``Enseigner la recherche en train de se faire''

COLLÈGE
DE FRANCE
1530

Chaire de
Physique de la Matière Condensée

THERMOELECTRICITE: CONCEPTS, MATERIAUX ET ENJEUX ENERGETIQUES

Antoine Georges

Cycle 2012-2013

Cours 5 et 6 – 24 avril 2013

- I. General expressions of transport coefficients from:
- Boltzmann equation
- Kubo formula

II. Metals and correlated metals

- III. Heavily-doped semiconductors and classic thermoelectric materials (Bi_2Te_3)

Slides: key steps only; details in the notes (web) and on the board

Séminaires – 15 et 22 mai

- 15 mai, 10h00: Prof.Ctirad Uher (University of Michigan)

`Skutterudites – efficient novel thermoelectric materials for power generation applications'

- 22 mai, 10h00*: Dr Marek Koza, (ILL Grenoble)
- *[Preliminary title]: `Neutron scattering studies on skutterudites and other open structures : mechanism for low thermal conductivity'*

PLEASE COME !

I. The Boltzmann equation approach

$F(\vec{k}, \vec{r}, t)$ Local distribution function

Relaxation-time approximation:

$$\frac{dF}{dt} = -\frac{F - F_0}{\tau}$$

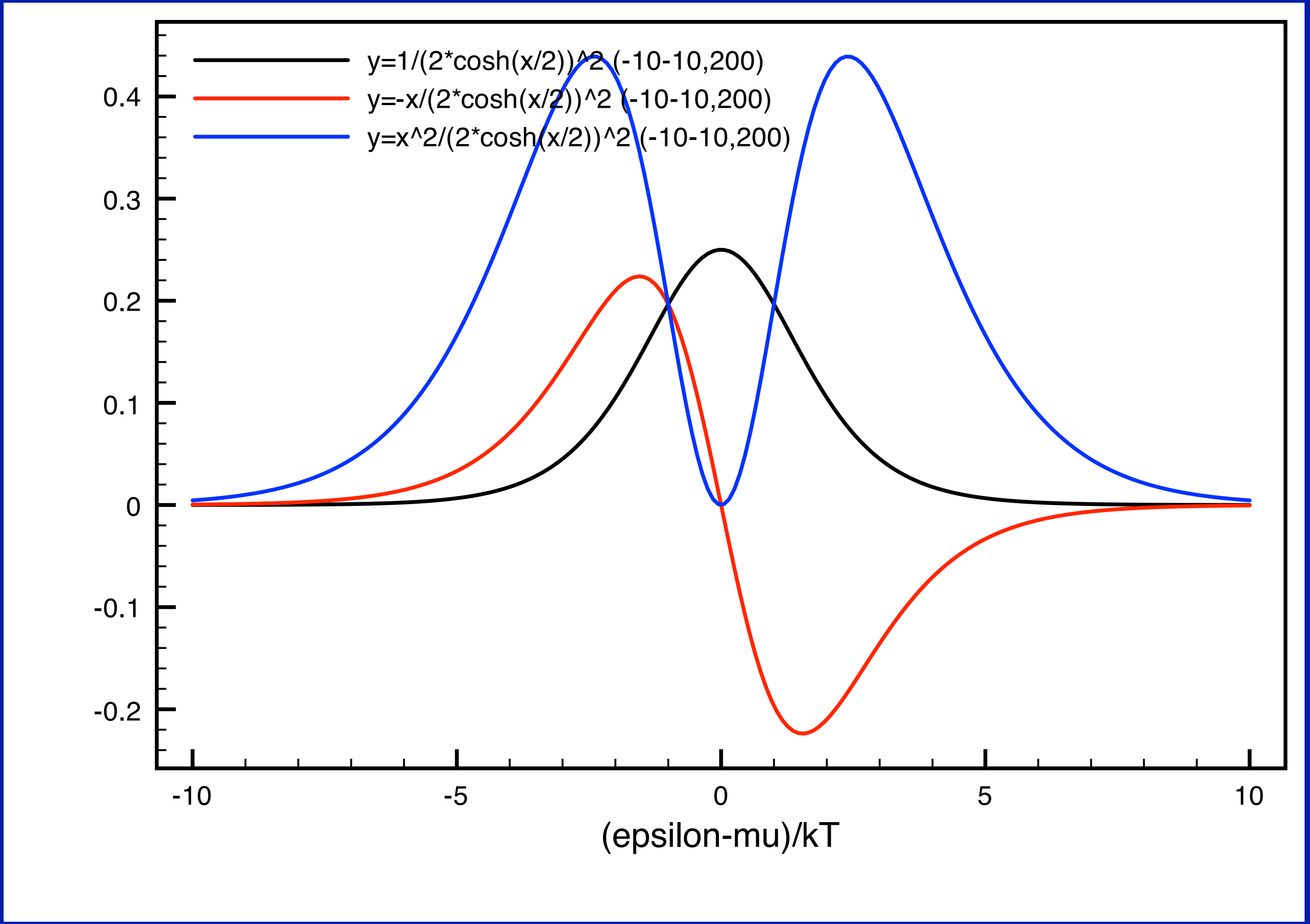
$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \dot{\boldsymbol{k}} \cdot \nabla_{\boldsymbol{k}} F + \dot{\boldsymbol{r}} \cdot \nabla_{\boldsymbol{r}} F$$

$$\mathcal{T}(\varepsilon) \equiv \frac{2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau(\varepsilon_{\mathbf{k}}) \left[\frac{1}{d} \sum_a (\nabla_{\boldsymbol{k}}^a \varepsilon_{\mathbf{k}})^2 \right] \delta(\varepsilon - \varepsilon_{\mathbf{k}})$$

(Dimensionality: $L^{2\text{-}d}$)

$$\begin{aligned} L_{11} &= \frac{1}{\hbar} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) \mathcal{T}(\varepsilon) \\ L_{12} &= \frac{1}{\hbar} \frac{1}{T} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) (\varepsilon - \mu) \mathcal{T}(\varepsilon) \\ L_{22} &= \frac{1}{\hbar} \frac{1}{T^2} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) (\varepsilon - \mu)^2 \mathcal{T}(\varepsilon) \end{aligned}$$

$$\sigma = e^2 L_{11} \; , \quad \alpha = -\frac{L_{12}}{e L_{11}} \; , \quad \kappa = T \left(L_{22} - \frac{L_{12}^2}{L_{22}} \right)$$



- Key role of particle-hole asymmetry
- Different coefficients probe different range of energy
- Conductivity → Fermi surface ; Thermal → A few kT away

II.1 Simple Metals

(with impurity/elastic scattering)

$$\sigma \simeq \frac{e^2}{\hbar} \mathcal{T}(\mu)$$

→ For free electron gas, Drude: $\sigma = \frac{ne^2\tau_i}{m}$

Cutler-Mott formula:

$$\boxed{\alpha \simeq -\frac{\pi^2}{3}\frac{k_B}{e}\frac{\mathcal{T}'(\mu)}{\mathcal{T}(\mu)} k_B T = -\frac{\pi^2}{3}\frac{k_B}{e} k_B T \frac{\partial}{\partial \mu} \ln \mathcal{T}(\mu)}$$

Wiedemann-Franz law:

$$\frac{\kappa/T}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

Lorenz number

Free-electron gas + impurities:

$$\alpha = -\frac{C_{el}/n}{e}$$

This relation
has apparently,
empirically,
a much wider
range of validity !
(including metals
with strong
electron
correlations)

Bhenia, Jaccard
& Flouquet
J Phys Cond Mat
16, 5187 (2004)

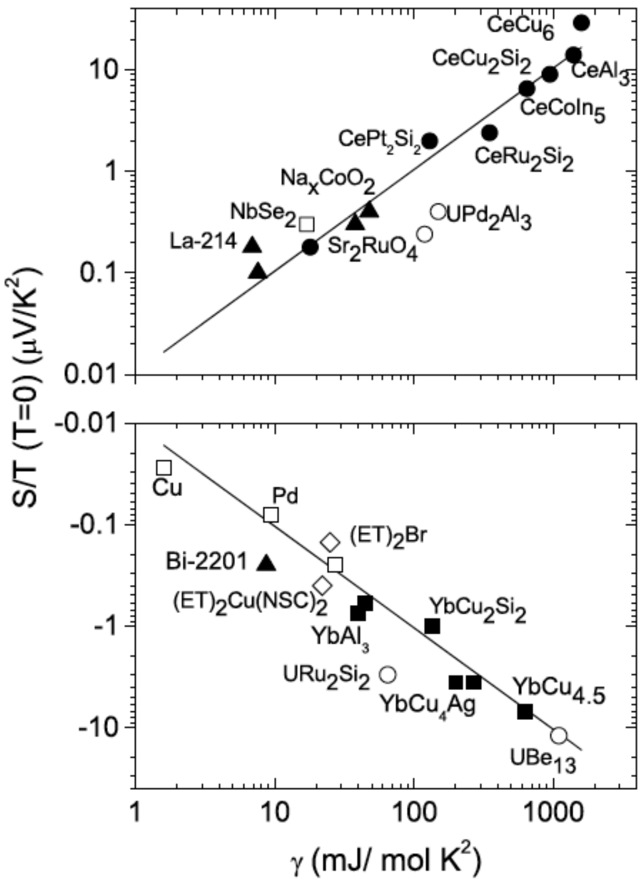


Figure 2. S/T versus γ for the compounds listed in table 1. Solid circles (squares) represent Ce (Yb) heavy-fermion systems. Uranium-based compounds are represented by open circles, metallic oxides by solid triangles, organic conductors by open diamonds, and common metals by open squares. For some data points, due to the lack of space, the name of the compound is not explicitly mentioned. See table 1 for the missing names. The two solid lines represent $\pm\gamma/(eN_{\mathrm{Av}})$.

I.2 - Onsager coefficients from Kubo formula

(continued from lecture 4)

- G.D. Mahan, Many-Particle Physics Sec. 3.8-3.9
- R. Kubo J.Phys Soc Jpn 12, 570 (1957)
- J.M. Luttinger Phys Rev 135, A1505 (1964)
- MR Peterson and BS Shastry PRB 82, 195105 (2010)
- Detailed derivation of thermal current and simplifications in DMFT: I.Paul and G.Kotliar PRB 67, 115131 (2003)

I will skip most details, just emphasizing some key (and sometimes subtle…) points

Currents and conjugate forces:

$$\frac{\partial S}{\partial t}\Big|_{\rm irr} = \sum_A J_A . X_A$$

$$A = N, S \;\Rightarrow\; X_N = -\frac{1}{T}\nabla\mu \;\; , \;\; X_S = -\frac{1}{T}\nabla T$$

Linear response: $J_A = \sum_B L_{AB}\, X_B$

$$\boxed{L_{AB} = -\frac{1}{\beta}\int_0^\infty dt e^{-st} \int_0^\beta d\tau\, {\rm Tr}\left[\hat{\rho}_0\, j_A(-t - i\tau) j_B(0)\right]}$$

$$L_{AB} = \pi \sum_{nm} e^{-\beta E_n} \langle n|j_A|m\rangle \langle m|j_B|n\rangle\, \delta(E_n - E_m)$$

Onsager symmetry is manifest on this form

Use of Kubo formula in practice –
- Two key steps:

- 1-Establish the expression of the currents
- (Easy for particle current, tricky for energy/heat current)
- 2-Evaluate correlation function
- Usually: perturbative or numerical methods

The currents

- Useful references:
- I.Paul & G.Kotliar Phys Rev B 67, 115131 (2003)
- M.Jonson and G.D.Mahan Phys Rev B 21, 4223 (1980)
- G.Beni Physical Review B 10, 2186 (1974)
- J.S. Langer, Phys Rev 128, 1101 (1962)

Key point:

- The particle/electrical current has a very simple expression, Which is teh free-particle one.
- The thermal current, in contrsat, involves in general quartic Terms which depend on the interaction part of the hamiltonian…

Apply Noether's method:

Symmetry of the action ←→ Conserved current/charge

$$
\begin{aligned}
L = {} & \frac{i}{2}\int d^3r(\psi^\dagger\dot{\psi} - \dot{\psi}^\dagger\psi) + \frac{1}{2m}\int d^3r\,\psi^\dagger(\boldsymbol{\nabla} - ie\mathbf{A}(r))^2\psi \\
& - \int d^3r\,V(r)\psi^\dagger\psi - \frac{e^2}{2}\int\int d^3r\,d^3r'\,\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}') \\
& \times \frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi(\mathbf{r}')\psi(\mathbf{r}). \qquad (1)
\end{aligned}
$$

- Number of particles: U(1)

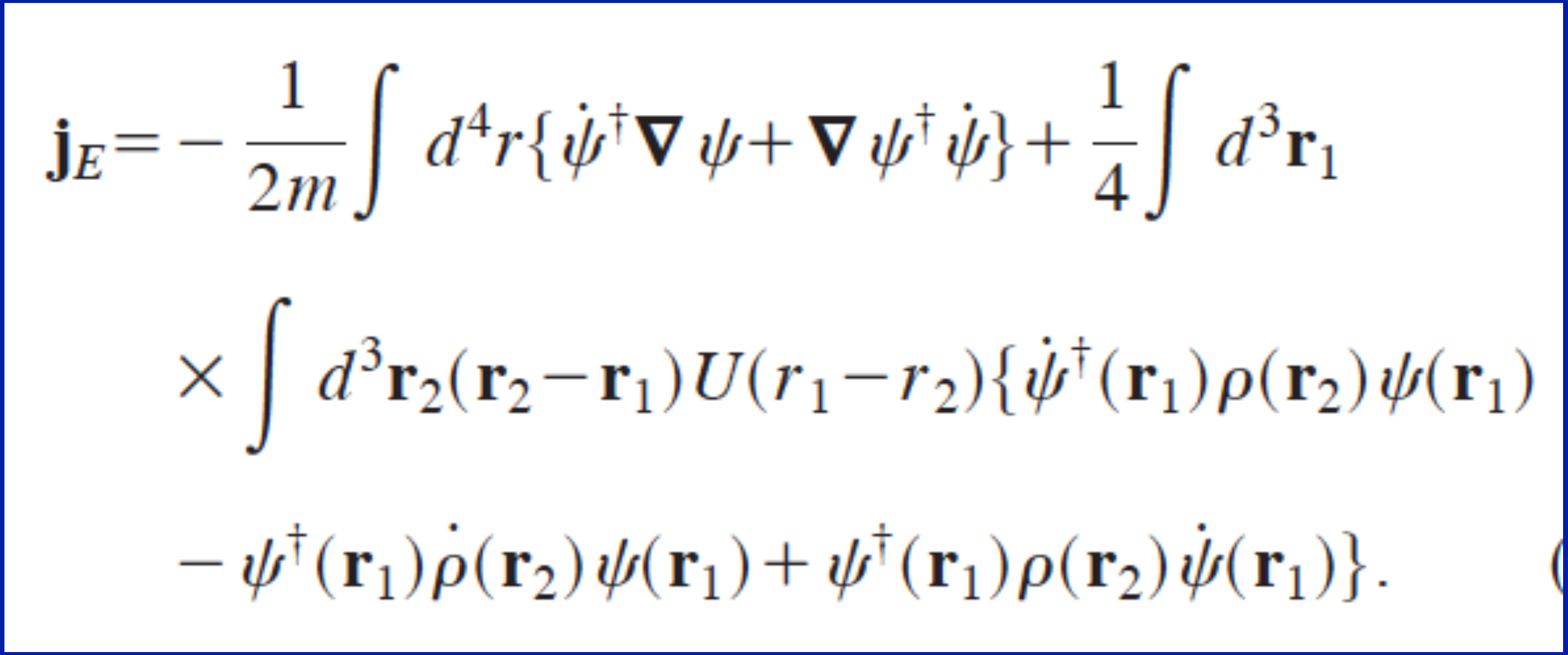
$$\psi(r) \to \psi(r)e^{i\phi(r)} \quad , \quad \psi^\dagger(r) \to \psi^\dagger(r)e^{-i\phi(r)}$$

Interaction term invariant (→ 0)

$$j = -\frac{ie}{m}\int dr\,\psi^\dagger(r)[\nabla - ieA(r)]\psi(r) \to -e\sum_k v_k c_k^\dagger c_k$$

Thermal (energy) current: this is NOT the case !

Ttime translation: $t \rightarrow t - \phi(r, t)$



$$\mathbf{j}_E = -\frac{1}{2m}\int d^4r\{\dot{\psi}^\dagger \boldsymbol{\nabla}\psi + \boldsymbol{\nabla}\psi^\dagger\dot{\psi}\} + \frac{1}{4}\int d^3\mathbf{r}_1$$

$$\times\int d^3\mathbf{r}_2(\mathbf{r}_2 - \mathbf{r}_1)U(r_1 - r_2)\{\dot{\psi}^\dagger(\mathbf{r}_1)\rho(\mathbf{r}_2)\psi(\mathbf{r}_1)$$

$$-\psi^\dagger(\mathbf{r}_1)\dot{\rho}(\mathbf{r}_2)\psi(\mathbf{r}_1) + \psi^\dagger(\mathbf{r}_1)\rho(\mathbf{r}_2)\dot{\psi}(\mathbf{r}_1)\}.$$

$$\mathcal{H}=\sum_{\substack{ij\\ \mu\nu\\ \sigma}} t_{ij}^{\mu\nu}c_{i\sigma}^{\dagger\mu}c_{j\sigma}^{\nu}+\sum_{\substack{ij\\ \mu\nu\\ \sigma\sigma'}} V_{ij,\sigma\sigma'}^{\mu\nu}n_{i\sigma}^{\mu}n_{j\sigma'}^{\nu}\,, \tag{12}$$

using the equation of motion technique. Here $n_{i\sigma}^{\mu}=c_{i\sigma}^{\dagger\mu}c_{i\sigma}^{\mu}$. The local energy density (h_i) is given by

$$h_i=\frac{1}{2}\sum_{\substack{j\\ \mu\nu\\ \sigma}} (t_{ij}^{\mu\nu}c_{i\sigma}^{\dagger\mu}c_{j\sigma}^{\nu}+t_{ji}^{\nu\mu}c_{j\sigma}^{\dagger\nu}c_{i\sigma}^{\mu})$$

$$+\frac{1}{2}\sum_{\substack{j\\ \mu\nu\\ \sigma\sigma'}} (V_{ij,\sigma\sigma'}^{\mu\nu}n_{i\sigma}^{\mu}n_{j\sigma'}^{\nu}+V_{ji,\sigma'\sigma}^{\nu\mu}n_{j\sigma'}^{\nu}n_{i\sigma}^{\mu}).$$

[redacted]

[redacted]

$$\dot{h}_i=\frac{1}{2}\sum_{\substack{j\\ \mu\nu\\ \sigma}} \{t_{ij}^{\mu\nu}(c_{i\sigma}^{\dagger\mu}\dot{c}_{j\sigma}^{\nu}-\dot{c}_{i\sigma}^{\dagger\mu}c_{j\sigma}^{\nu})+t_{ji}^{\nu\mu}(\dot{c}_{j\sigma}^{\dagger\nu}c_{i\sigma}^{\mu}-c_{j\sigma}^{\dagger\nu}\dot{c}_{i\sigma}^{\mu})\}$$

$$+\frac{1}{2}\sum_{\substack{j\\ \mu\nu\\ \sigma\sigma'}} V_{ij,\sigma\sigma'}^{\mu\nu}(-\dot{c}_{i\sigma}^{\dagger\mu}c_{j\sigma'}^{\dagger\nu}c_{j\sigma'}^{\nu}c_{i\sigma}^{\mu}+c_{i\sigma}^{\dagger\mu}\dot{c}_{j\sigma'}^{\dagger\nu}c_{j\sigma'}^{\nu}c_{i\sigma}^{\mu}$$

$$+c_{i\sigma}^{\dagger\mu}c_{j\sigma'}^{\dagger\nu}\dot{c}_{j\sigma'}^{\nu}c_{i\sigma}^{\mu}-c_{i\sigma}^{\dagger\mu}c_{j\sigma'}^{\dagger\nu}c_{j\sigma'}^{\nu}\dot{c}_{i\sigma}^{\mu})$$

$$+\frac{1}{2}\sum_{\substack{j\\ \mu\nu\\ \sigma\sigma'}} V_{ji,\sigma'\sigma}^{\nu\mu}(\dot{c}_{j\sigma'}^{\dagger\nu}c_{i\sigma}^{\dagger\mu}c_{i\sigma}^{\mu}c_{j\sigma'}^{\nu}-c_{j\sigma'}^{\dagger\nu}\dot{c}_{i\sigma}^{\dagger\mu}c_{i\sigma}^{\mu}c_{j\sigma'}^{\nu}$$

$$-c_{j\sigma'}^{\dagger\nu}c_{i\sigma}^{\dagger\mu}\dot{c}_{i\sigma}^{\mu}c_{j\sigma'}^{\nu}+c_{j\sigma'}^{\dagger\nu}c_{i\sigma}^{\dagger\mu}c_{i\sigma}^{\mu}\dot{c}_{j\sigma'}^{\nu}), \tag{13}$$

$$
\begin{aligned}
\mathbf{j}_E = & \frac{i}{2} \sum_{\substack{\mathbf{k} \\ \mu\nu \\ \sigma}} \boldsymbol{\nabla}_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\mu\nu} \left(c_{\mathbf{k},\sigma}^{\dagger\mu} \dot{c}_{\mathbf{k},\sigma}^{\nu} - \dot{c}_{\mathbf{k},\sigma}^{\dagger\mu} c_{\mathbf{k},\sigma}^{\nu} \right) \\
& + \frac{i}{2} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ \mu\nu \\ \sigma\sigma'}} \boldsymbol{\nabla}_{\mathbf{k}} V_{\mathbf{k},\sigma\sigma'}^{\mu\nu} \left(c_{\mathbf{k}',\sigma}^{\dagger\mu} \dot{n}_{\mathbf{k},\sigma'}^{\nu} c_{\mathbf{k}'-\mathbf{k},\sigma}^{\mu} \right. \\
& \left. - \dot{c}_{\mathbf{k}',\sigma}^{\dagger\mu} n_{\mathbf{k},\sigma'}^{\nu} c_{\mathbf{k}'-\mathbf{k},\sigma}^{\mu} - c_{\mathbf{k}',\sigma}^{\dagger\mu} n_{\mathbf{k},\sigma'}^{\nu} \dot{c}_{\mathbf{k}'-\mathbf{k},\sigma}^{\mu} \right),
\end{aligned}
$$

Single-band Hubbard model:

$$\mathbf{j}_Q = \frac{i}{2} \sum_{\mathbf{k},\sigma} \mathbf{v}_{\mathbf{k}} \left(c^{\dagger}_{\mathbf{k},\sigma} \dot{c}_{\mathbf{k},\sigma} - \dot{c}^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} \right)$$

$$= \frac{1}{2} \sum_{\substack{\langle ij \rangle \\ \sigma}} (\mathbf{R}_i - \mathbf{R}_j) t_{ij} \left(c^{\dagger}_{i,\sigma} \dot{c}_{j,\sigma} - \dot{c}^{\dagger}_{i,\sigma} c_{j,\sigma} \right).$$

But, beware…

$$\dot{c}_{i,\sigma} = -i \Sigma_l t_{il} c_{l,\sigma} - i U c_{i,\sigma} n_{i,\bar{\sigma}} + i \mu c_{i,\sigma}$$

cf. Beni, PRB 1974

Interacting system: Evaluation of correlators in DMFT

Vertex corrections and quartic terms in the thermal current do not contribute and one can simply evaluate <j.j> from its factorized term involving 2 Green’s functions (Proof: Paul & Kotliar, PRB 2003)

$$L_{11}(i\omega_n) = -\left(\frac{e^2}{d}\right)\left(\frac{1}{\beta i\omega_n V}\right)\sum_{\mathbf{k},\sigma} v_{\mathbf{k}}^2 \frac{1}{\beta} \times \sum_{ip_n} \mathcal{G}_\sigma(\mathbf{k}, i\omega_n + ip_n)\mathcal{G}_\sigma(\mathbf{k}, ip_n).$$

→

$$\boxed{\mathcal{T}(\omega) = \frac{2}{\hbar}\int d\varepsilon \Phi(\varepsilon)\, A(\varepsilon,\omega)^2}$$

Note formal similarity betwen the expressions established in the Boltzmann and Kubo frameworks

$$\mathcal{T}(\omega) = \frac{2}{\hbar}\int d\varepsilon \Phi(\varepsilon)\, A(\varepsilon,\omega)^2$$

Transport function (d.o.s weighted by velocities):

$$\Phi(\varepsilon) = \int \frac{d^d k}{(2\pi)^d} \left[\frac{1}{d}\sum_a (\nabla_{\boldsymbol{k}}^a \varepsilon_{\mathbf{k}})^2\right] \delta(\varepsilon - \varepsilon_{\mathbf{k}})$$

Also, formal similarity with Landauer formula: transmission coefficient $\mathcal{T}(\varepsilon)$ → Lectures in Fall 2013

II.2 Metals with strong electron correlations

Low T → Focus on low-energy quasiparticles

$$\mathcal{T}(\omega,T) \simeq \frac{1}{\pi\hbar}\,\Phi\left[\overline{\mu}(T)+\frac{\omega}{Z}\right]\,\tau_{ee}(\omega,T)$$

$$\gamma(\omega,T) \equiv \frac{\hbar}{\tau_{ee}(\omega,T)} = |\Sigma_2(\omega,T)| \simeq C_\Sigma^{-1}\left[(\hbar\omega)^2+(\pi k_B T)^2\right]$$

Note: the quasiparticle weight Z does NOT enter
(not to be confused with QP lifetime)

Conductivity (electrical and thermal)

Wiedemann-Franz law for correlated metals

Assume first no impurity scattering:

T^2 resistivity:

$$\rho = AT^2 \quad , \quad A = \frac{\hbar}{e^2}\,\frac{\pi k_B^2}{I_1^0 C_\Sigma\, \Phi(\varepsilon_F)}$$

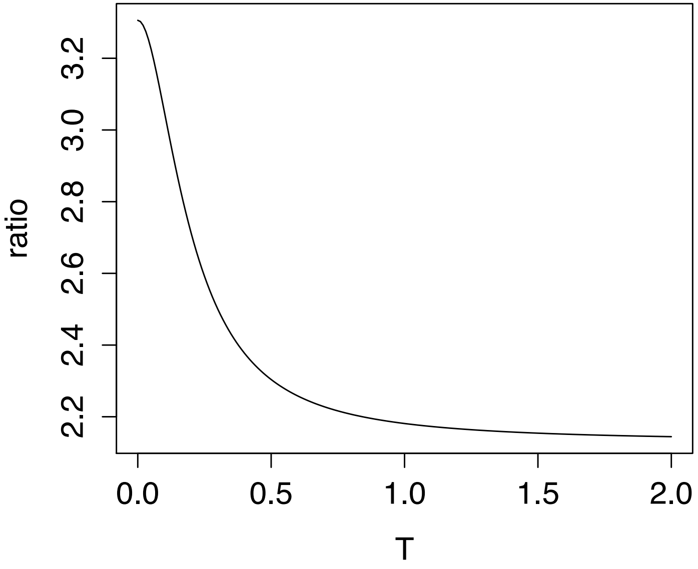
Non-standard value of the Lorenz number:

$$\mathcal{L}_{ee} \equiv \frac{\kappa/T}{\sigma} = \left(\frac{k_B}{e}\right)^2 \frac{I_1^2}{I_1^0} \simeq 2.14 \left(\frac{k_B}{e}\right)^2$$

Combining (naively) e-e interactions and impurity scattering:

$$\rho(\overline{T}) = \rho_i \frac{I_0(0)}{I_0(\overline{T})} \;,\; \mathcal{L}(\overline{T}) = \left(\frac{k_B}{e}\right)^2 \frac{I_2(\overline{T})}{I_0(\overline{T})}$$

$$I_{\{0,2\}}(\overline{T}) \equiv \int_{-\infty}^{+\infty} dx \frac{1}{4\cosh^2\frac{x}{2}} \frac{\{1, x^2\}}{1+\overline{T}^2(x^2+\pi^2)}$$



$$\overline{T} = \sqrt{I_1^0}\sqrt{\frac{AT^2}{\rho_i}} \simeq 0.29\sqrt{\frac{AT^2}{\rho_i}}$$

Experimental observation ?

Thermopower of correlated metals at low-T: The dominant linear low-T behaviour involves **corrections to Fermi Liquid theory !** [Particle-hole asymmetry of the scattering rate]

(Haule and Kotliar, arXiv:0907.0192) in "Properties and Applications of Thermoelectric Materials", Edited by V. Zlatic and A.C. Hewson, Springer

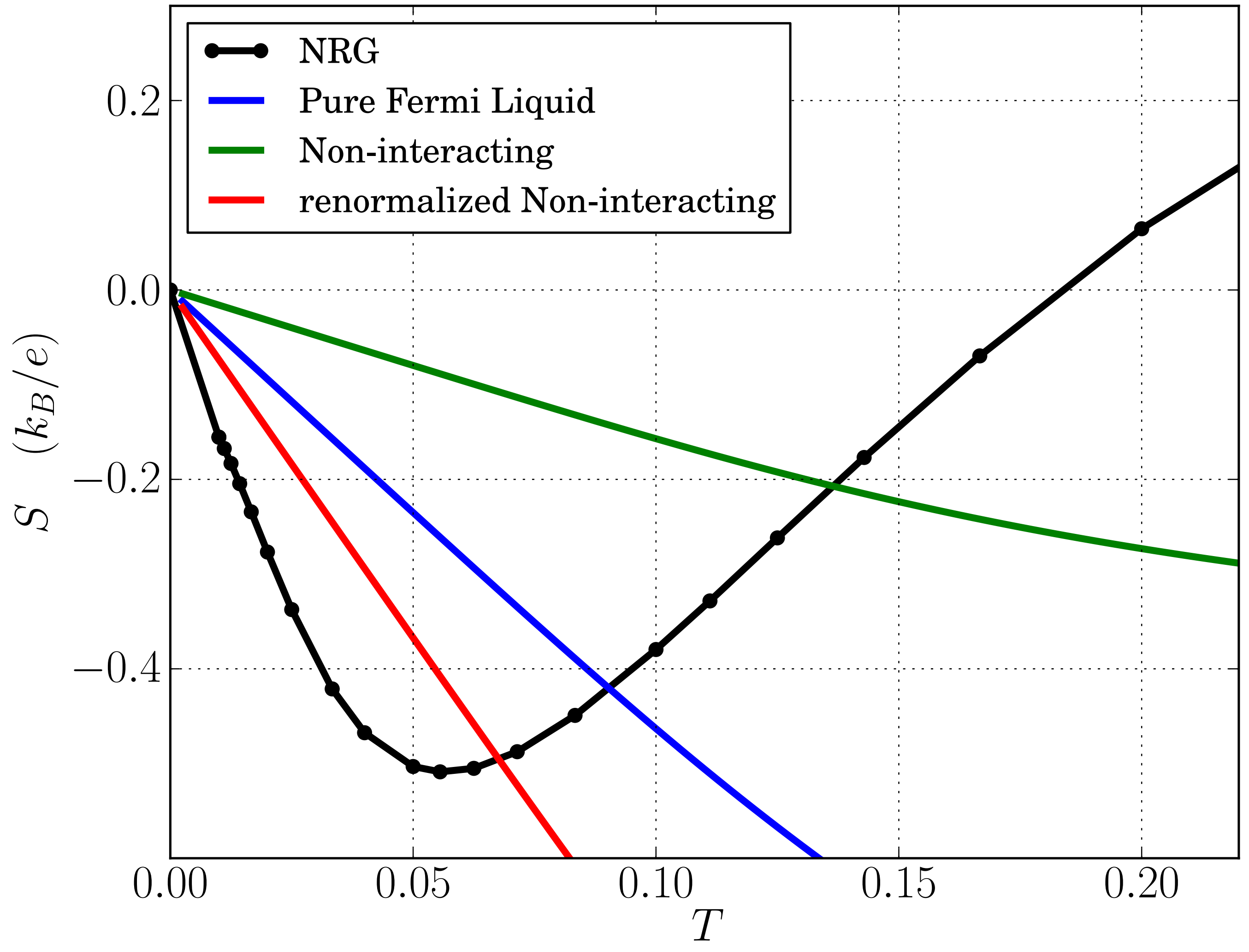
$$\Sigma''(\omega) = \Sigma^{(2)}(\omega) + \Sigma^{(3)}(\omega) + \cdots$$

$$\Sigma^3(\omega) = \frac{(a_1\omega^3 + a_2\,\omega T^2)}{Z^3}$$

Slope enhanced by 1/Z
ss in specific heat cf. `BJF law’

$$E_n^k = \int_{-\infty}^{\infty} \frac{x^n dx}{4\cosh^2(x/2)[1+(x/\pi)^2]^k}$$

$$S = \boxed{-\frac{k_B}{|e|}\frac{k_B T}{Z}} \left[\boxed{\frac{\Phi'(\mu_0)}{\Phi(\mu_0)}\frac{E_2^1}{E_0^1}} - \boxed{\frac{a_1 E_4^2 + a_2 E_2^2}{\gamma_0 E_0^1}} \right]$$

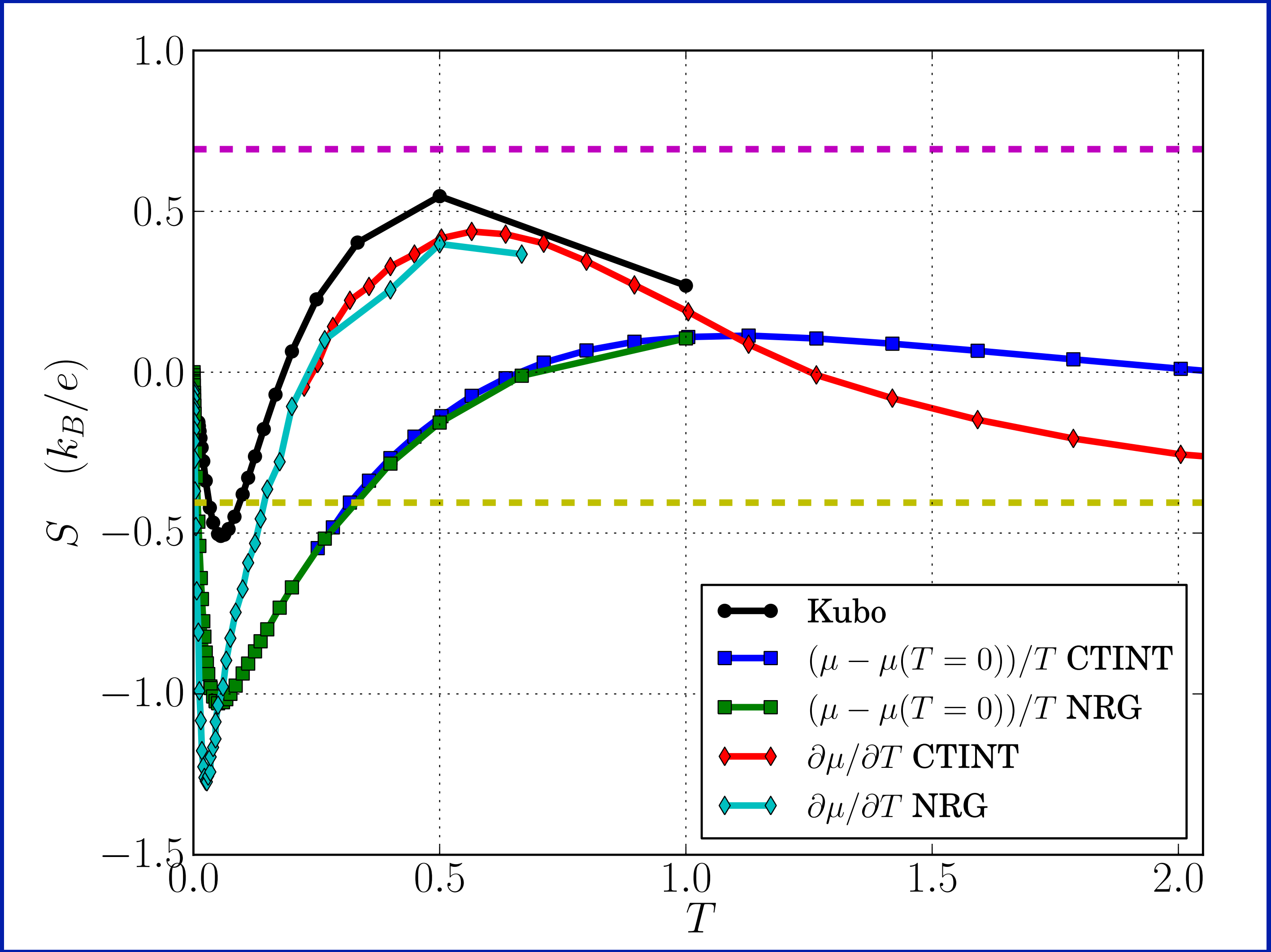



PRL **110,** 086401 (2013) PHYSICAL REVIEW LETTERS week ending 22 FEBRUARY 2013

How Bad Metals Turn Good: Spectroscopic Signatures of Resilient Quasiparticles

Xiaoyu Deng,[1,2,3] Jernej Mravlje,[4,1,5] Rok Žitko,[5] Michel Ferrero,[1] Gabriel Kotliar,[3] and Antoine Georges[4,1,6,2]

Much broader range of temperature: crossover into Heikes-like hi-T regimes (cf. lecture 3).



III. Heavily doped semiconductors

As already emphasized in lecture 1 and
in the seminars, most thermoelectric materials
of current prcatical interest (e.g. Bi_2Te_3) are
semiconductors, with rather large density of carriers
(~ 10^{20} /cm^3) i.e. in the intermediate range
between semiconductors and metals

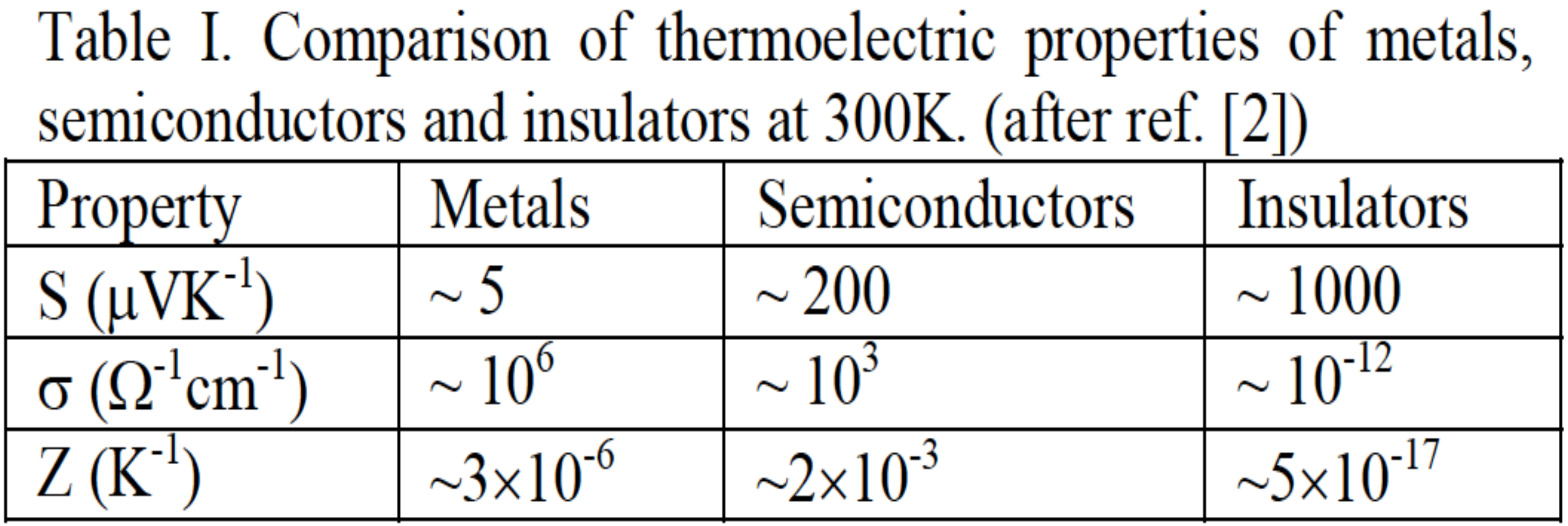
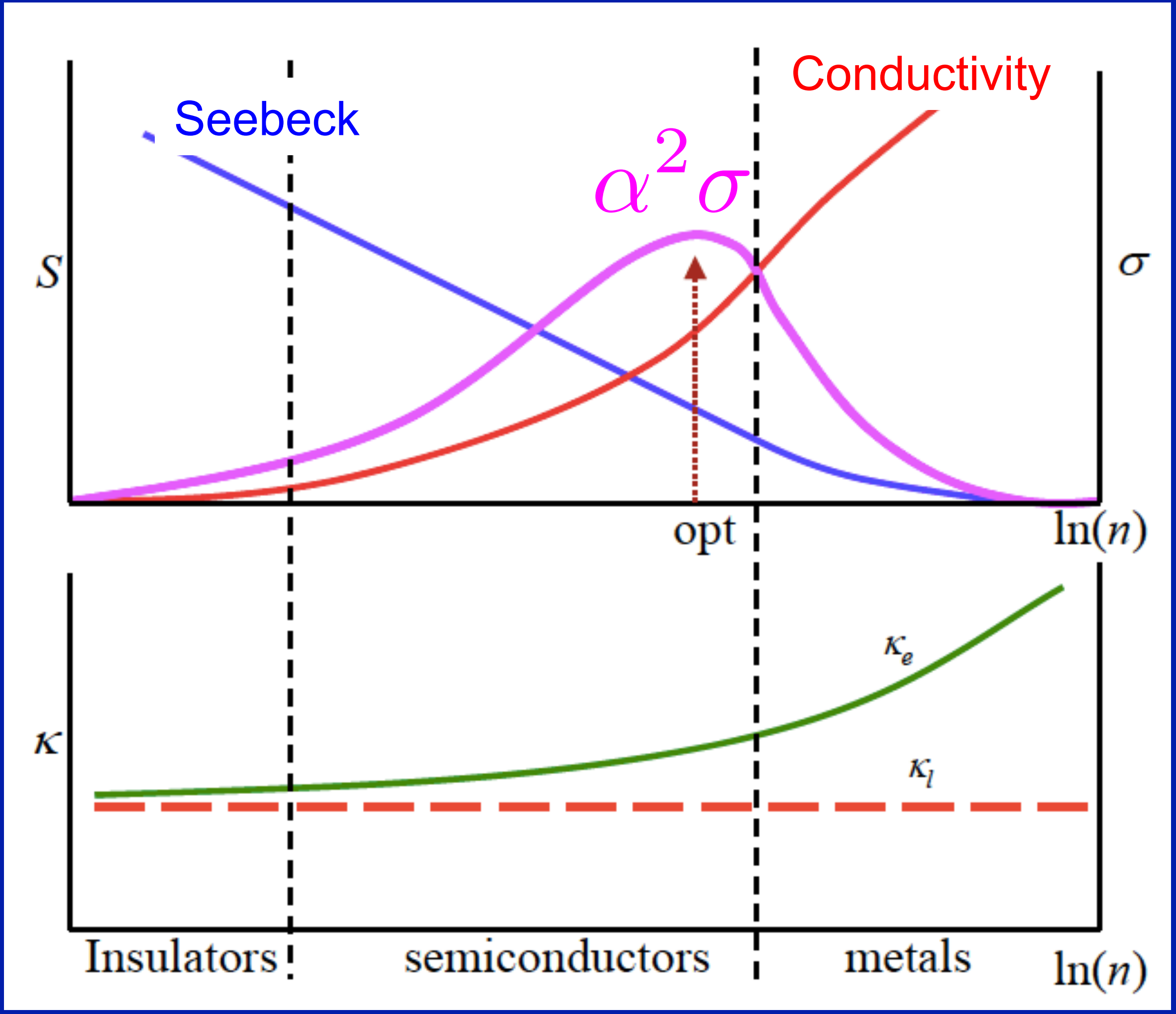


Table I. Comparison of thermoelectric properties of metals, semiconductors and insulators at 300K. (after ref. [2])

Property	Metals	Semiconductors	Insulators
S (μVK^{-1})	~ 5	~ 200	~ 1000
σ ($\Omega^{-1}cm^{-1}$)	~ 10^{6}	~ 10^{3}	~ 10^{-12}
Z (K^{-1})	~3×10^{-6}	~2×10^{-3}	~5×10^{-17}

Semiconductors and the first golden age of thermoelectricity: 1950 → ~ 1965



→ Optimal range of carrier concentration (~ 10^{19}-10^{20} /cm^3)

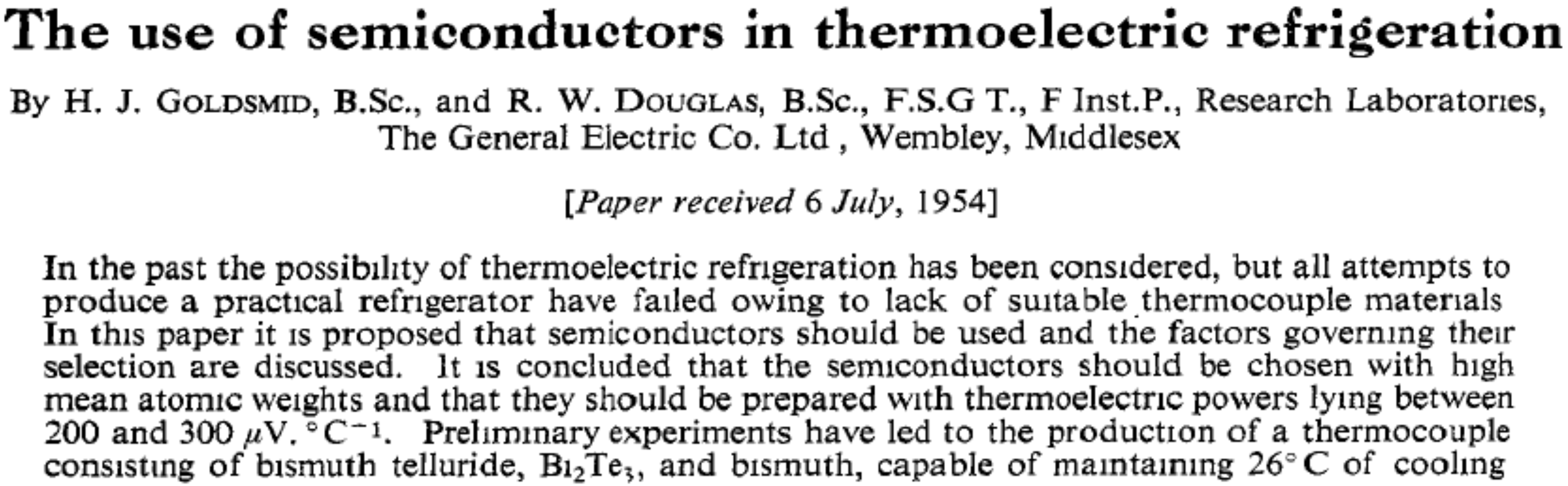
Abram Ioffe (1880-1960)

- Prominent physicist, Soviet Union
- Pioneer of semiconductor physics, use of semiconductors as thermoelectrics, and much more…
- Also the author of the `Ioffe-Regel – Mott' criterion
- Directed PhD's of Aleksandrov, Davydov, Frenkel, Kapitsa, Kurchatov, etc…
- Ioffe Physico-Technical Institute in St Petersburg bears his name
- Stalin Prize, Lenin prize, Hero of Socialist Labor
- Author of books `Semiconductor thermoelements' and `Thermoelectric cooling' (1957)

H.J. Goldsmid (U. of New South Wales, Australia): Bi_2Te_3 and thermoelectric cooling (1954)

Author of several books, especially: `Introduction to Thermoelectricity’ (Springer, 2010)
– Recommended reading

(British J. Appl. Phys. 5 (1954) 386)



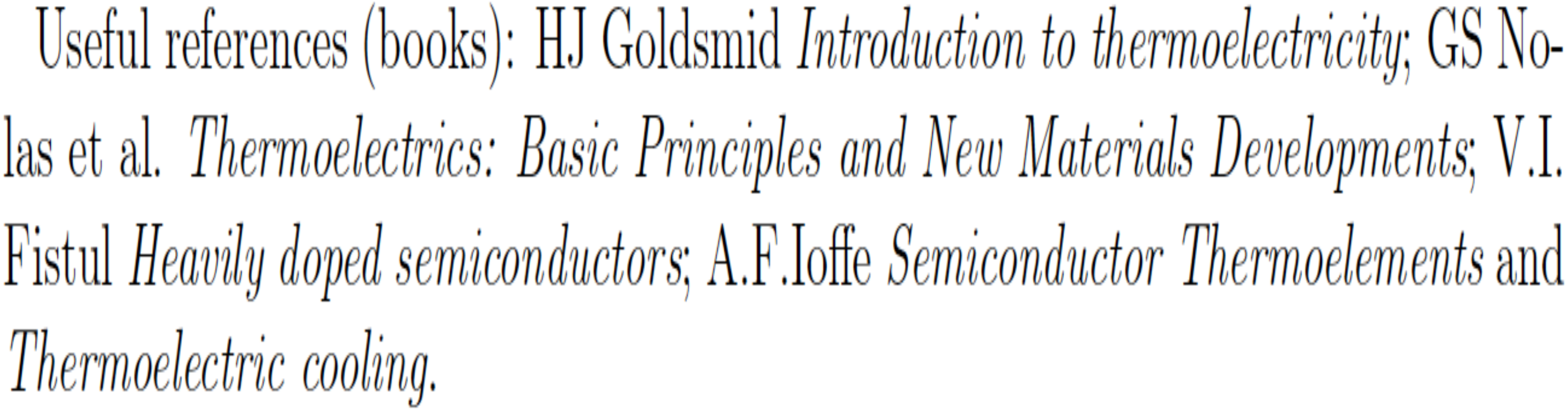
The use of semiconductors in thermoelectric refrigeration

By H. J. GOLDSMID, B.Sc., and R. W. DOUGLAS, B.Sc., F.S.G T., F Inst.P., Research Laboratories,
The General Electric Co. Ltd , Wembley, Middlesex

[*Paper received 6 July*, 1954]

In the past the possibility of thermoelectric refrigeration has been considered, but all attempts to produce a practical refrigerator have failed owing to lack of suitable thermocouple materials In this paper it is proposed that semiconductors should be used and the factors governing their selection are discussed. It is concluded that the semiconductors should be chosen with high mean atomic weights and that they should be prepared with thermoelectric powers lying between 200 and 300 $\mu V. {}^\circ C^{-1}$. Preliminary experiments have led to the production of a thermocouple consisting of bismuth telluride, Bi_2Te_3, and bismuth, capable of maintaining 26° C of cooling

Useful references (books) :


Useful references (books): HJ Goldsmid *Introduction to thermoelectricity*; GS Nolas et al. *Thermoelectrics: Basic Principles and New Materials Developments*; V.I. Fistul *Heavily doped semiconductors*; A.F.Ioffe *Semiconductor Thermoelements* and *Thermoelectric cooling*.

Summary of key expressions

(Derivation on blackboard, see notes on the website)

These expressions are for a single type of carriers
(e.g. electrons in the conduction band)

Chemical potential
counted from the bottom of the conduction band :

$$\delta\mu \quad , \quad \left(\eta \equiv \frac{\delta\mu}{k_B T}\right)$$

Scattering time and Transport function:

$$\tau(\varepsilon) \sim (\varepsilon - \varepsilon_c)^r \quad , \quad \Phi(\varepsilon) \sim (\varepsilon - \varepsilon_c)^\phi$$

[Scattering by acoustic phonons: r = -1/2]
[Parabolic band: φ=3/2]

Thermopower:

(Note the first term δμ/kT)

$$\alpha = \frac{k_B}{e}\left[\eta - \frac{r+\phi+1}{r+\phi}\,\frac{F_{r+\phi}(\eta)}{F_{r+\phi-1}(\eta)}\right]$$

Lorenz number:

$$\left(\frac{e}{k_B}\right)^2 \mathcal{L}_e(\eta) = \frac{r+\phi+2}{r+\phi}\,\frac{F_{r+\phi+1}(\eta)}{F_{r+\phi-1}(\eta)} - \left(\frac{r+\phi+1}{r+\phi}\right)^2 \left(\frac{F_{r+\phi}(\eta)}{F_{r+\phi-1}(\eta)}\right)^2$$

Fermi integrals:

$$F_n(\eta) \equiv \int_0^\infty dx\, \frac{x^n}{1+e^{x-\eta}}$$

- Density of carriers (parabolic band):

$$\boxed{n \;=\; 4\pi\,\left(\frac{2m_c k_B T}{h^2}\right)^{3/2}\;F_{1/2}(\eta)} \qquad (5$$

- Mobility (parabolic band) - not to be confused with chemical potential-:

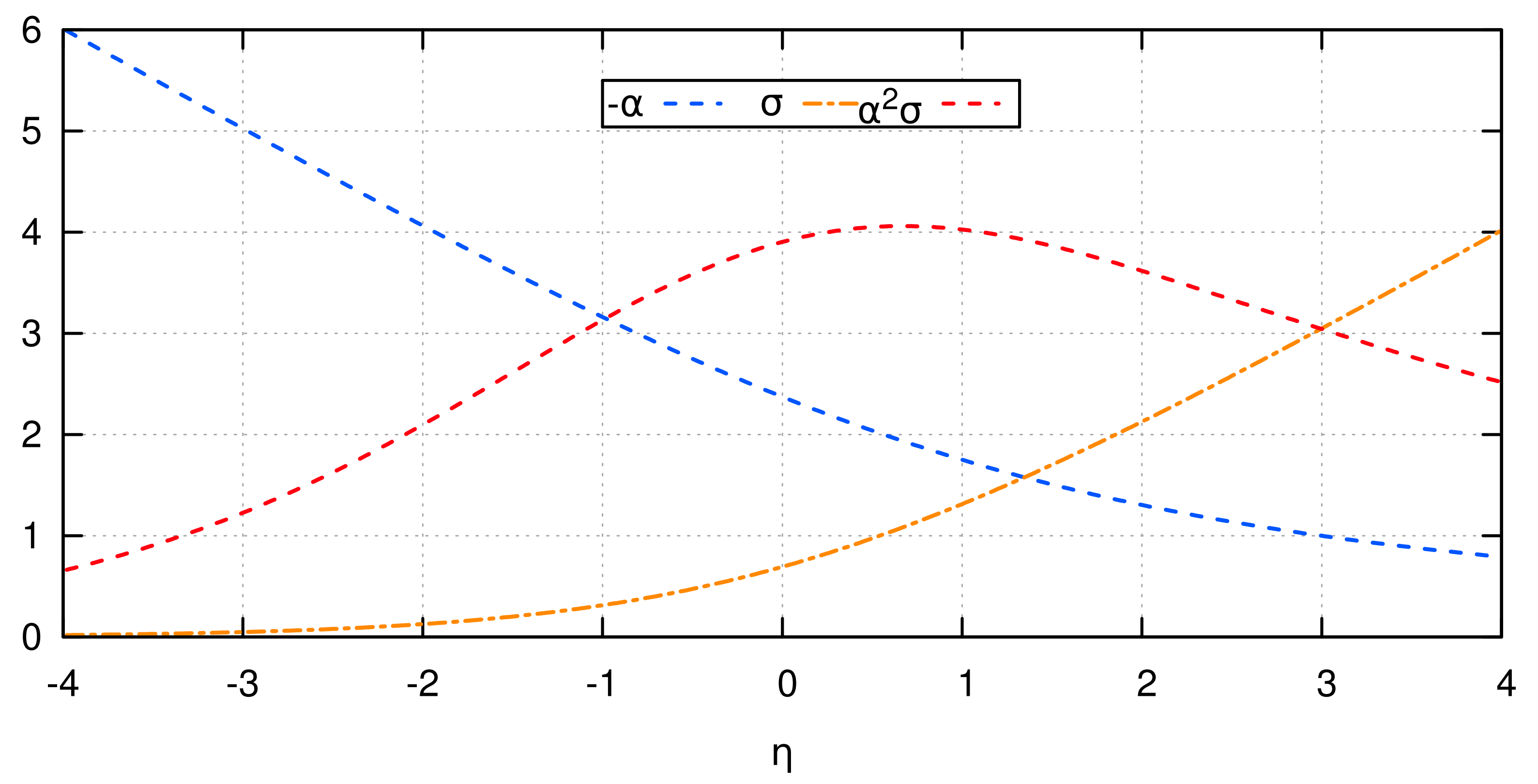
$$\boxed{\mu(T,\eta) \;=\; \frac{e\,\tau(T)}{m_c}\,\frac{2}{3}(r+\frac{3}{2})\,\frac{F_{r+1/2}(\eta)}{F_{1/2}(\eta)} \;\;,\;\; \tau(T) \equiv \tau(\varepsilon = k_B T) \simeq C_\tau (k_B T)^r}$$

- Conductivity (parabolic band):

$$\boxed{\sigma \;=\; n\,e\,\mu(T,\eta) \;=\; \sigma_0(T)\,\frac{F_{r+1/2}(\eta)}{\Gamma(r+3/2)} \;\;,}$$

$$\boxed{\sigma_0(T) = \frac{8\pi}{3}\Gamma(r+\frac{5}{2})\,\left(\frac{2m_c k_B T}{h^2}\right)^{3/2}\,\frac{e\,\tau(T)}{m_c}}$$

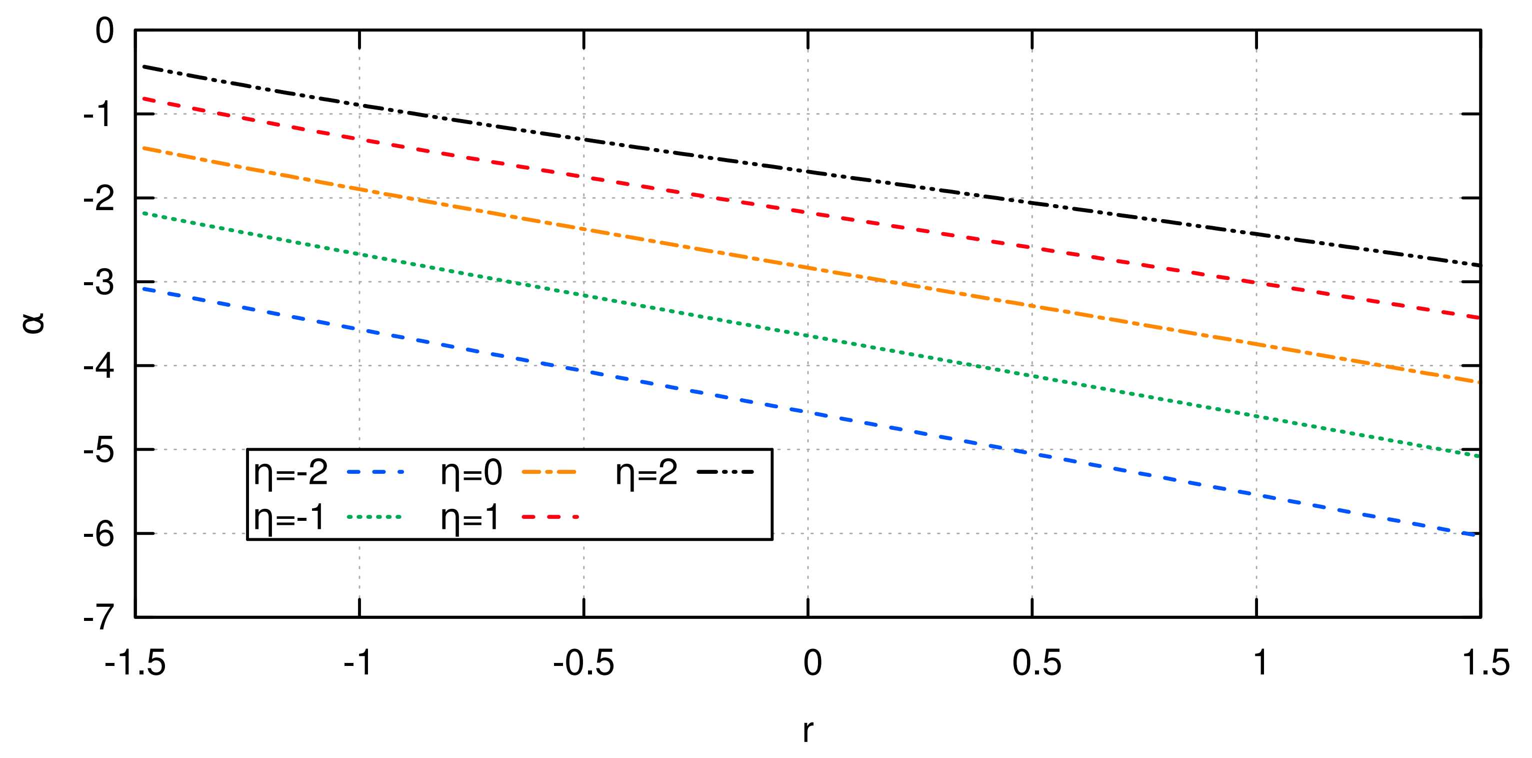
Power factor, conductivity and Seebeck vs. chemical potential:



Optimum for η ~ 0-1, corresponding to n ~ 10^{20}/cm^3
Optimum ZT for η ~ -0.5, n~10^{19}
→ Optimum Seebeck around 200 μV/K

Acoustic phonon scattering r=-1/2 assumed in this plot

N.B: Dependence on scattering mechanism (r-parameter)



Materials selection criteria

Introduce materials-specific parameter :
(Chasmar and Stratton, 1959)

$$\boxed{\beta \equiv \left(\frac{k_B}{e}\right)^2 \frac{\sigma_0}{\kappa_L/T}}$$

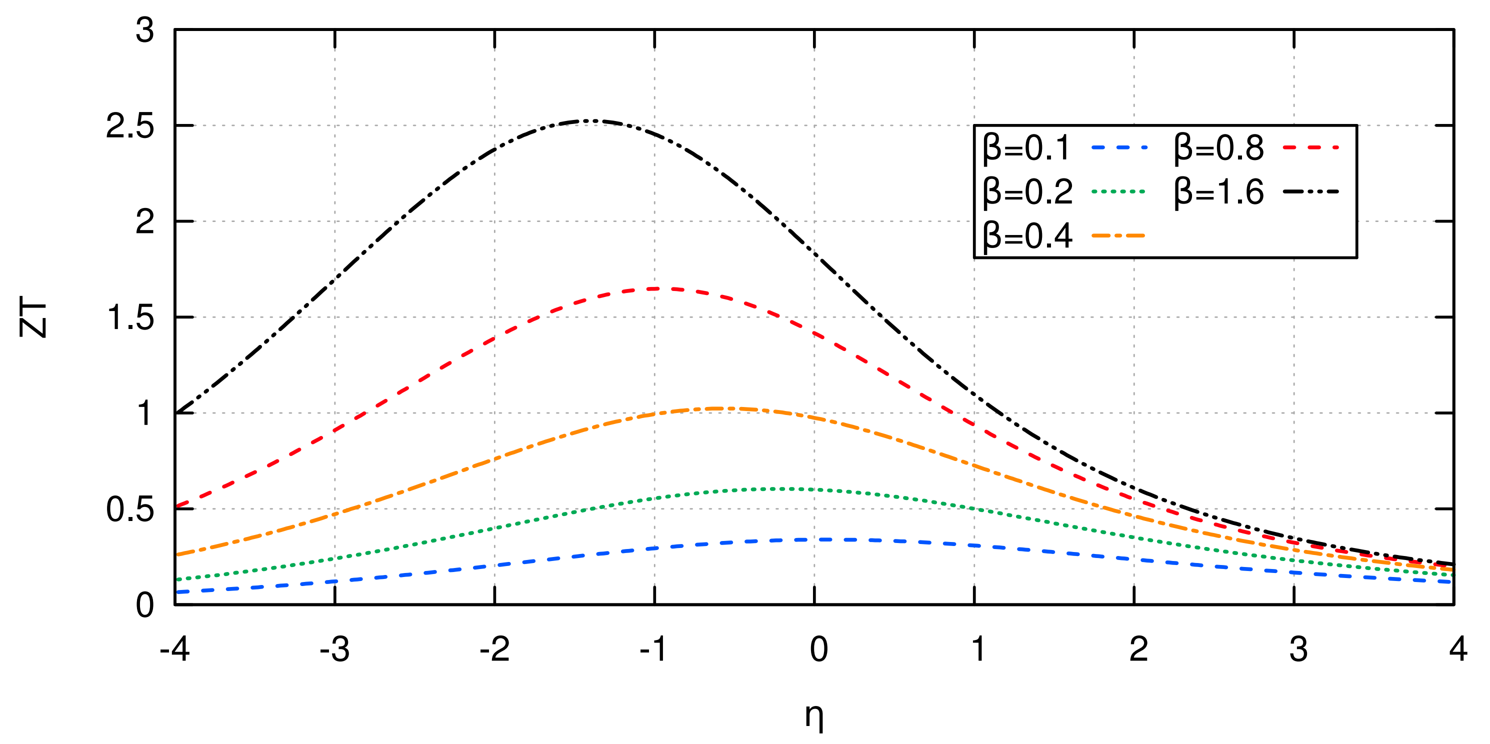
$$\sigma_0(T) = \frac{8\pi}{3}\Gamma(r+\frac{5}{2}) \left(\frac{2m_c k_B T}{h^2}\right)^{3/2} \frac{e\,\tau(T)}{m_c}$$

The parameter β is the inverse of a Lorenz number comparing the LATTICE thermal conductivity to ~ the mobility

Large β is desirable !

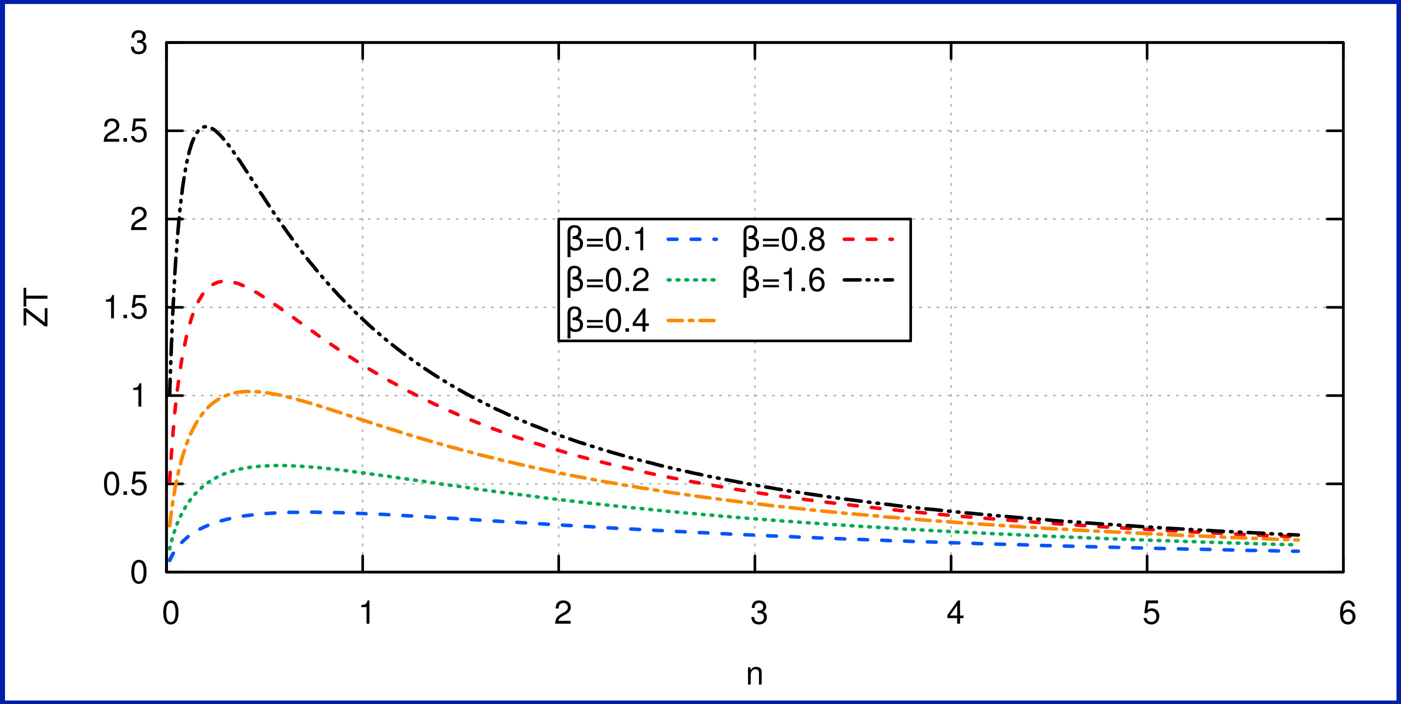
Dimensionless figure of merit :

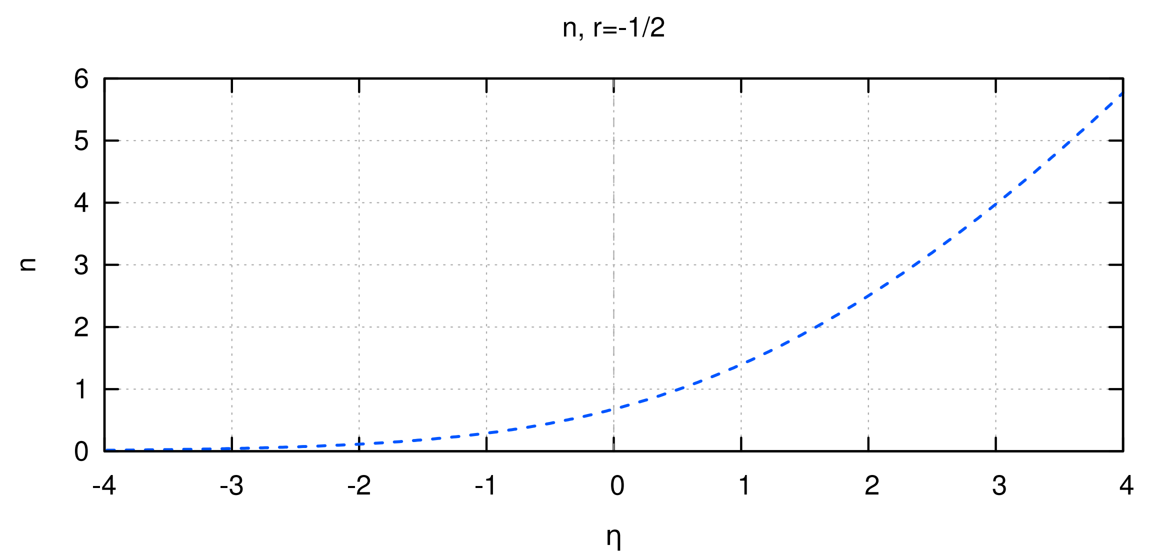
$$ZT = \frac{\overline{\alpha}^2}{\overline{\mathcal{L}}_e + \beta^{-1}\frac{\Gamma(r+3/2)}{F_{r+1/2}(\eta)}} \rightarrow \frac{[\eta-(r+5/2)]^2}{r+5/2+\beta^{-1}e^{-\eta}}$$



(all curves for r = -1/2)

Standard materials have β ~ 0.4…
Hence zT ~ 1
Optimal regime is the crossover regime between SC and metal


ZT
3
2.5
2
1.5
1
0.5
0
0
1
2
3
4
5
6
n
β=0.1
β=0.2
β=0.4
β=0.8
β=1.6


n, r=-1/2
n
6
5
4
3
2
1
0
-4
-3
-2
-1
0
1
2
3
4
η

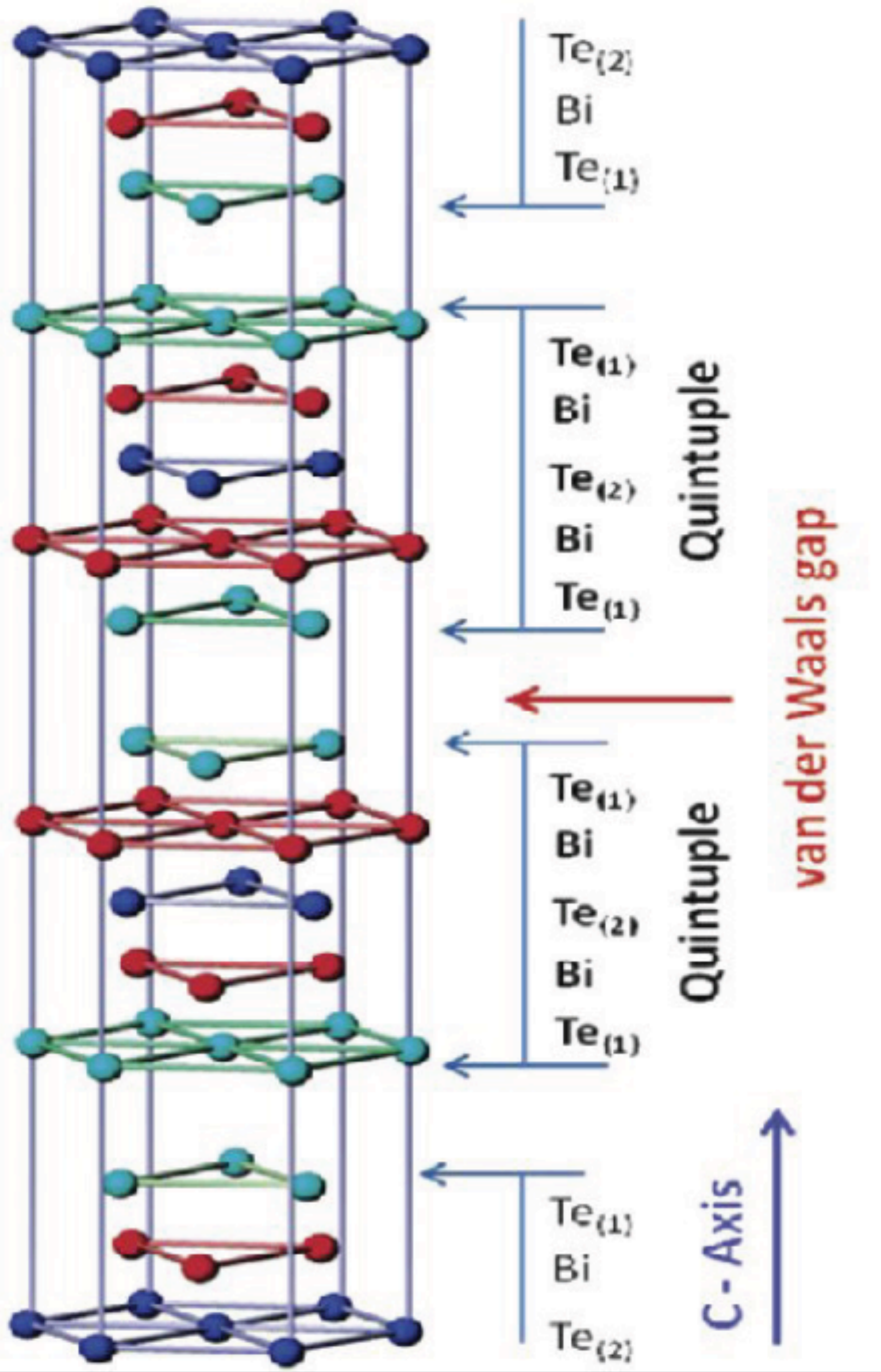
CRITERIA:

$$\boxed{\beta \equiv \left(\frac{k_B}{e}\right)^2 \frac{\sigma_0}{\kappa_L/T}}$$

$$\sigma_0 = 2e\,\mu \left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2}$$

- <u>LOW LATTICE THERMAL CONDUCTIVITY !!</u>
- High-enough mobility
- Large effective mass as appearing in density of states
- (e.g. multivalley semiconductor with not too light masses)
- Small (large carrier density) but not too small band gap (→ `bipolar effects', ie both types of carriers → bad)

Bi_2Te_3


Te(2)
Bi
Te(1)
Te(1)
Bi
Te(2)
Bi
Te(1)
Quintuple
van der Waals gap
Te(1)
Bi
Te(2)
Bi
Te(1)
Quintuple
Te(1)
Bi
Te(2)
C - Axis

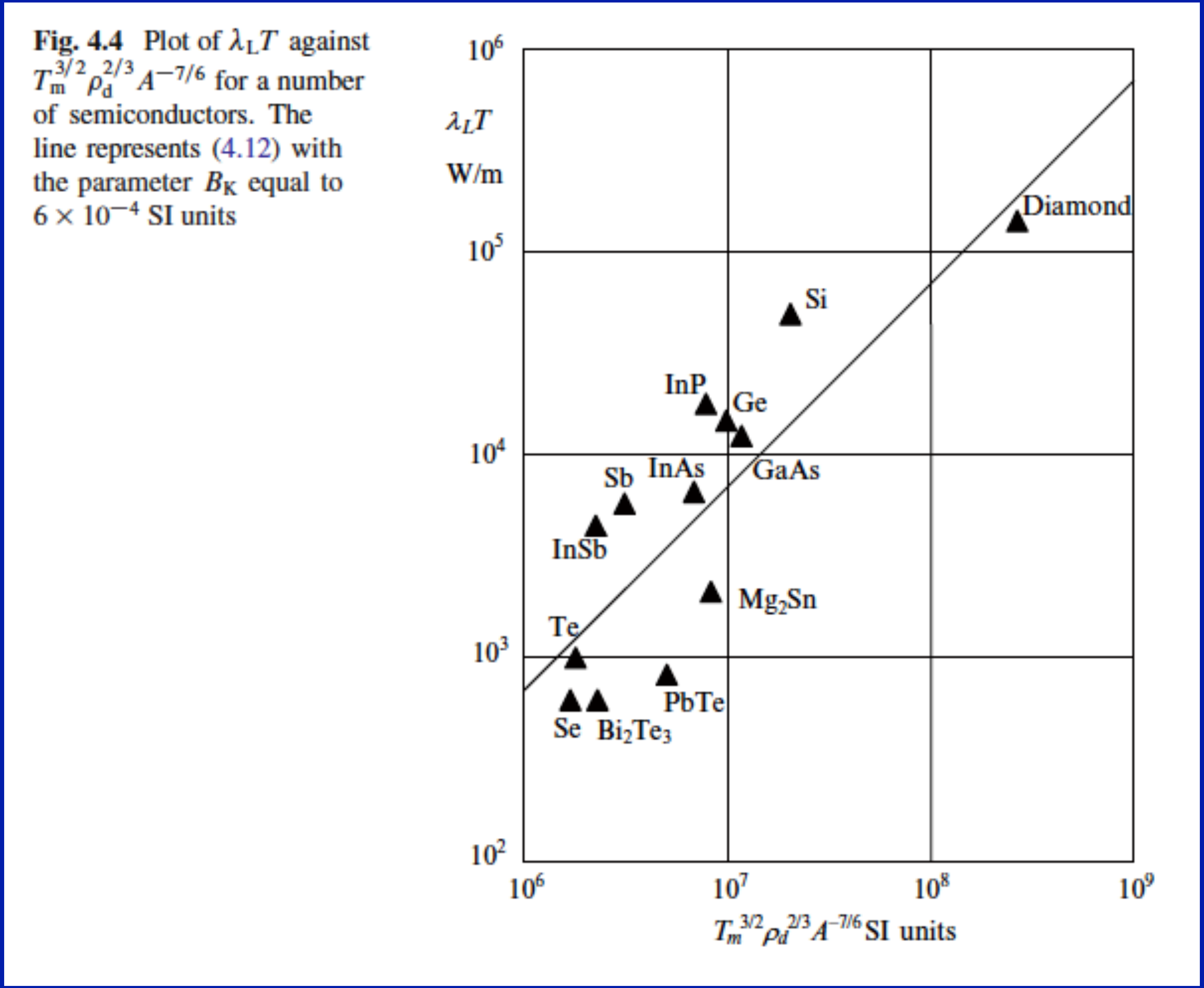
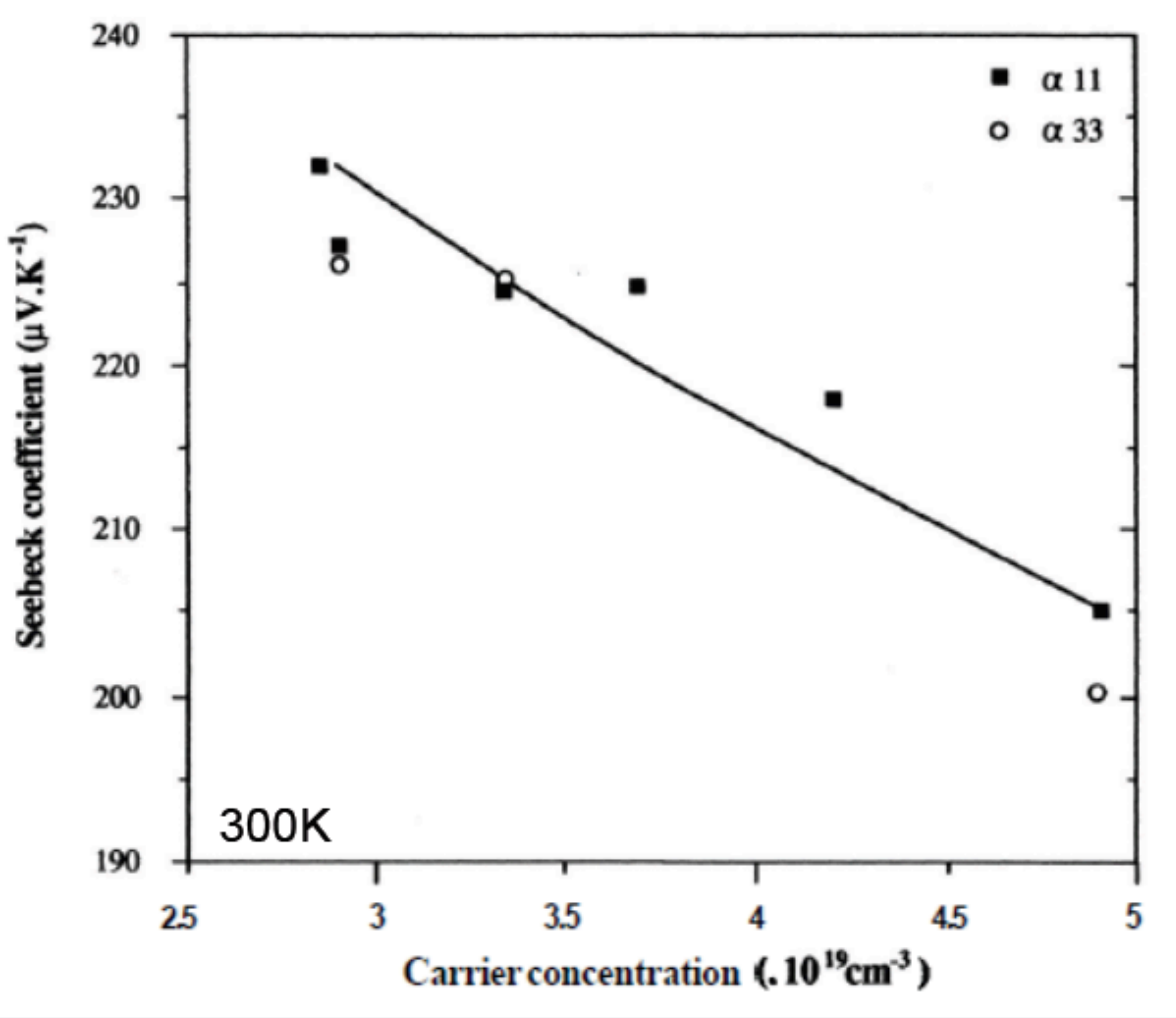


Fig. 4.4 Plot of $\lambda_L T$ against $T_m^{3/2}\rho_d^{2/3}A^{-7/6}$ for a number of semiconductors. The line represents (4.12) with the parameter B_K equal to 6×10^{-4} SI units

Heavy elements, low melting temperature → low thermal cond.

Basic electronic properties

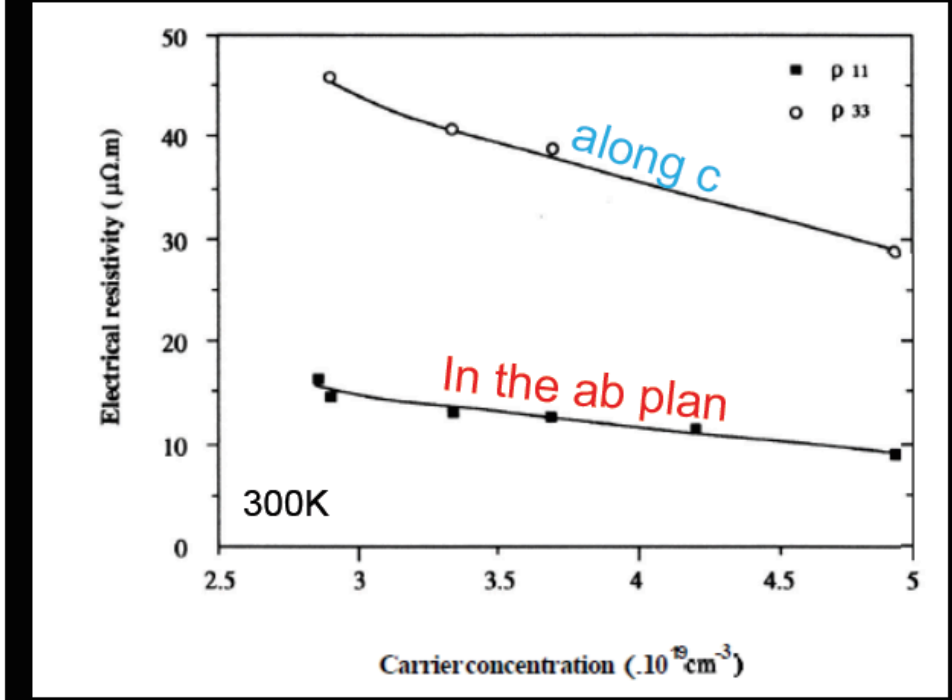
- Energy gap: about 0.13 eV
- Multivalley (6 in c-band, 6 in v-band)
- Relatively low effective masses in each valley
- But because of multivalley: d.o.s effective mass sizeable (0.5 m_e → 1.5 m_e)
- Scattering exponent $r = -1/2$ observed
- Lattice thermal cond. of order 1W/m/K @ 300K (anisotropic, see below)

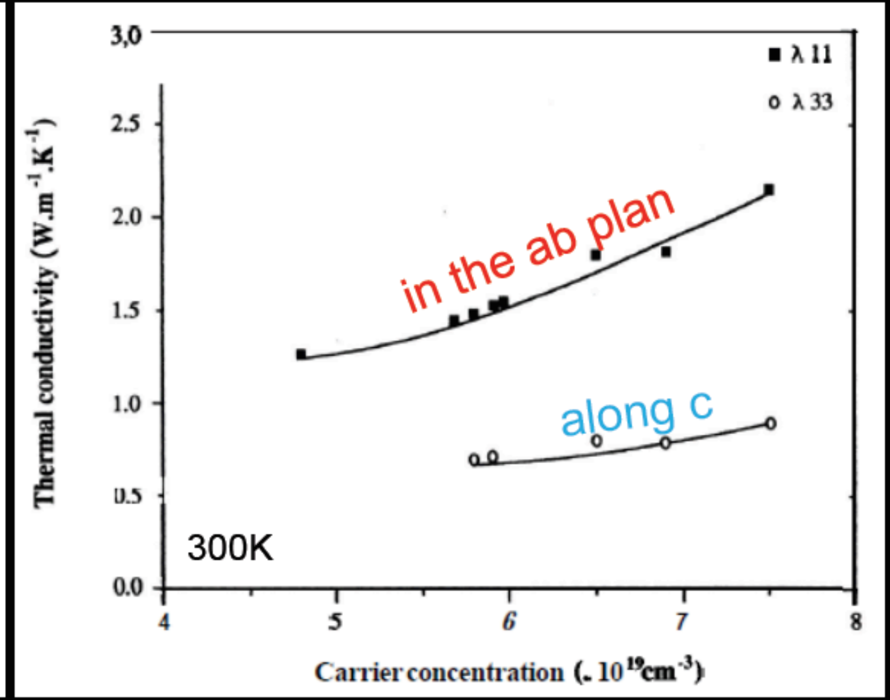


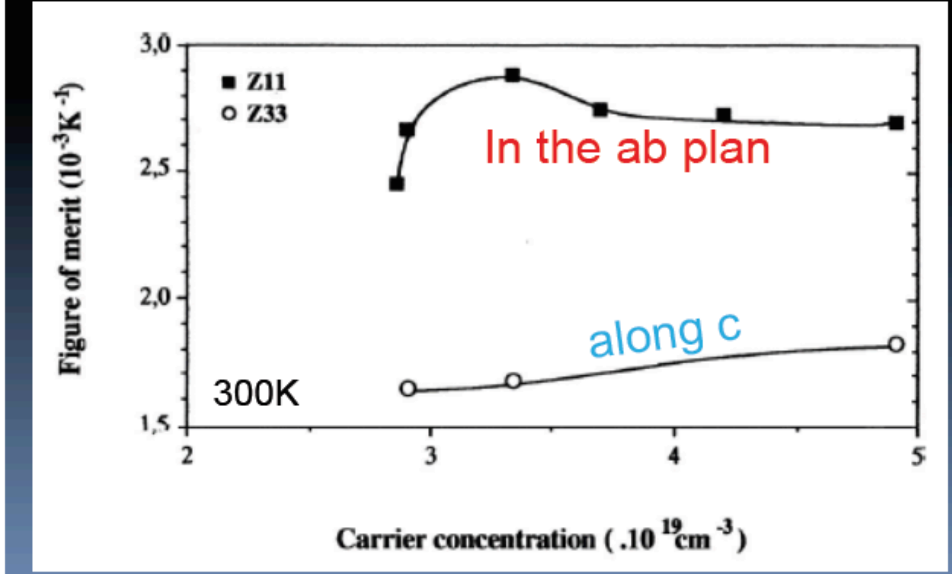
Slides from F.Gascoin’s seminar

Bi_2Te_3 - Anisotropy of transport properties

In single crystals !







For n or p: ZT (ab) > ZT(along c) !

Must orient the TE legs when making a module
(commercial module : ZT_p~1-1,1 and ZT_n~0.9)

The most studied TE material
…still today…
(Cf 2^{ième} partie)

Comparison of measurements to above model:

T.Caillat et al. J.Phys Chem Sol 54, 575 (1993)

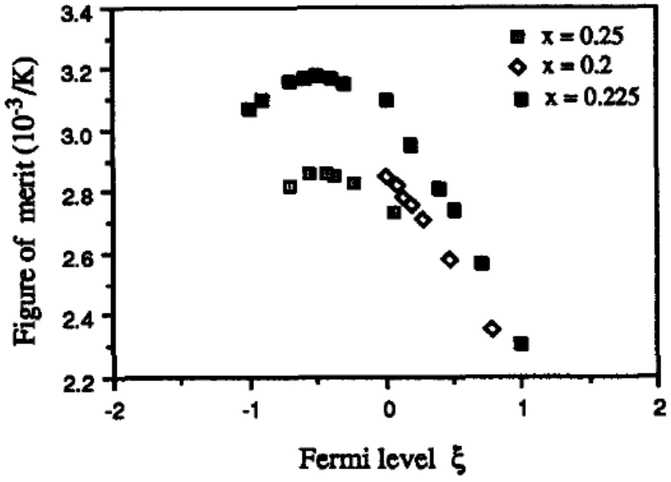


Fig. 8. The calculated values of the figure of merit (Z) as a function of the Fermi level ξ for the $(Bi_xSb_{1-x})_2Te_3$ solid solutions with $x = 0.225$, 0.2 and 0.25.

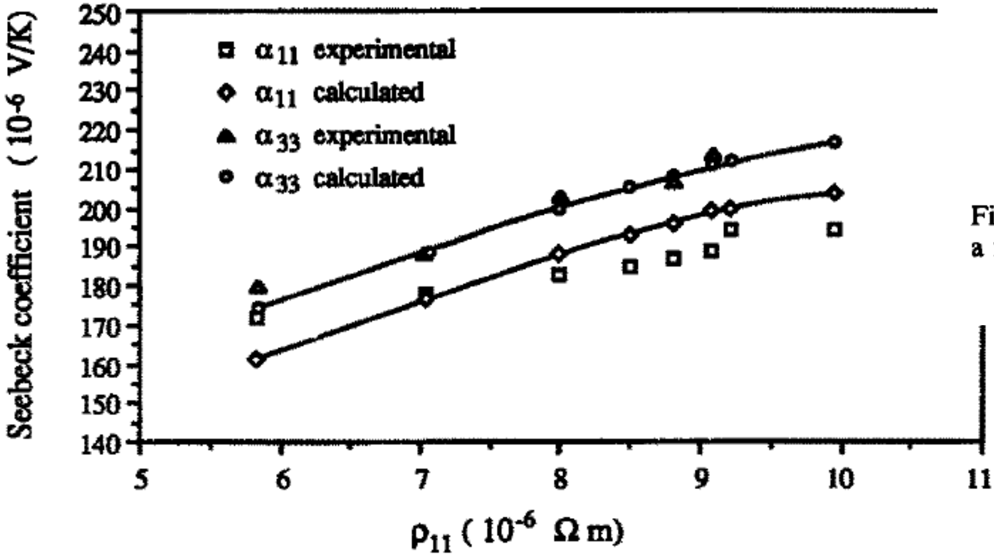
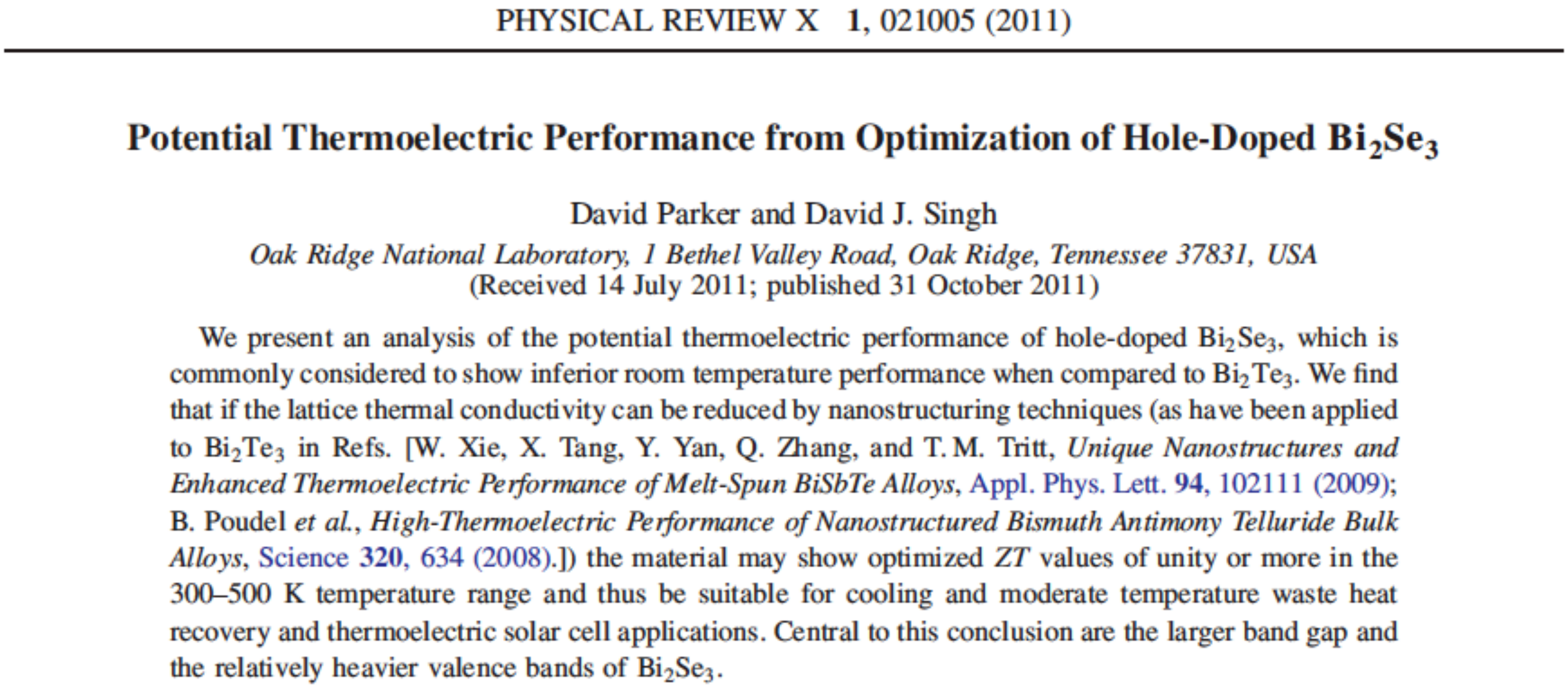


Fig. 4. The calculated and experimental Seebeck coefficients α_{11} and α_{33} as a function of the electrical resistivity ρ_{11} for the $(Bi_xSb_{1-x})_2Te_3$ solid solution with $x = 0.2$.

Electronic structure calculations



PHYSICAL REVIEW X 1, 021005 (2011)

Potential Thermoelectric Performance from Optimization of Hole-Doped Bi_2Se_3

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(Received 14 July 2011; published 31 October 2011)

We present an analysis of the potential thermoelectric performance of hole-doped Bi_2Se_3, which is commonly considered to show inferior room temperature performance when compared to Bi_2Te_3. We find that if the lattice thermal conductivity can be reduced by nanostructuring techniques (as have been applied to Bi_2Te_3 in Refs. [W. Xie, X. Tang, Y. Yan, Q. Zhang, and T. M. Tritt, *Unique Nanostructures and Enhanced Thermoelectric Performance of Melt-Spun BiSbTe Alloys*, Appl. Phys. Lett. **94**, 102111 (2009); B. Poudel *et al.*, *High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys*, Science **320**, 634 (2008).]) the material may show optimized ZT values of unity or more in the 300–500 K temperature range and thus be suitable for cooling and moderate temperature waste heat recovery and thermoelectric solar cell applications. Central to this conclusion are the larger band gap and the relatively heavier valence bands of Bi_2Se_3.

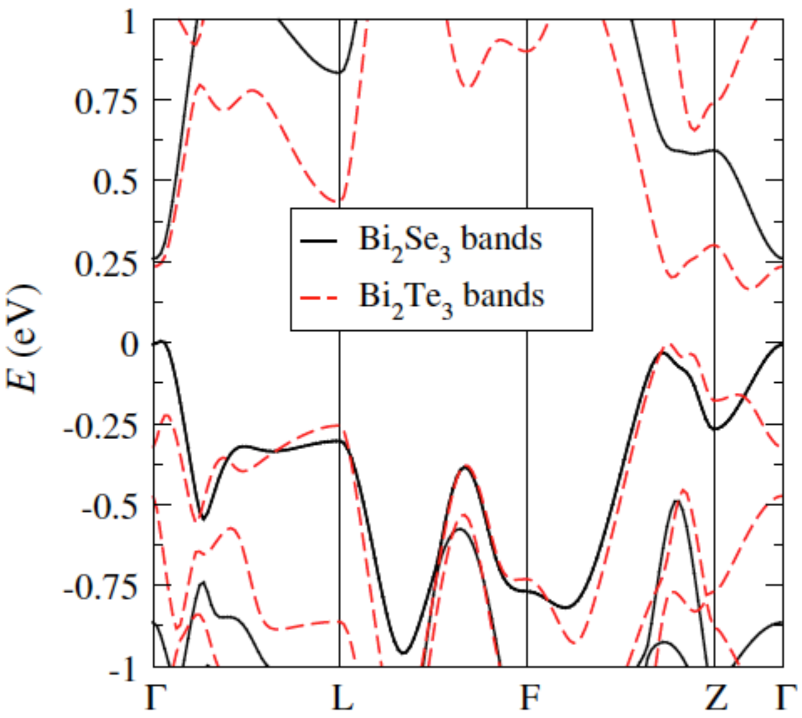


FIG. 1. The calculated band structure for Bi_2Se_3 and Bi_2Te_3 in the rhombohedral Brillouin zone. The valence band maximum is set to the energy zero.

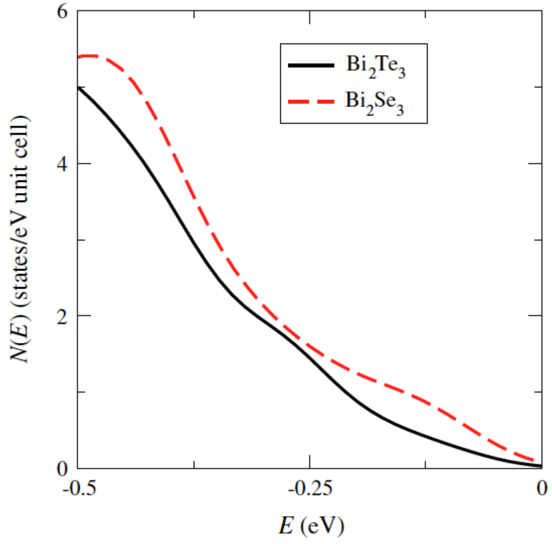
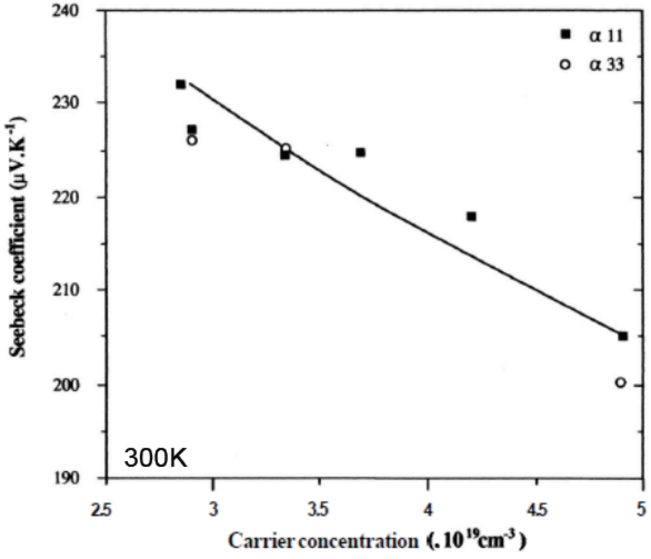
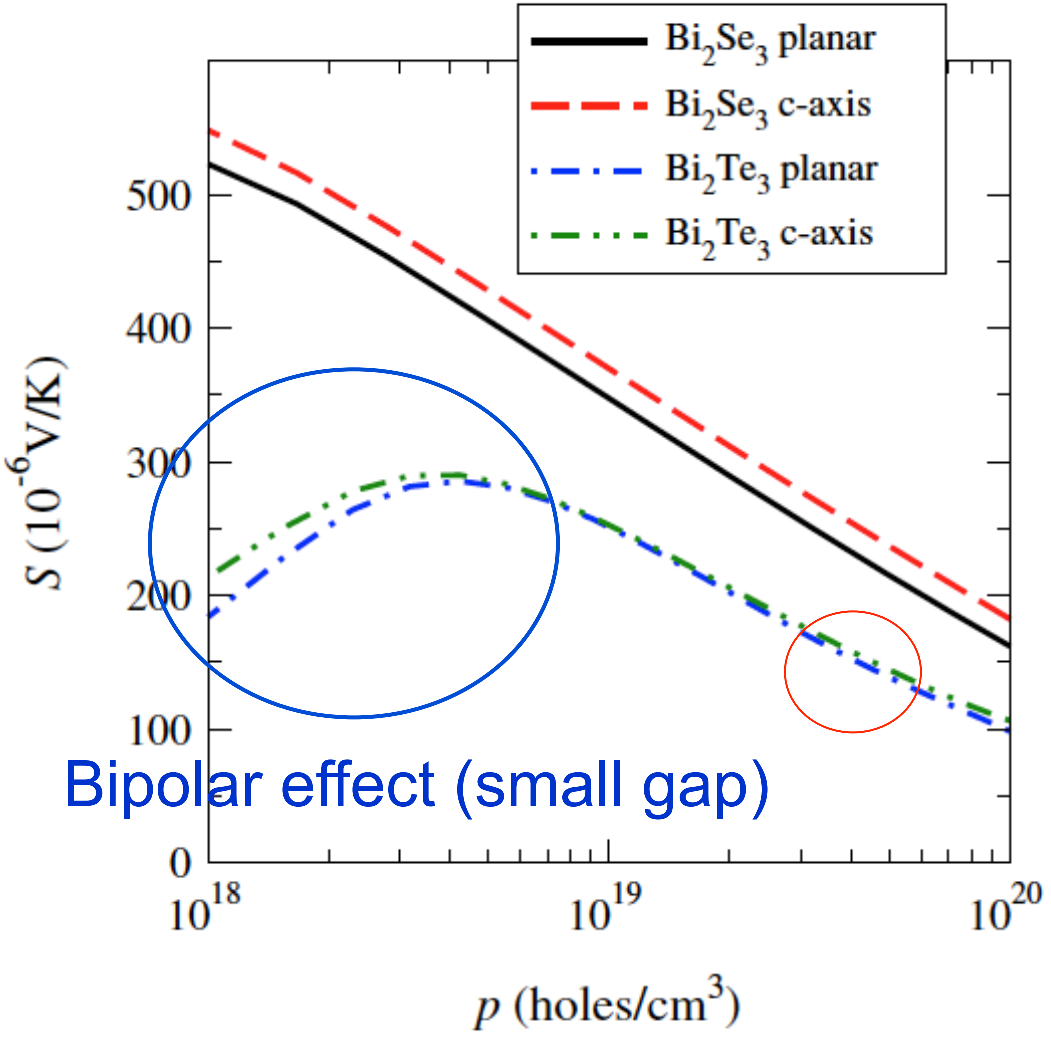


FIG. 2. The calculated density-of-states for the valence bands of Bi_2Se_3 and Bi_2Te_3. Note the larger values for Bi_2Se_3 just below the valence band maximum, particularly in the first quarter eV—the most important region for temperatures below 500 K. For both compounds, the valence band maximum is set to the energy zero.

[redacted]





Bipolar effect (small gap)

FIG. 3. The calculated thermopower for Bi_2Se_3 and Bi_2Te_3 at 300 K.

[redacted]

Some take-home messages

- A delicate materials-optimisation problem
- Several competing factors, often antagonistic
- Lowering thermal conductivity is KEY
- → Cf. Seminars of May,15 and 22 on skutterudites