LVB}}{\sigma_{ratio} + 1}$$

Ioffe, Physics of Semiconductors

Pisarenko Relation for Bi_2Te_3 at 300K

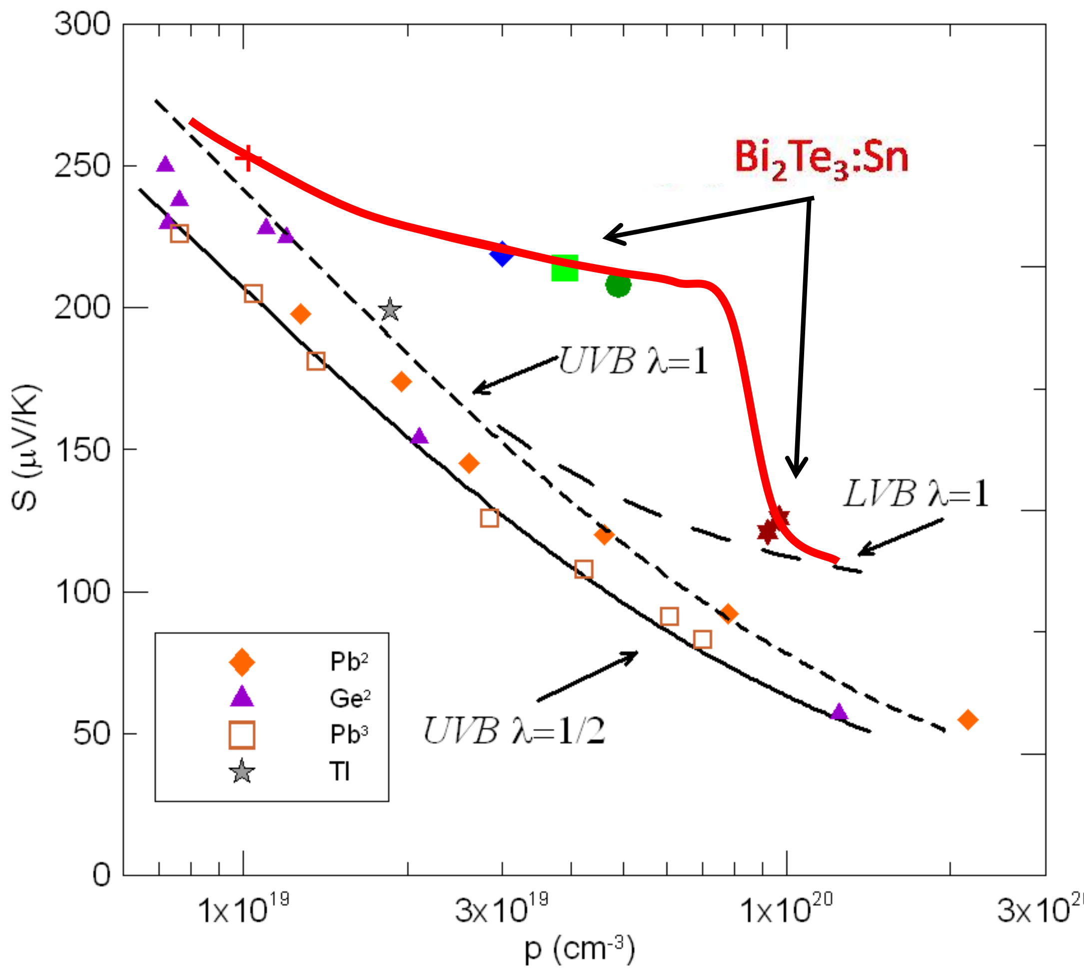
- Calculation of thermopower as function of carrier density
- UVB: λ =1/2, 1
- LVB: λ =1
- LVB starts at 20 meV below UVB

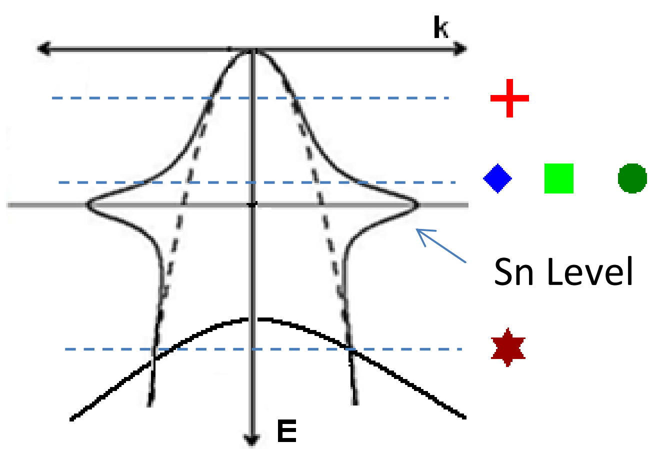


1. Ioffe, Physics of Semiconductors, 1961
2. Bergmann. 1169, s.l. : Z Natuforsch, 1963, Vol. 18a.
3. Philosophical Magazine, Volume 84, Issue 21 July 2004 , pages 2217 - 2228

Pisarenko Relation for Bi_2Te_3 at 300K

- Middle Sn concentrations have increased Seebeck over Ge and Pb doped Bi_2Te_3
- Resonant level
- Highest Sn concentrations fall with 2nd valence band

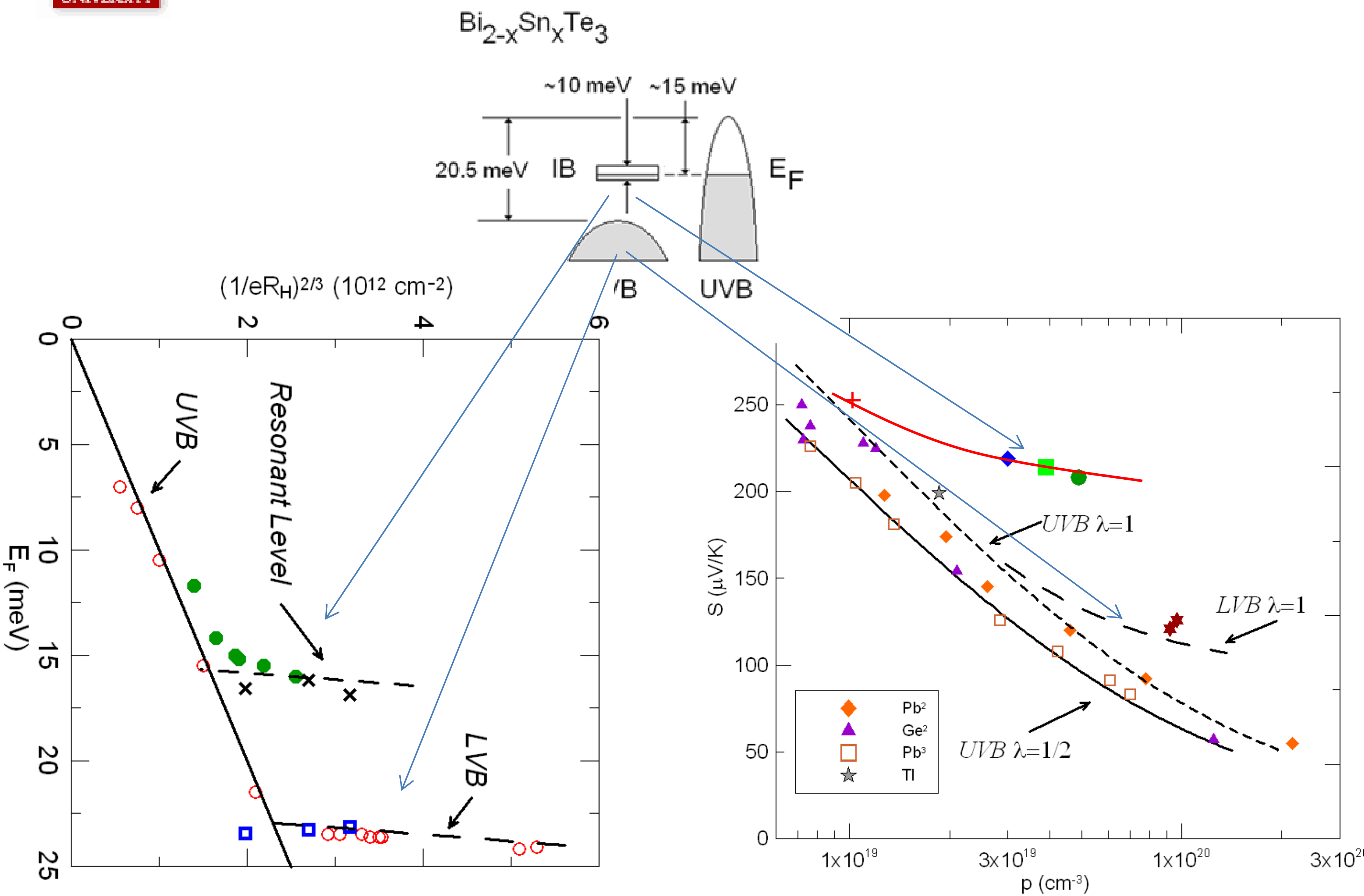




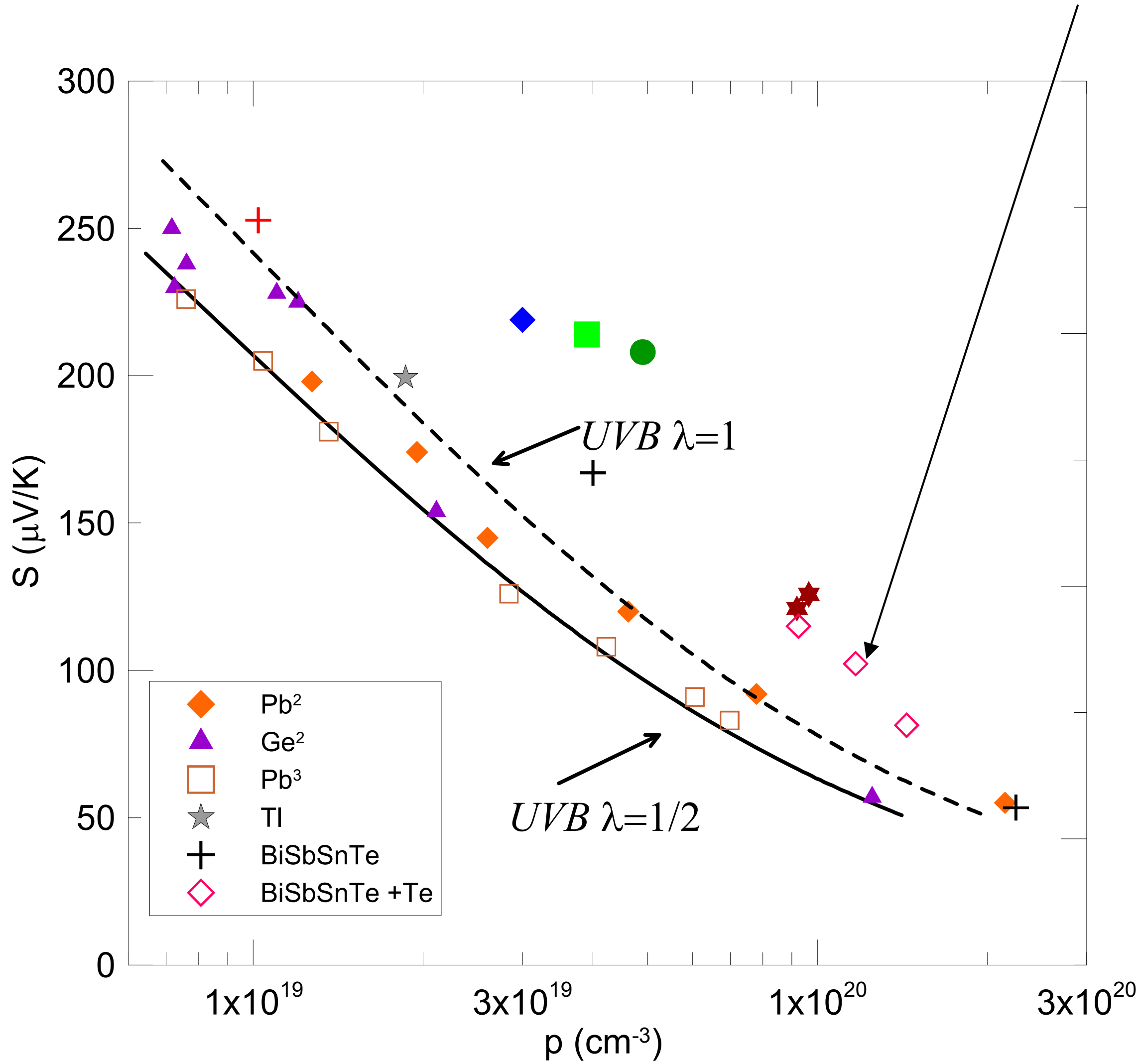
Resonant level much narrower (10 meV) than thallium in PbTe (30meV)

=> Optimization of Fermi level more delicate

Consistent data: SdH / Pisarenko



Extend to $(Bi_{30} Sb_{70})_2Te_3$

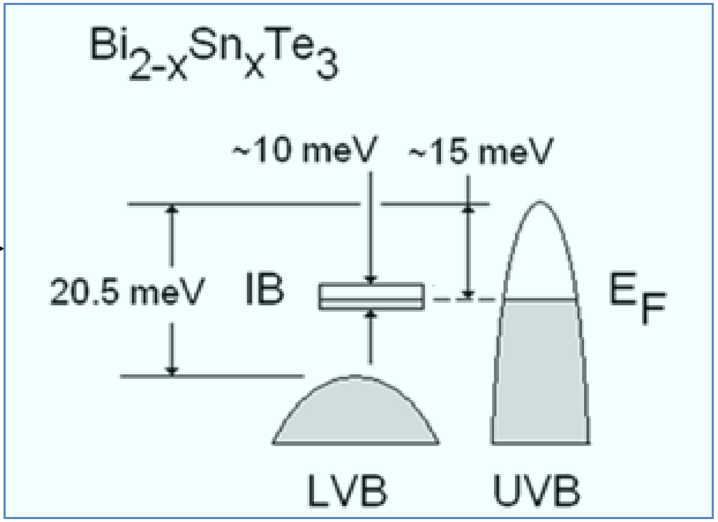


Sb more prone to antisite defects than Bi

=> Fermi level optimization is harder.

Conclusions

1. Correct picture for Bi2Te3 from SdH & method of 4 coefficients



2. Pisarenko relation for Bi2Te3 : Sn different from Bi2Te3 : (Ge, Sn, Pb)

3. Effect is due to an increase in effective mass,
   NOT resonant scattering as suggested by Zhitinskaya

4. Sn boosts thermopower EVEN at room temperature: Sn enhances power factor S^2n at useful temperatures for Peltier coolers

5. Resonant level much narrower (10 meV) than thallium in PbTe (30meV)
   => Optimization of Fermi level more delicate

6. Applicable to commercial $(Bi_{0.3}Sb_{0.7})_2Te_3$ – type alloys?
   YES: **ONGOING WORK**

Resonant scattering

Blandin & Friedel J. Phys. Rad. ***20*** *160 1959*