Opis zjawisk transportu elektronów

w materii skondensowanej

konwersja termoelektryczna

Pierwsza kwantowa teoria elektronów w metalach (model Drude-Sommerfeld) - przypomnienie

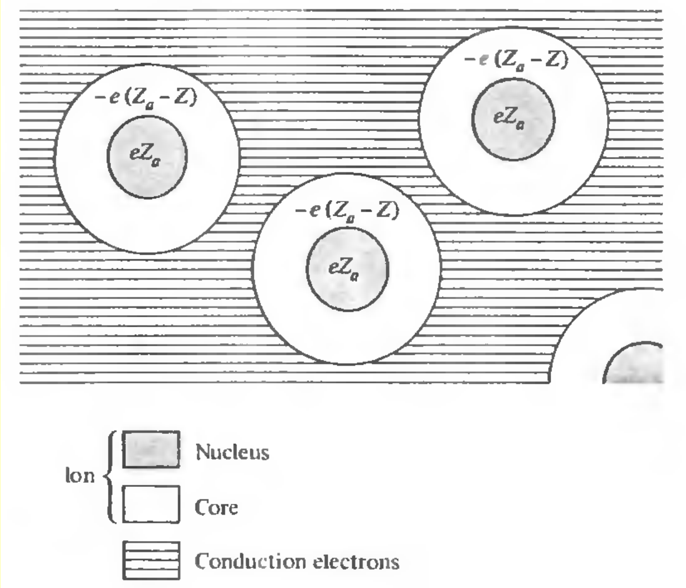
1838 Michael Faraday obserwuje przepływ prądu przez rozrzedzone powietrze, pomiędzy anodą i katodą wytwarza się łuk świetlny oprócz okolicy katody (tzw. ciemnia Faradaya) odkrycie promieni katodowych

1897 Joseph John Thomson odkrywa elektron w podobnym eksperymencie, ale z przyłożonym poprzecznym polem **E**, którym można kierować wiązkę „promieni katodowych"; wyznacza *e/m*.

1900 Paul Drude formułuje pierwszą elektronową teorię metali

1927 Arnold Sommerfeld używa statystyki Fermiego-Diraca do modelu Drudego i proponuje pierwszą kwantową teorię ruchu elektronów w metalach dając początek tzw. modelowi Drudego-Sommerfelda elektronów swobodnych.

$$\mathbf{j} = -e\, n\, \mathbf{v}$$



Współczynnik Halla wybranych pierwiastków w słabych i średnich polach B.

METAL	VALENCE	$-1/R_H nec$
Li	1	0.8
Na	1	1.2
K	1	1.1
Rb	1	1.0
Cs	1	0.9
Cu	1	1.5
Ag	1	1.3
Au	1	1.5
Be	2	−0.2
Mg	2	−0.4
In	3	−0.3
Al	3	−0.3

[a] These are roughly the limiting values assumed by R_H as the field becomes very large (of order 10^4 G), and the temperature very low, in carefully prepared specimens. The data are quoted in the form n_0/n, where n_0 is the density for which the Drude form (1.21) agrees with the measured R_H: $n_0 = -1/R_H ec$. Evidently the alkali metals obey the Drude result reasonably well, the noble metals (Cu, Ag, Au) less well, and the remaining entries, not at all.

dobra zgodność

słaba zgodność

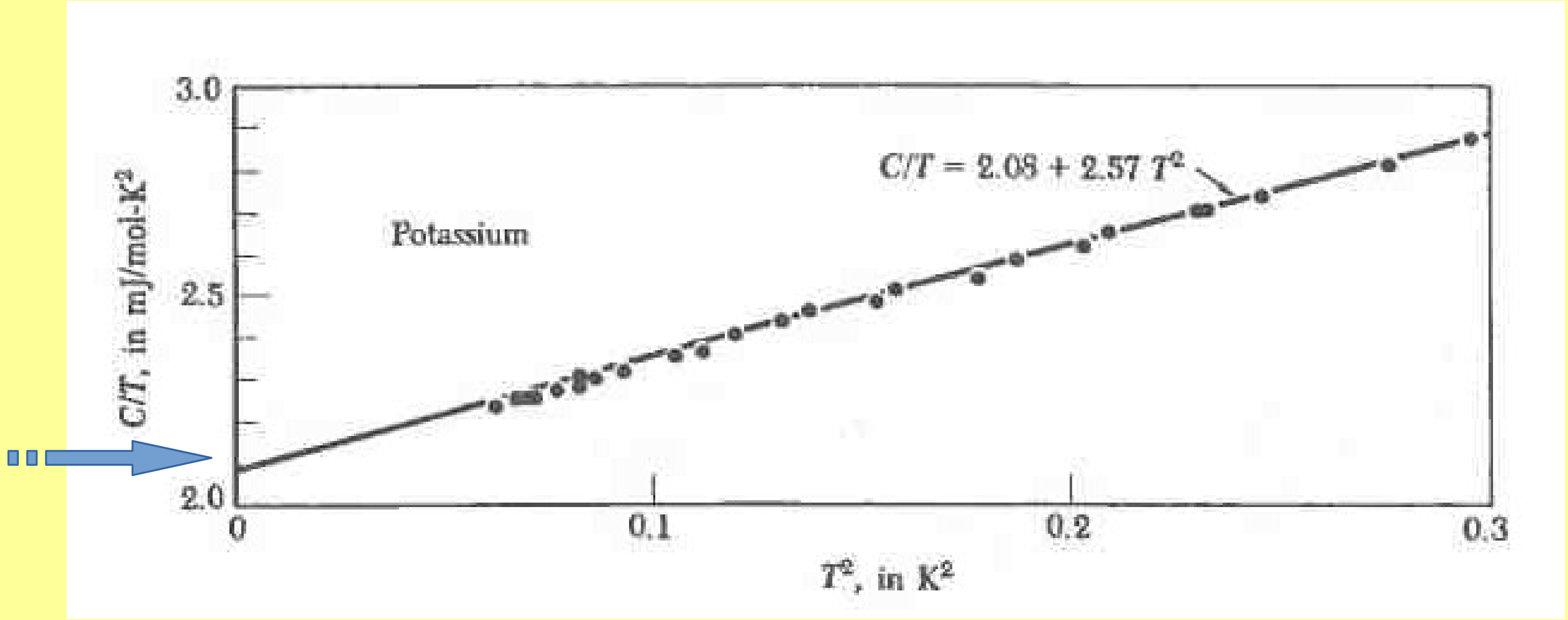
niezgodność

Eksperymentalne wartości przewodności cieplnych i liczb Lorenza dla wybranych metal

	273 K		373 K	
ELEMENT	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K^2)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K^2)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-8}
Na	1.38	2.12		
K	1.0	2.23		
Rb	0.6	2.42		
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Be	2.3	2.36	1.7	2.42
Mg	1.5	2.14	1.5	2.25
Nb	0.52	2.90	0.54	2.78
Fe	0.80	2.61	0.73	2.88
Zn	1.13	2.28	1.1	2.30
Cd	1.0	2.49	1.0	
Al	2.38	2.14	2.30	2.19
In	0.88	2.58	0.80	2.60
Tl	0.5	2.75	0.45	2.75
Sn	0.64	2.48	0.60	2.54
Pb	0.38	2.64	0.35	2.53
Bi	0.09	3.53	0.08	3.35
Sb	0.18	2.57	0.17	2.69

Source: G. W. C. Kaye and T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966.

Pomiar doświadczalny ciepła właściwego w metalicznym potasie



Współczynniki elektronowe dla ciepła właściwego (pomiar/teoria)

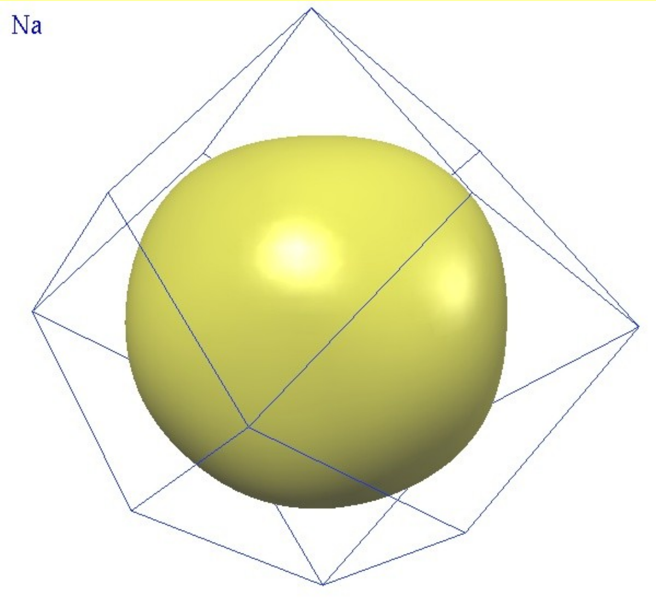
Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).)

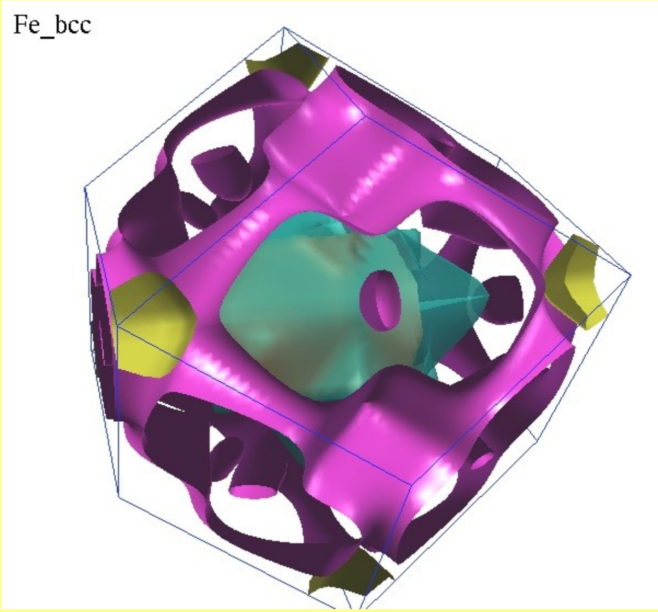
Observed γ in mJ mol^{-1} K^{-2}.
Calculated free electron γ in mJ mol^{-1} K^{-2}.
m_{th}/m = (observed γ)/(free electron γ).

Li 1.63 0.749 2.18	Be 0.17 0.500 0.34											B	C	N
Na 1.38 1.094 1.26	Mg 1.3 0.992 1.3											Al 1.35 0.912 1.48	Si	P
K 2.08 1.668 1.25	Ca 2.9 1.511 1.9	Sc 10.7	Ti 3.35	V 9.26	Cr 1.40	Mn(γ) 9.20	Fe 4.98	Co 4.73	Ni 7.02	Cu 0.695 0.505 1.38	Zn 0.64 0.753 0.85	Ga 0.596 1.025 0.58	Ge	As 0.19
Rb 2.41 1.911 1.26	Sr 3.6 1.790 2.0	Y 10.2	Zr 2.80	Nb 7.79	Mo 2.0	Tc —	Ru 3.3	Rh 4.9	Pd 9.42	Ag 0.646 0.645 1.00	Cd 0.688 0.948 0.73	In 1.69 1.233 1.37	Sn (w) 1.78 1.410 1.26	Sb 0.11
Cs 3.20 2.238 1.43	Ba 2.7 1.937 1.4	La 10.	Hf 2.16	Ta 5.9	W 1.3	Re 2.3	Os 2.4	Ir 3.1	Pt 6.8	Au 0.729 0.642 1.14	Hg(α) 1.79 0.952 1.88	Tl 1.47 1.29 1.14	Pb 2.98 1.509 1.97	Bi 0.008

Investigations of electronic states near the Fermi surface $E(\mathbf{k})=E_F$



$$ZT=\frac{S^2}{\rho\,\kappa}$$



$$E(k)=\frac{\hbar\left(k_x^2+k_y^2+k_z^2\right)}{2m}$$

Electron motion in solids (semi-classical)

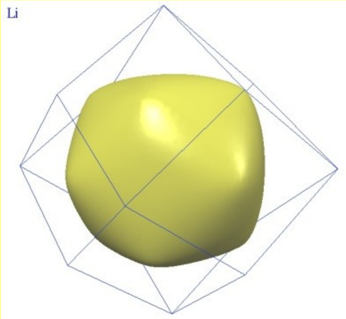
Group velocity of electrons

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k} = \nabla_k E(k) = v(k)$$

In general **v-**vector is NOT parallel to **k**–vector (e.g. ellipsoid), but it is perpendicular to isoenergetic surface E(**k**)

$$v = \frac{\hbar k}{m} \quad \Leftrightarrow \quad E(k) = \frac{\hbar^2 k^2}{2m}$$

v(**k**) parallel to **k** only if Fermi surface is spherical



Acceleration of electrons

$$F = \hbar\frac{dk}{dt} \quad \Rightarrow \quad a_k = \frac{dv_k}{dt} = \frac{1}{\hbar}\frac{\partial^2 E(k)}{\partial k\,\partial k}\frac{dk}{dt} = \frac{1}{\hbar^2}\frac{\partial^2 E(k)}{\partial k\,\partial k}F$$

$$a_k = (m)^{-1} F \quad \text{where} \quad (m_{ij})^{-1} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j}$$

In general, tensor of effective mass is independent on electron velocity

$$n(E_F) \propto \frac{\partial E(k)}{\partial k}$$

How to measure ?

$$(m_{ij})^{-1} \propto \frac{\partial^2 E}{\partial k_i \partial k_j}$$

DOS near E=E_F can be detected in specific heat and magnetic susceptibility measurements

Effective masses can be detected in dH-vA or transport measurements

Thermoelectric „tetragon"

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ -\nabla T \end{bmatrix}$$

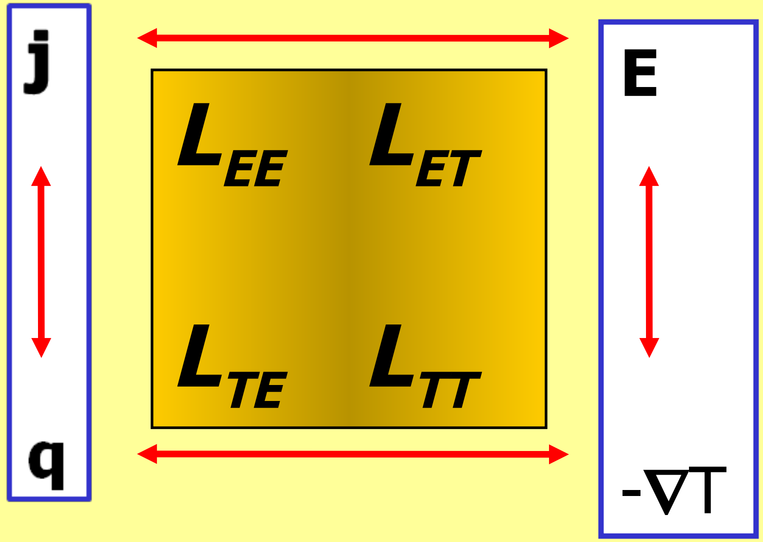
Ohm, 1826

Electrical current

Electrical field

Peltier, 1834

Seebeck, 1821



Heat current

Temperature gradient

Fourier, 1822

$S = \Pi T$ (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), …

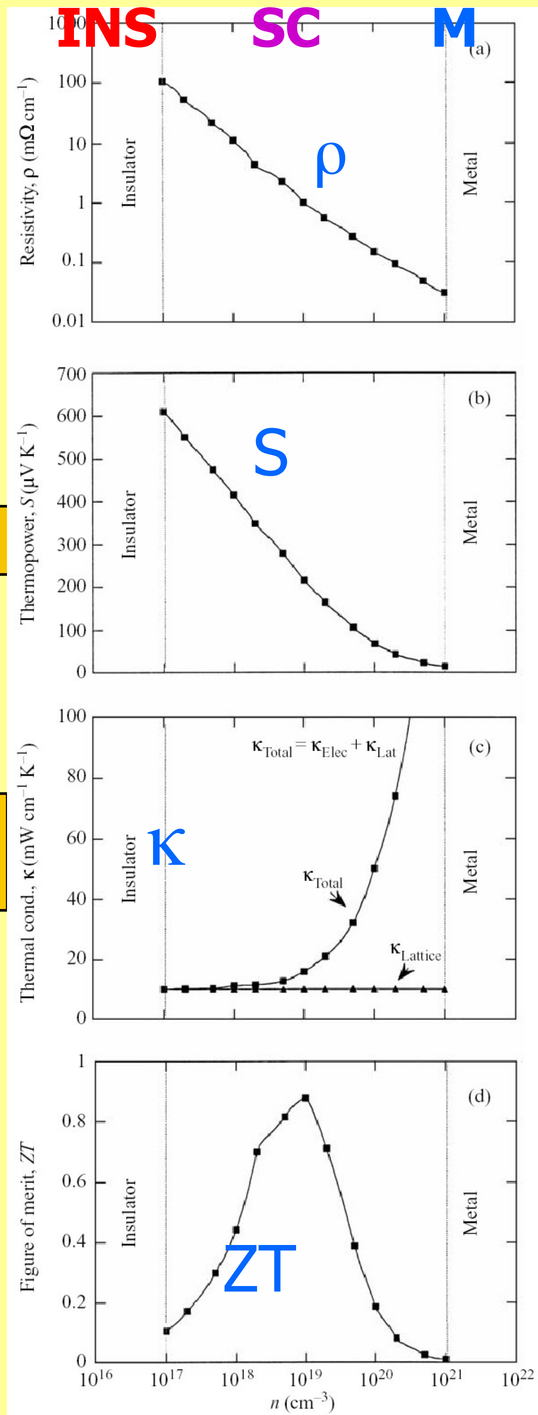
Thermoelectric properties

Resitivity

Thermopower

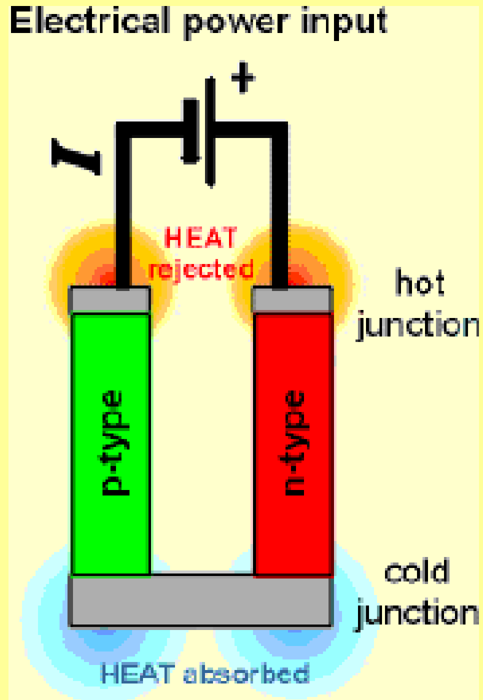
Thermal conductivity

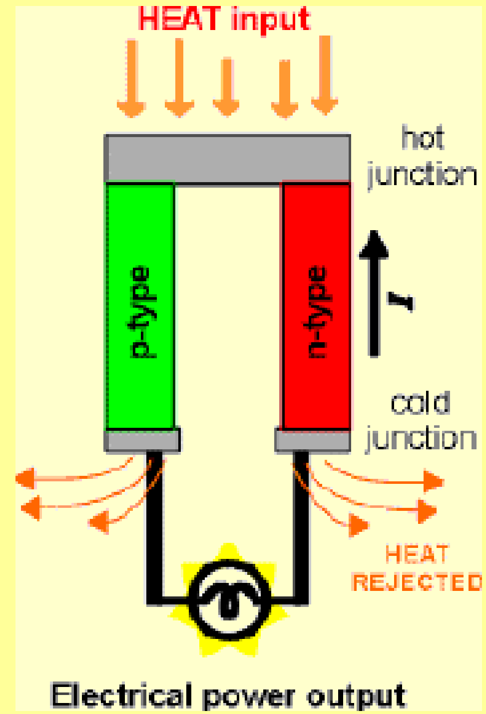
ZT
Figure of merit



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

A. Joffe





Thermoelectric properties - search for optimum

Carnot limit

COOLING ELEMENTS

$COP = (T_H - T_C)(\gamma - 1)(T_C + \gamma T_H)^{-1}$

POWER GENERATORS

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

Improvement of figure of merit

Geometry of the devices

Physical properties of the system

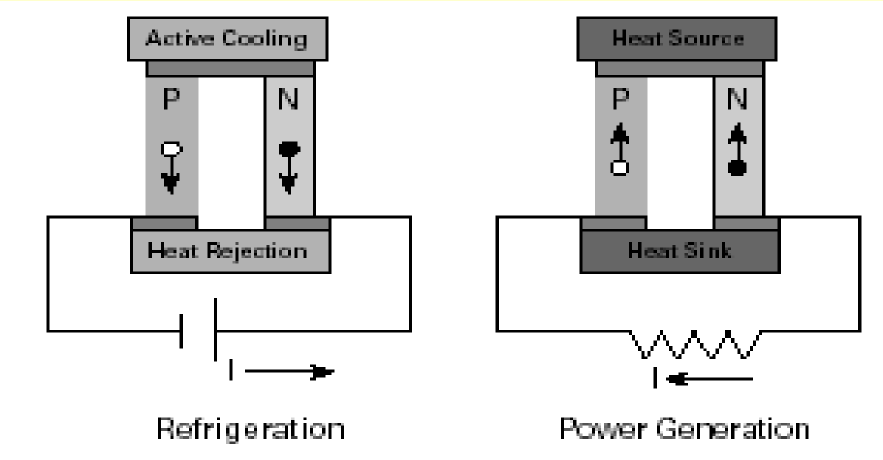
$\gamma = (1+ZT)^{1/2}$

$$ZT = \frac{S^2\sigma}{\kappa} T = \underbrace{\frac{S^2}{L}}_{calculated} \frac{1}{1+\frac{\kappa_L}{\kappa_e}}$$

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

Lorentz factor

Thermal conductivity (phonons /electrons)



$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ -\nabla T \end{bmatrix}$$

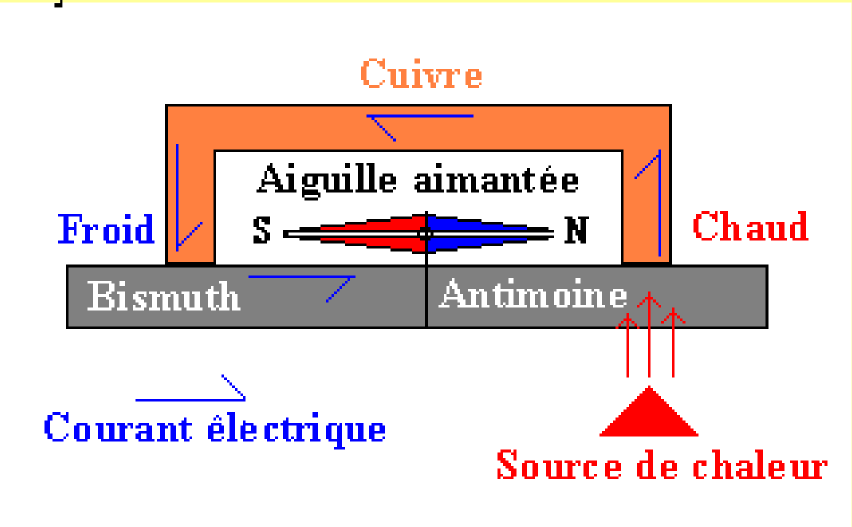
Seebeck effect (1821)

Electric field $\mathbf{E} = S \nabla T$ Temperature gradient

$\left[\frac{\mu V}{K}\right]$ thermopower

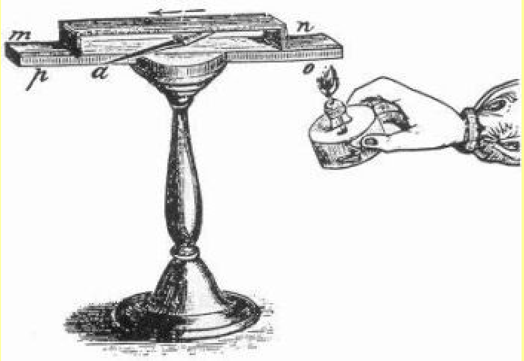
$S = L_{EE}^{-1} L_{ET}$

1770 Tallin
1854 Berlin



Vivid personality of the Romaticism

temperature gradient causes changes of magnetic field of Earth !!, Oersted's experiments (1820) „blind" scientists.



Explanation : thermomagnetism - „magnetic" polarisation of metals and alloys due to the difference of temperature !!

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ -\nabla T \end{bmatrix}$$

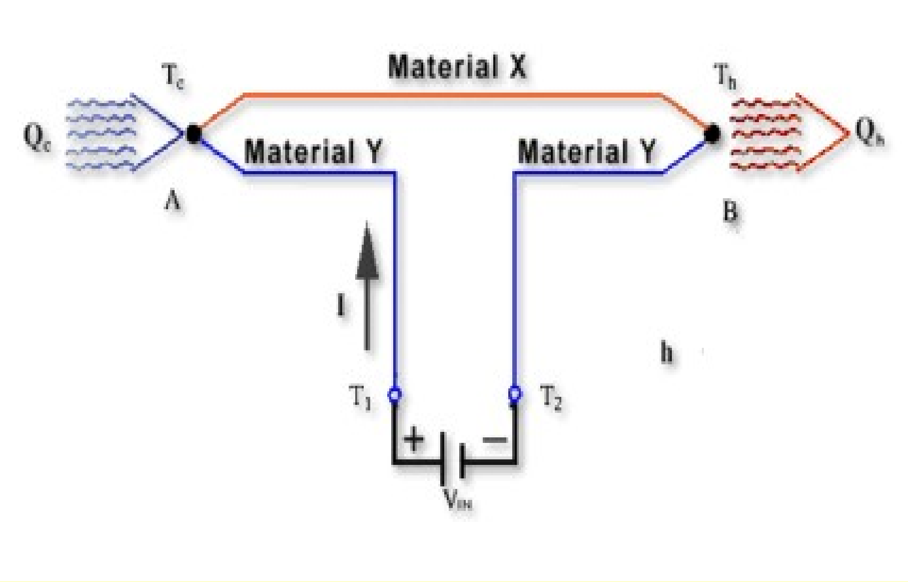
Peltier effect (1834)

1785 Ham
1845 Paris

Heat current **$q = \Pi j$** Electrical density current

Peltier coefficient $\Pi = L_{TE} L_{EE}^{-1}$

"Reverse" process to Seebeck effect



Thomson effect (1834)

<u>Heat generation</u> in the presence of electrical current **j** and temperature gradient **dT/dx**

$$Q = j^2/\sigma \;+/-\; \mu \; j \; dT/dx$$

Joule Thomson

$\mu = T\, dS/dT$

$\Pi T = S$ (Thomson)

$L_{ET} = L_{TE} / T$

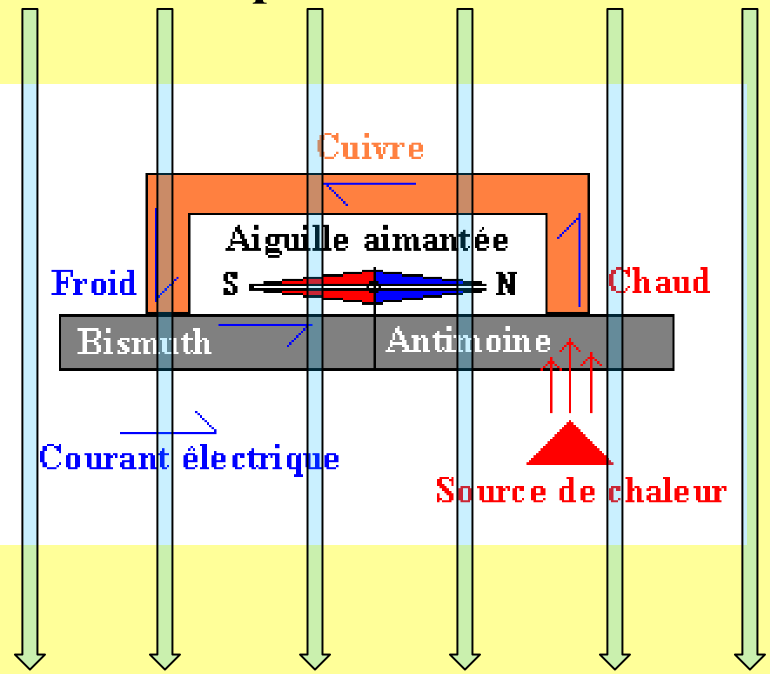
Nernst-(Ettingshausen) effect (1886)

1864 Wąbrzeźno
1941 Niwica

Thermo-magneto-electric effect

$$|N| = \frac{E_Y / B_Z}{dT/dx} \qquad \left[\frac{\mu V}{KT}\right]$$

"Reverse" process to Nernst effect = Ettingshausen effect



magnetic field **B**

Phenomenon observed when a sample conducting electrical current is subjected to a magnetic field **B** and a temperature gradient **dT/dx** perpendicular to each other.

E_Y is the *y*-component of the electric field that results from the magnetic field's *z*-component B_Z and the temperature gradient dT/dx.

N ~ 0 in metals

N large in semiconductors, superconductors, heavy-fermions, Dirac electrons in Bi, graphen, Landau levels cross Fermi level

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} & L_{ET} \\ L_{TE} & L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ -\nabla T \end{bmatrix}$$

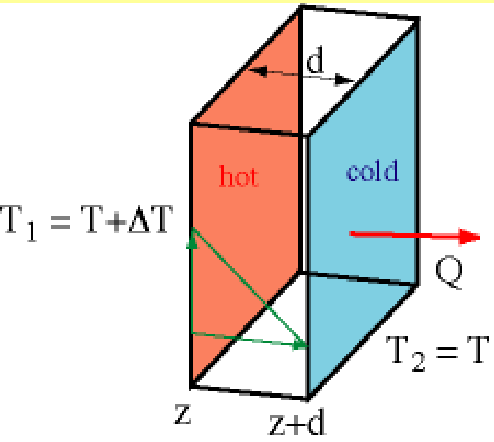
Fourier relation (1822)

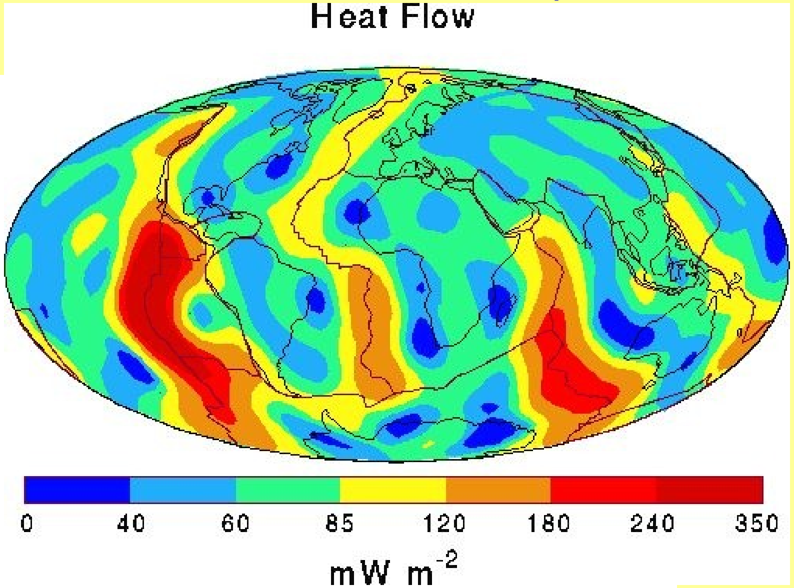
1768 Auxerre
1830 Paris

Heat current $\mathbf{q} = -\kappa \nabla T$ Temperature gradient

Thermal conductivity $\kappa = L_{TE} L_{EE}^{-1} L_{ET} - L_{TT}$

Heat conducted (balance) = **Heat generated** in system - **Heat accumulated** in system





in differential form: $Q(z) = -k \frac{dT}{dz}$

$\nabla \mathbf{q} = q_{gen} - du/dt$

$du/dt = \rho\, c\, dT/dt$

$\nabla(-\kappa \nabla T) + \partial T/\partial t = q_{gen}$

$\nabla^2 T + (\rho c/k)\, \partial T/\partial t = 0$

when $q_{gen} = 0$

Heat conduction equation

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} L_{ET} \\ L_{TE} L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ -\nabla T \end{bmatrix}$$

Ohm law (1826)

Electrical density current

$$\mathbf{j} = \sigma \mathbf{E}$$

Electric field

Electrical conductivity

$$\sigma = L_{EE} = ne\mu = ne\tau/m$$

1789 Erlangen
1854 Munchen

Ohm’s study inspired by works of Fourier and Seebeck

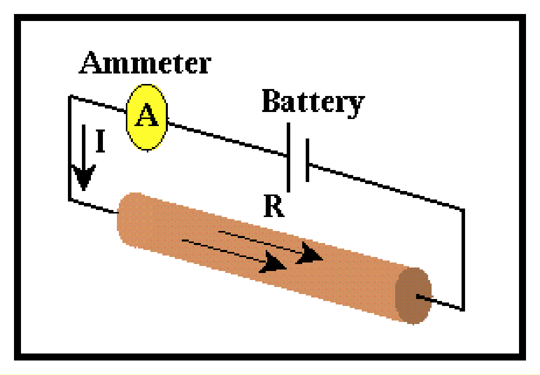
Metallic wire in cyllinder

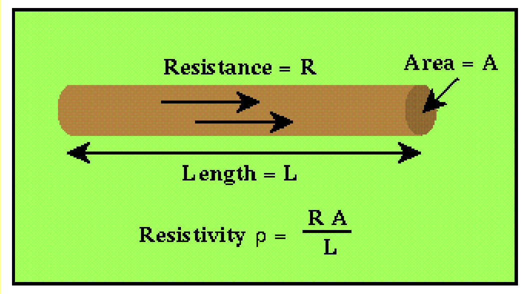
*Declination of magnetic needle proportional to electric current I

* Seebeck thermocouple – a source of electrical potential V

V/I = R = constant

when R=const. !!





„The Galvanic Circuit Investigated Mathematically” (1827)

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

$$J(r,t) = \frac{e}{4\pi^3} \int v_k f(k,r,t)\, dk$$

Transport equation

$$\frac{df}{dt} = -\frac{dk}{dt} \cdot \nabla_k f - v \cdot \nabla_r f + \frac{\partial f}{\partial t} + \left(\frac{\partial f}{\partial t} \right)_{coll.}$$

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

$$\left(\frac{\partial f}{\partial t} \right)_{coll} = -\frac{f - f_0}{\tau}$$

Onsager coefficients

1-electron Boltzmann eq. in the presence of fields :

E, **B** & ∇T

$$\vec{v}_k \cdot \vec{\nabla} T \frac{\partial f}{\partial T} + \frac{q}{\hbar}(\vec{E} + \vec{v}_k \times \vec{B}) \cdot \frac{\partial f}{\partial \vec{k}} = -\frac{f - f_0}{\tau}$$

After linearisation

$$f = f_0 - \left(q\vec{E} - \frac{\nabla T}{T}(\varepsilon_k - \mu) \right) \frac{\partial f_0}{\partial \varepsilon} \cdot \vec{\Lambda}_k$$ where $\vec{\Lambda}_k = \tau \vec{v}_k$ Mean-free path

Electric current density

$$\vec{j} = \frac{1}{V}\sum_k q\vec{v}_k f_k = \left(\int d\varepsilon\, \sigma(\varepsilon) \frac{\partial f_0}{\partial \mu} \right) \vec{E} + \left(\int d\varepsilon \frac{1}{q} \sigma(\varepsilon)(\varepsilon - \mu) \frac{\partial f_0}{\partial \mu} \right) \left(-\frac{\nabla T}{T} \right)$$

Heat density current

$$\vec{j}^Q = \frac{1}{V}\sum_k (\varepsilon_k - \mu)\vec{v}_k f_k = \left(\int d\varepsilon \frac{1}{q} \sigma(\varepsilon)(\varepsilon - \mu) \frac{\partial f_0}{\partial \mu} \right) \vec{E} + \left(\int d\varepsilon \frac{1}{q^2} \sigma(\varepsilon)(\varepsilon - \mu)^2 \frac{\partial f_0}{\partial \mu} \right) \left(-\frac{\nabla T}{T} \right),$$

$$\vec{j} = L_{11}\vec{E} + L_{12}\left(-\frac{\nabla T}{T} \right)$$

$$\vec{j}^Q = L_{21}\vec{E} + L_{22}\left(-\frac{\nabla T}{T} \right)$$

Transport functions

With applied **E** and **∇**T (**B=0**)

Transport function

$$\sigma(\varepsilon) = \frac{q^2\tau}{V}\sum_k \vec{v}_k\vec{v}_k\delta(\varepsilon_k - \varepsilon)$$

Applying additional magnetic field **B** (Hall effect)

Mean free path of electrons

$$\vec{\Lambda}_k = \tau\vec{v}_k - \frac{q\tau}{\hbar}\left(\vec{v}_k \times \vec{B}\cdot\frac{\partial}{\partial\vec{k}}\right)\vec{\Lambda}_k$$

Electrical current density

$$\vec{j} = \frac{1}{V}\sum_k q\vec{v}_k f_k = \left(\int d\varepsilon\,\sigma_B(\varepsilon)\frac{\partial f_0}{\partial\mu}\right)\vec{E} = \sigma(\vec{B})\vec{E}$$

Magnetic transport function

$$\sigma_B(\varepsilon) = \frac{q^2}{V}\sum_k \vec{v}_k\vec{\Lambda}_k\delta(\varepsilon_k - \varepsilon)$$

Transport coefficients

Electrical conductivity

$$\sigma = L_{11},$$

when $\nabla T = 0$

Thermopower

$$S = \frac{L_{11}^{-1} L_{12}}{T},$$

when $\mathbf{j} = 0$

Thermal conductivity

$$\kappa_e = \frac{1}{T}\left(L_{22} - \frac{L_{21} L_{12}}{L_{11}}\right),$$

Hall coefficient

$$R_H = \frac{\rho_{yx}}{B},$$

Hall concentration

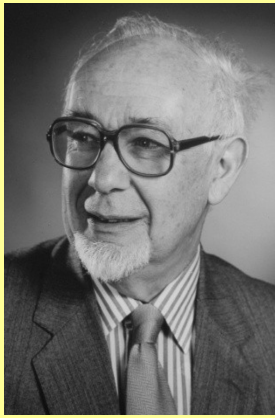
$$n_H \equiv \frac{1}{R_H q} = \alpha(n) n$$

Lorenz factor

$$L = \frac{\kappa_e}{T\sigma} = \frac{1}{T} \frac{L_{22} - L_{21}(L_{11})^{-1} L_{12}}{L_{11}}.$$

$$\begin{bmatrix} \vec{j} \\ q \end{bmatrix} = \begin{bmatrix} L_{EE} L_{ET} \\ L_{TE} L_{TT} \end{bmatrix} \begin{bmatrix} \vec{E} \\ -\nabla T \end{bmatrix}$$

Kinetic theory of Ziman



$$\sigma(T) = e^2/3 \int dE\, N(E)\, v^2(E)\, \tau(E,T)\, [-\partial f(E)/\partial E]$$

Electrical conductivity

$$S(T) = e(3T\sigma)^{-1} \int dE\, N(E)\, v^2(E)\, E\, \tau(E,T)\, [-\partial f(E) / \partial E] =$$

$$(3eT\sigma)^{-1} \int dE\, \sigma(E,T)\, E\, [-\partial f(E) / \partial E]$$

Thermopower (Seebeck coefficient)

$$N(E) = (2\pi)^{-3} \int \delta(E(\mathbf{k})-E)\, d\mathbf{k}$$

DOS (density of states)

Thermal conductivity

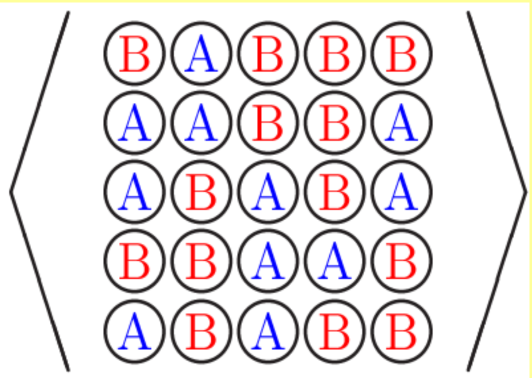
$$\kappa/\sigma \approx L_0 T,\ L_0 = \text{const} \quad \kappa \approx -L_{TT}$$

Wiedemann-Franz law, L_0 Lorentz number

Relaxation time in transport Boltzman equation

KKR-CPA method & complex bands

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



CPA "trick"

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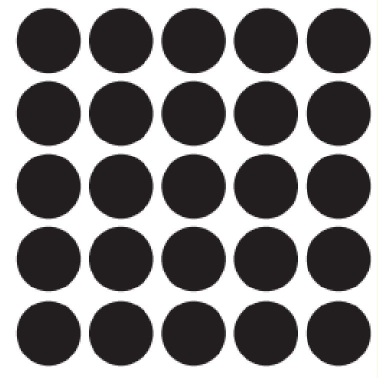


CPA condition

$$c_A T^A + c_B T^B = T^{CP}.$$

In multi-atomic systems more imagination needed !

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

CPA crystal - restored periodicity

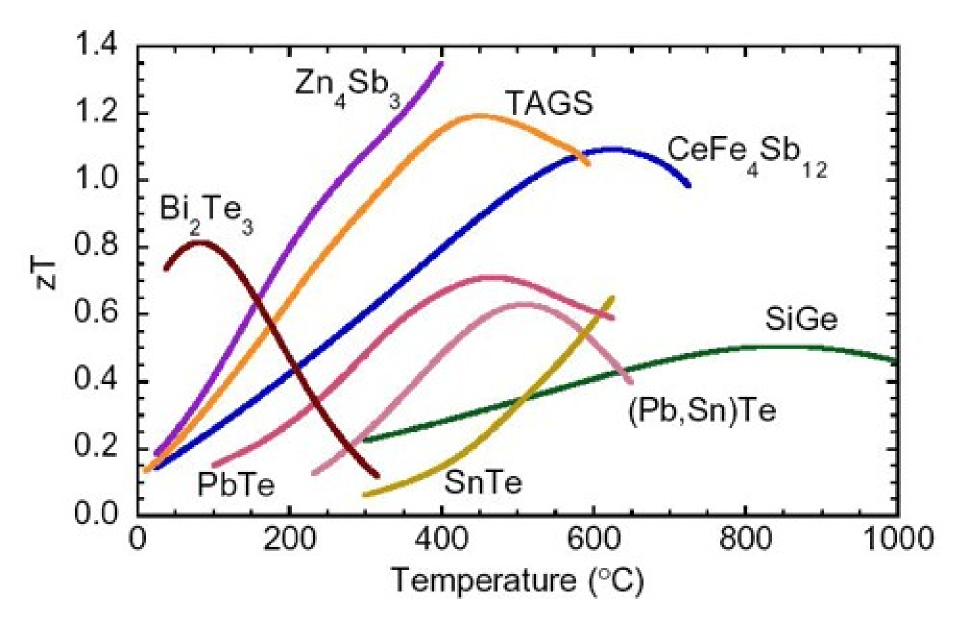
- **price: complex potential**

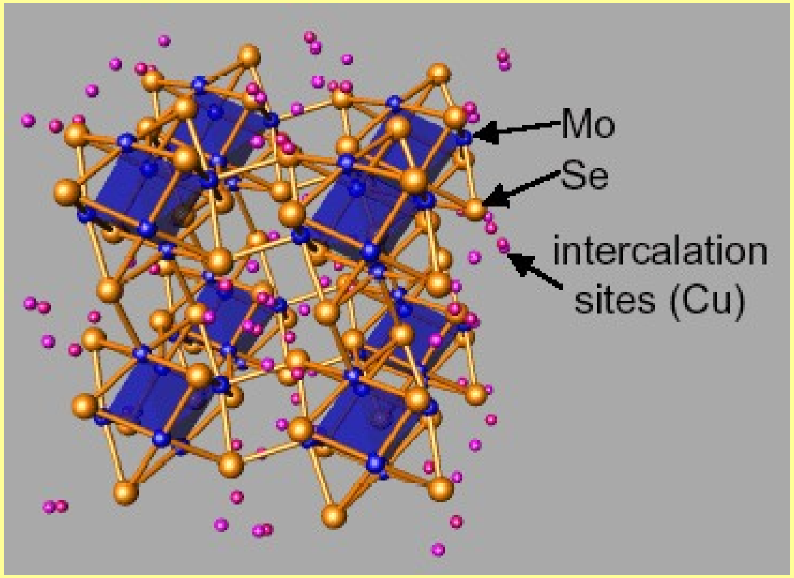
CPA much better than virtual crystal approx. V_{VCA}

Present KKR-CPA code allows for treatment of more than 2 atoms on disordered site, but within *muffin-tin* potential (problem with CPA condition), CPA is also solved self-consistently; imaginary part of $E(\mathbf{k})$ related to electron life-time due to disorder !

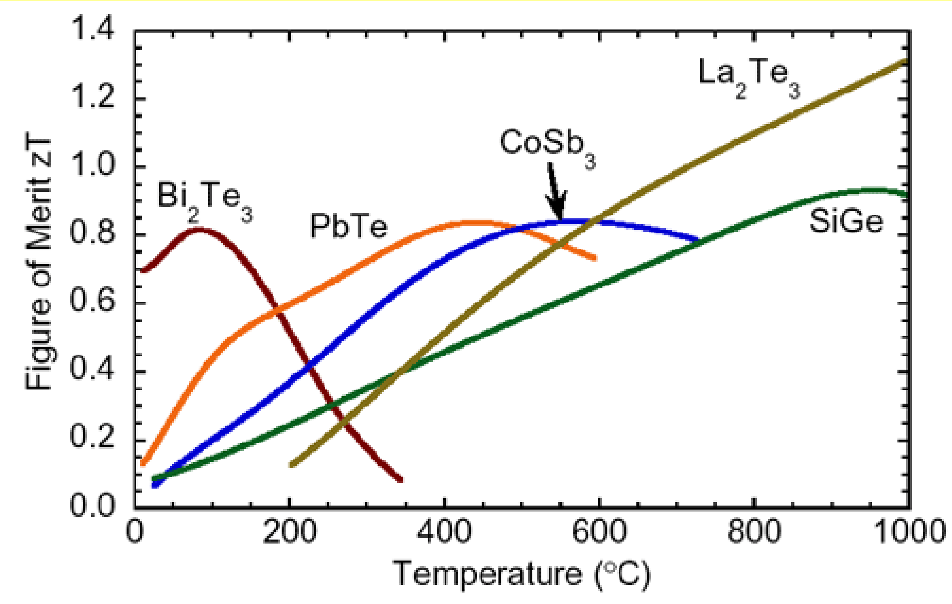
Thermoelectric materials

$$ZT = \frac{S^2}{\rho\,\kappa}$$

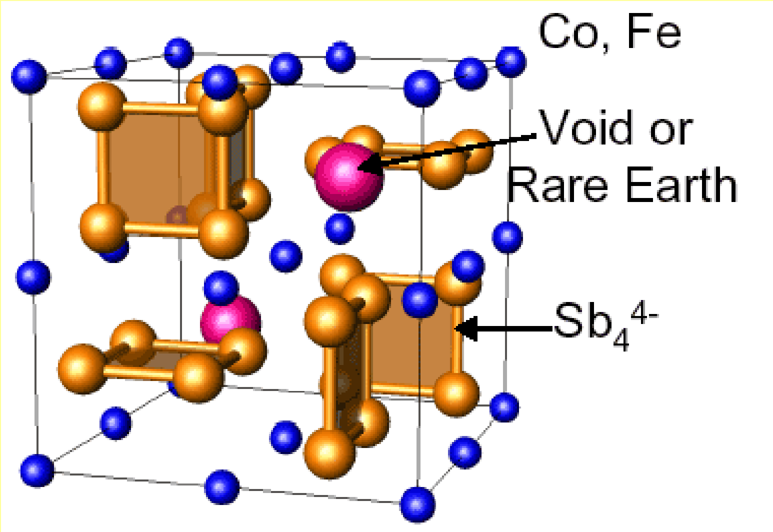




Chevrel phases



J. Snyder, JPL-NASA



Skutterudites

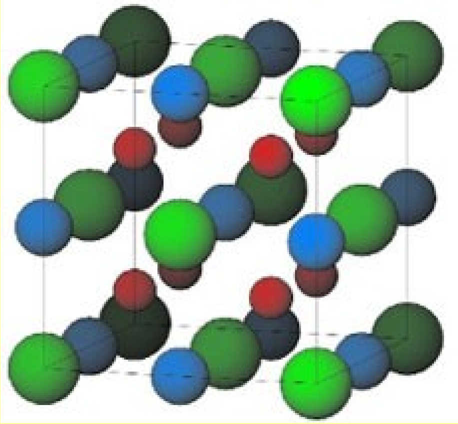
Electronic structure peculiarities

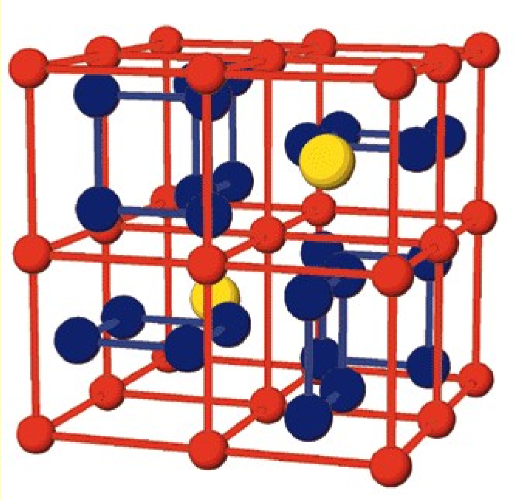
<u>Half-Heusler</u> (VEC=18)

Semiconductors/semimetals

(CoTiSb, NiTiSn, FeVSb, ...)

<u>9 + 4 + 5=18</u> **wide variety !!**





<u>Skutterudites</u> (VEC=96)

semiconductors/semimetals

($CoSb_3$, $RhSb_3$, $IrSb_3$, CoP_3 ...)

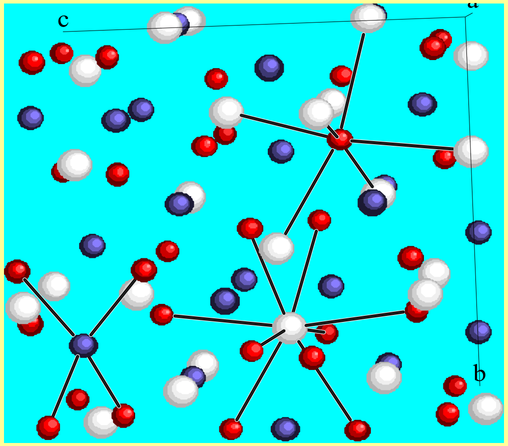
<u>4 x 9 +12 x 5 = 96</u>

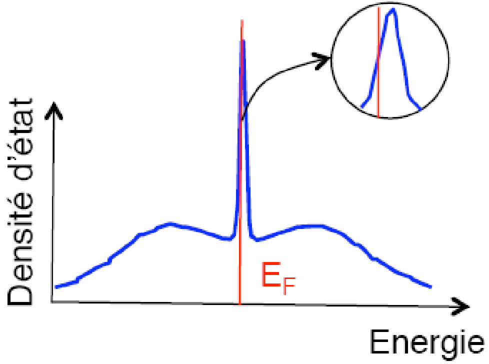
<u>Zintl phases</u> (VEC=62)

semiconductors/semimetals

($Y_3Cu_3Sb_4$, $Y_3Au_3Sb_4$, ...)

<u>3 x 4 + 3 x 10 + 4 x 5 = 62</u>

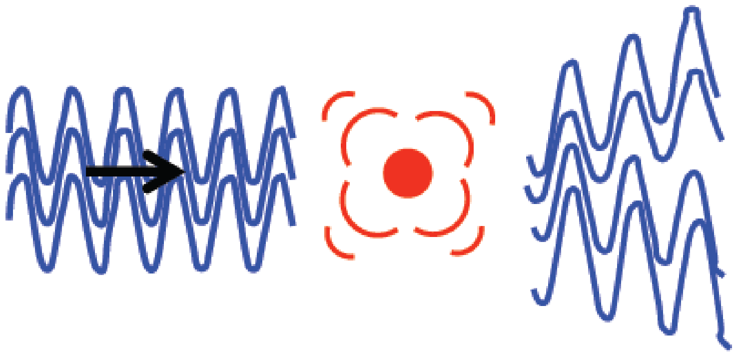


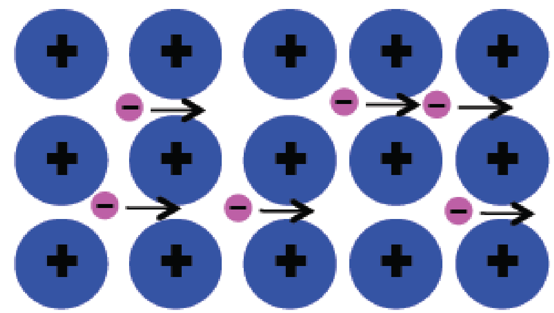


Concepts of ZT improvement

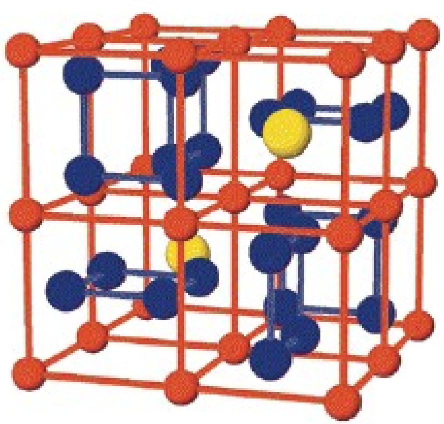
Sharp DOS (heavy fermions, QC, low dimension).

PGEC – „phonon glass” + „electron crystal” (Slack, ‘95)

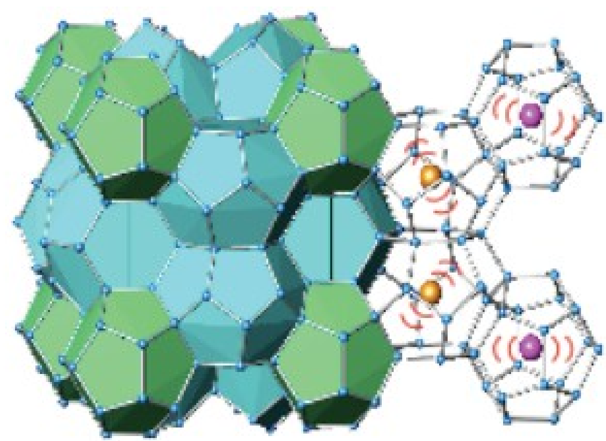




more complex structures + specific vibrations (rattling, phonon, magnon)



skutterudites



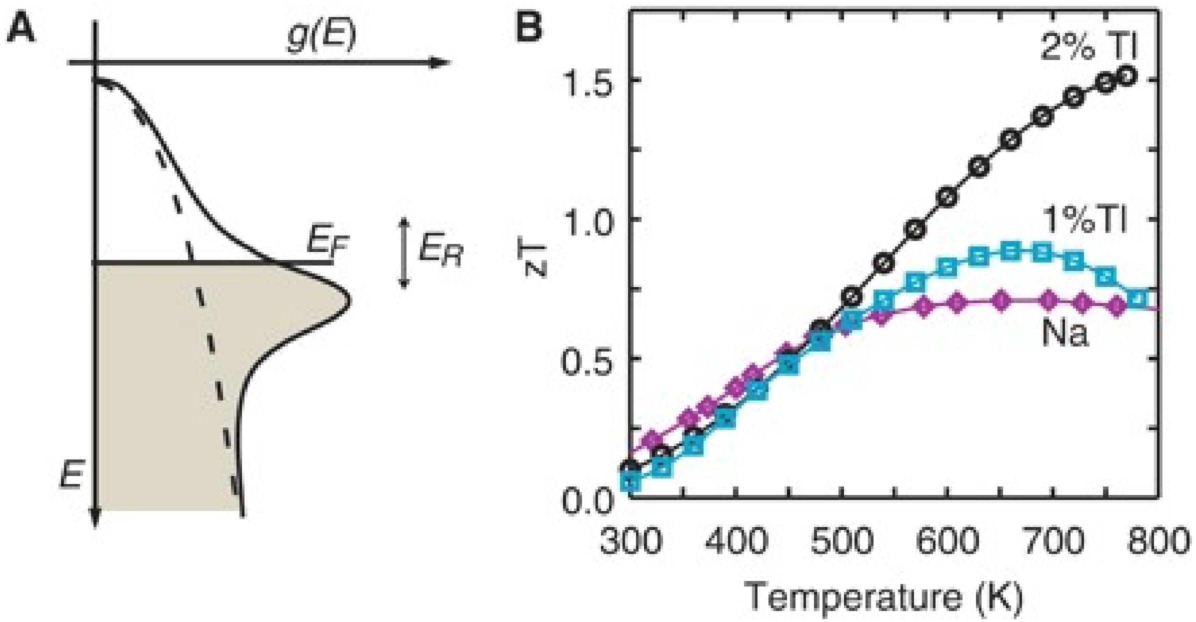
clathrates

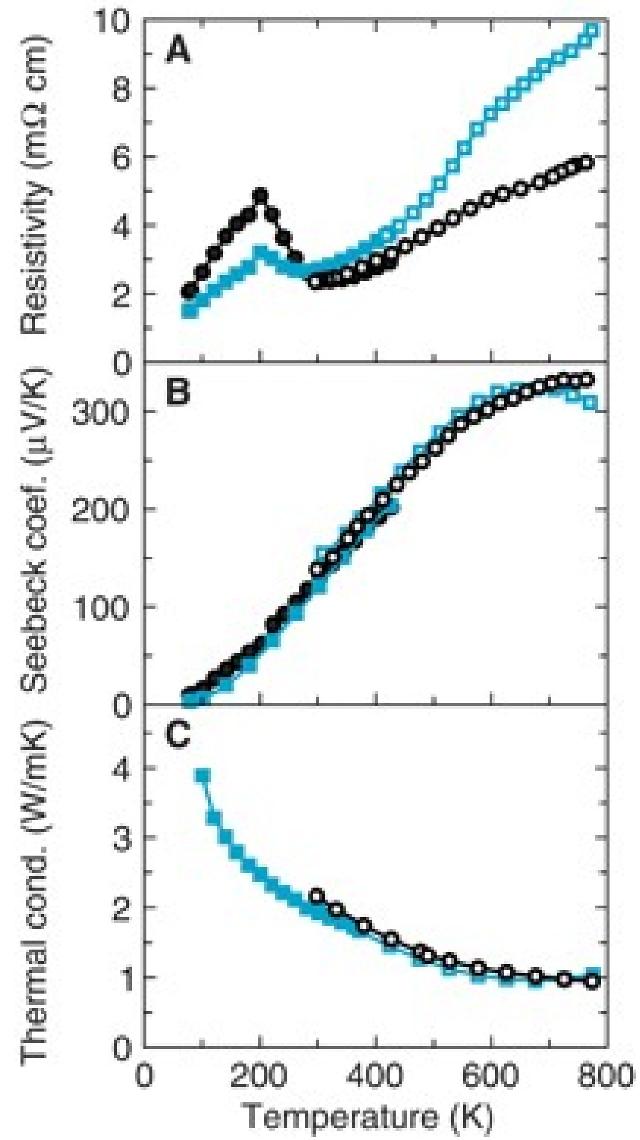
B. Lenoir, GDR-Thermo, Bordeaux (2008)

Enhancement of TE efficiency in PbTe
(distortion of electronic DOS)

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

Mott's formula for thermopower





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

Electron transport coefficients

$$\boldsymbol{\sigma}_e = \mathscr{L}^{(0)},$$

Electrical conductivity

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

Seebeck coefficient (thermopower)

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

Electronic thermal conductivity

$$L(T) = \frac{\kappa_e(T)}{\sigma(T)T}$$ Wiedemman-Franz-Lorenz

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

$$PF = S^2\sigma$$

Onsager-related functions

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

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

$L(T,n)$

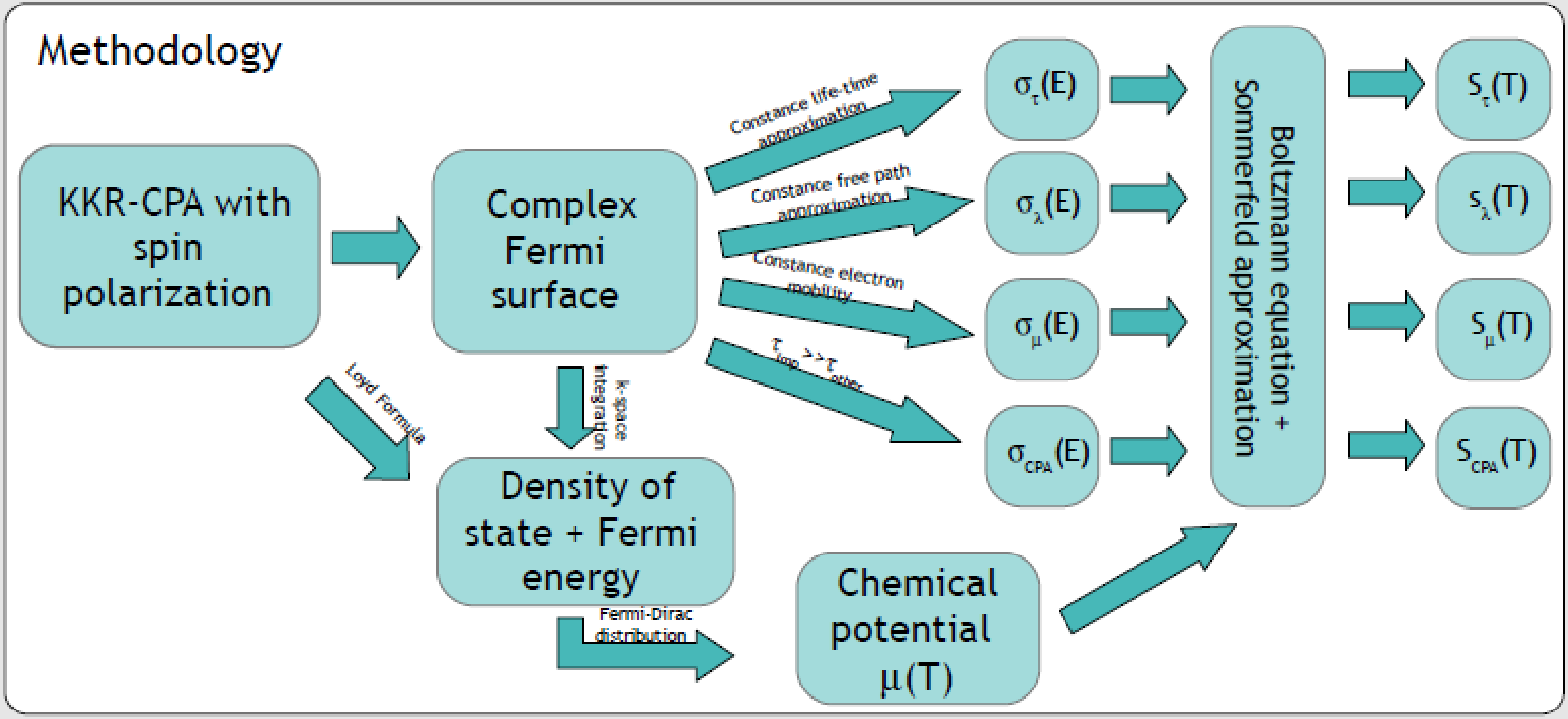
$PF(T,n)$

Transport functions (in general tensors)

$ZT(T,n)$

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

Boltzmann transport & KKR-CPA calculations of complex energy bands and thermopower



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

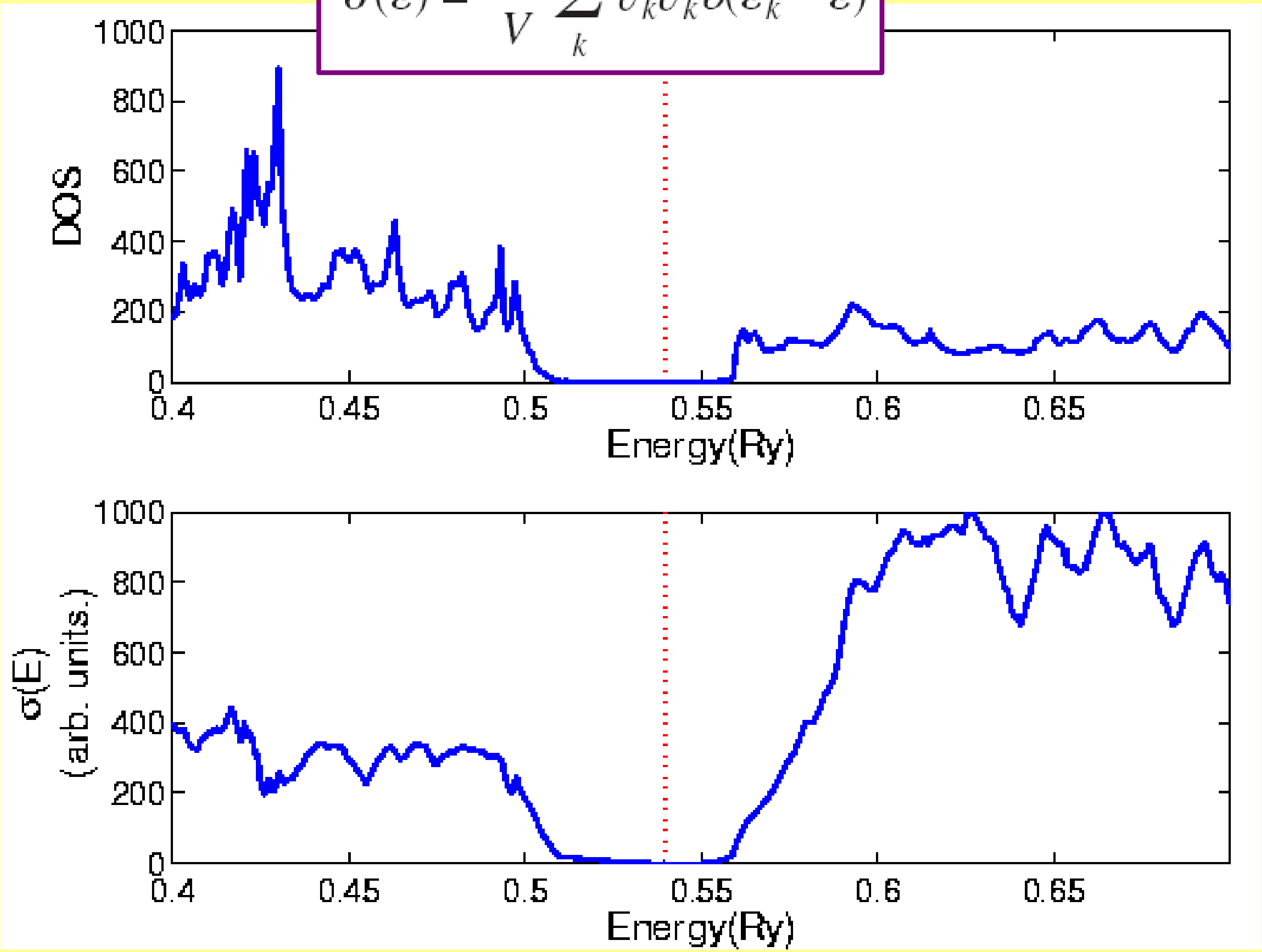
Different approximations used

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

DOS vs. transport function σ(E)

$$\sigma(\varepsilon) = \frac{q^2\tau}{V}\sum_k \vec{v}_k\vec{v}_k\delta(\varepsilon_k - \varepsilon)$$

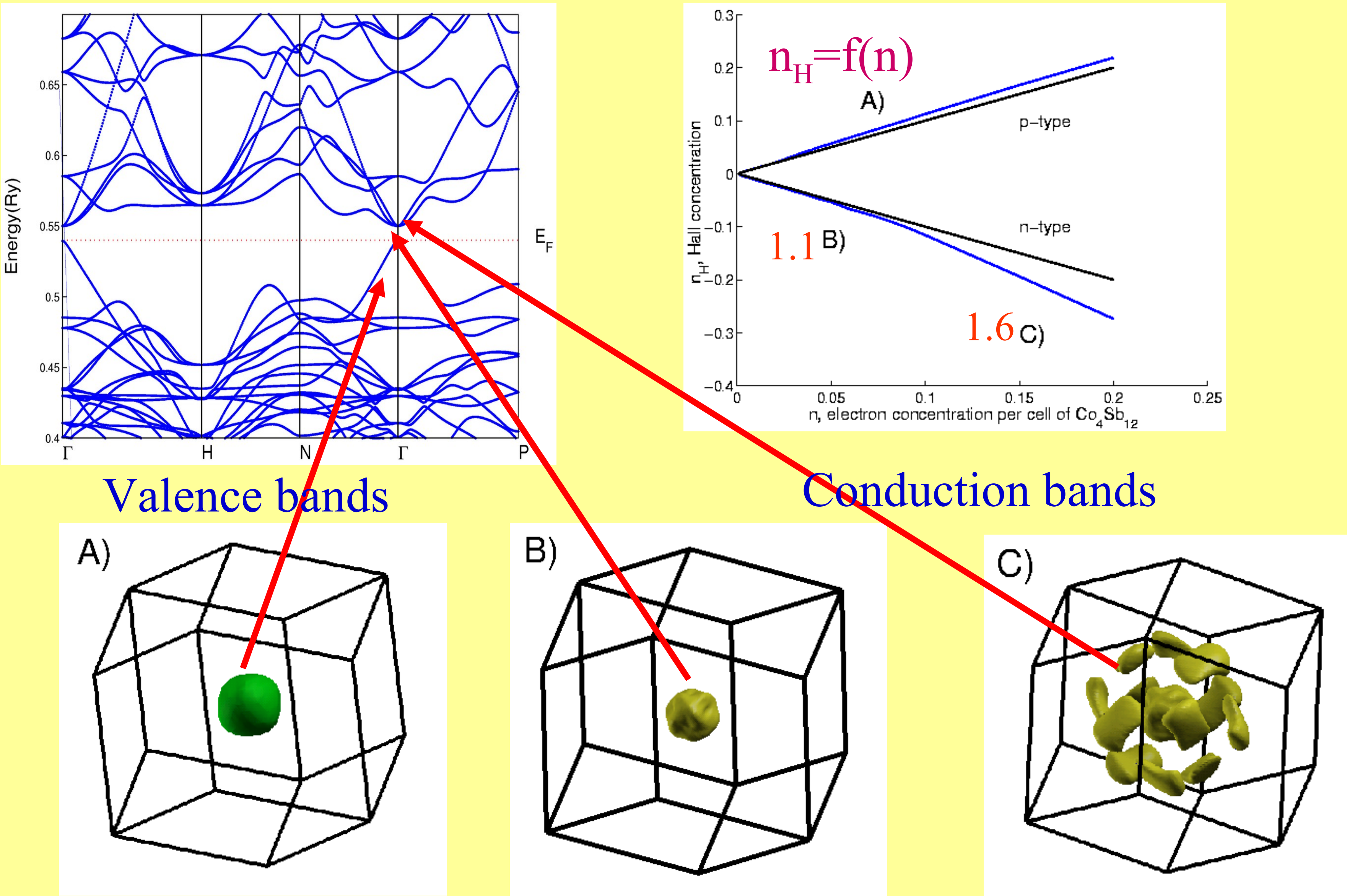
Chaput, ... JT, PRB (2005)



Small substitution/doping 0.01-0.05 el. per Co_4Sb_{12} → $\Delta E_F \approx 1\text{-}2$ mRy

Doped $CoSb_3$: FS vs. Hall concentration (rigid band)

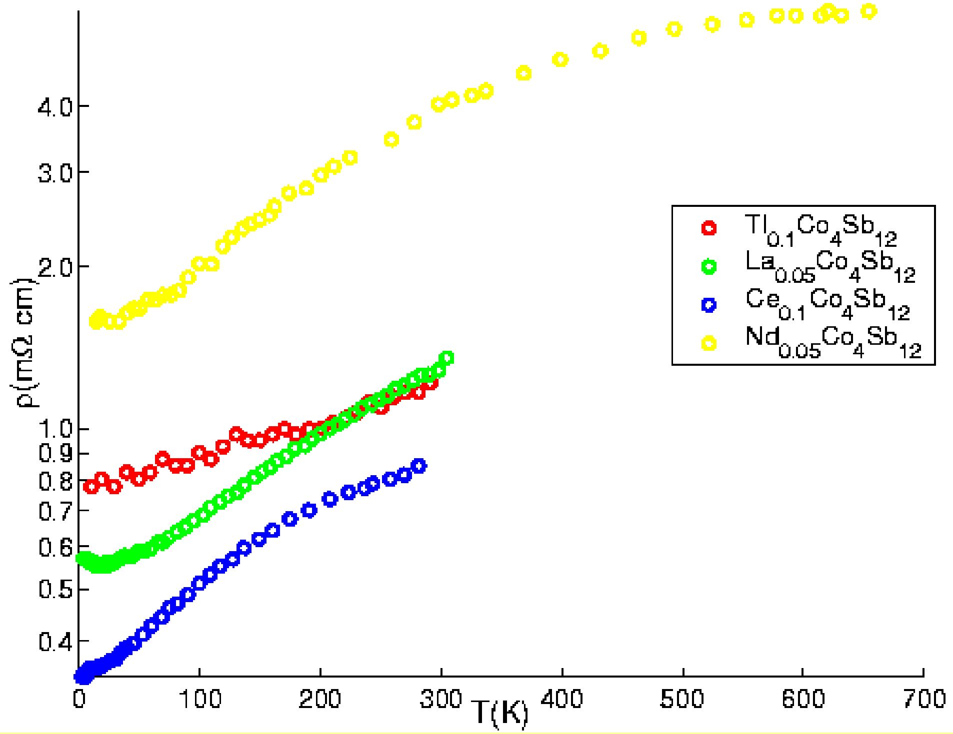
Chaput, ... JT, PRB (2005)



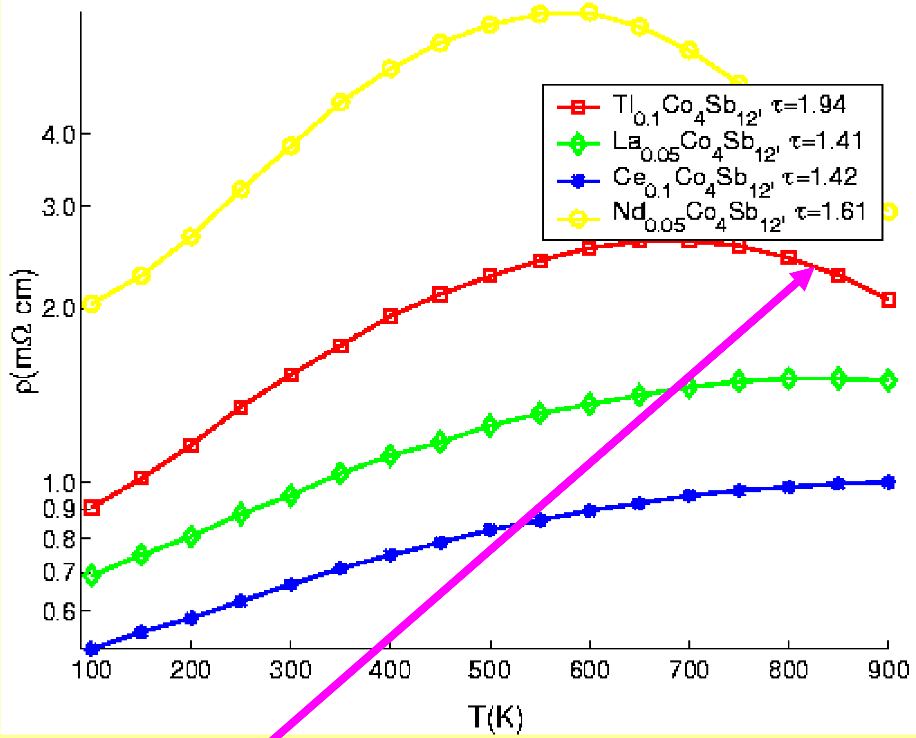
E_F=0.5191 Ry, n=0.01 E_F=0.5570 Ry, n=0.01 E_F=0.5585 Ry, n=0.06

Doped $CoSb_3$: electrical resistivity

Experiment (literature)



FLAPW calculations

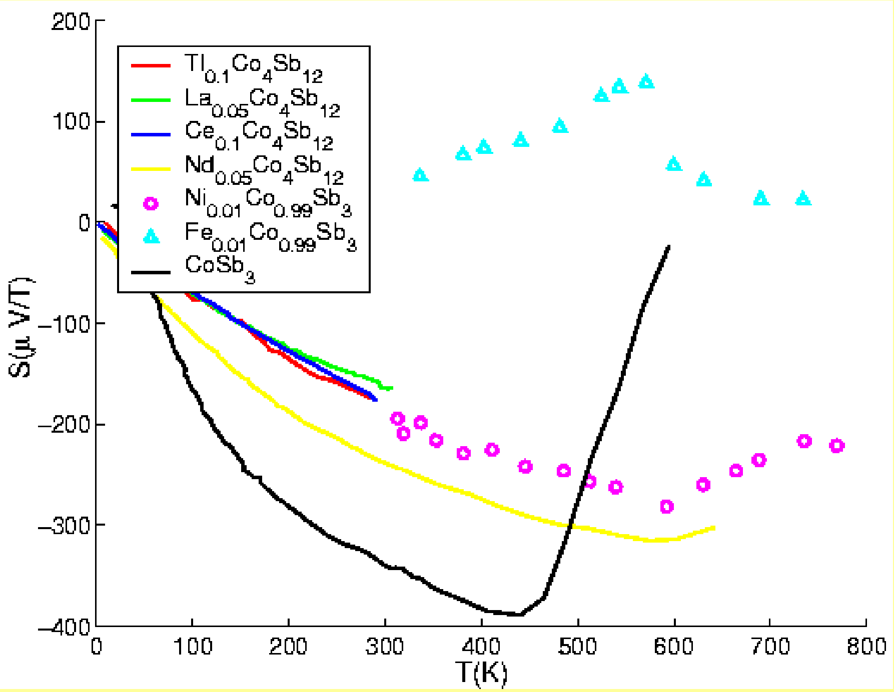


Constant relaxation time (only one free parameter selected in order to gain the best fits to experimental resistivity curves, includes also lattice contribution) ($\tau \sim 10^{-14}$ s), concentration of carriers taken from Hall measurements (not from nominal composition !)

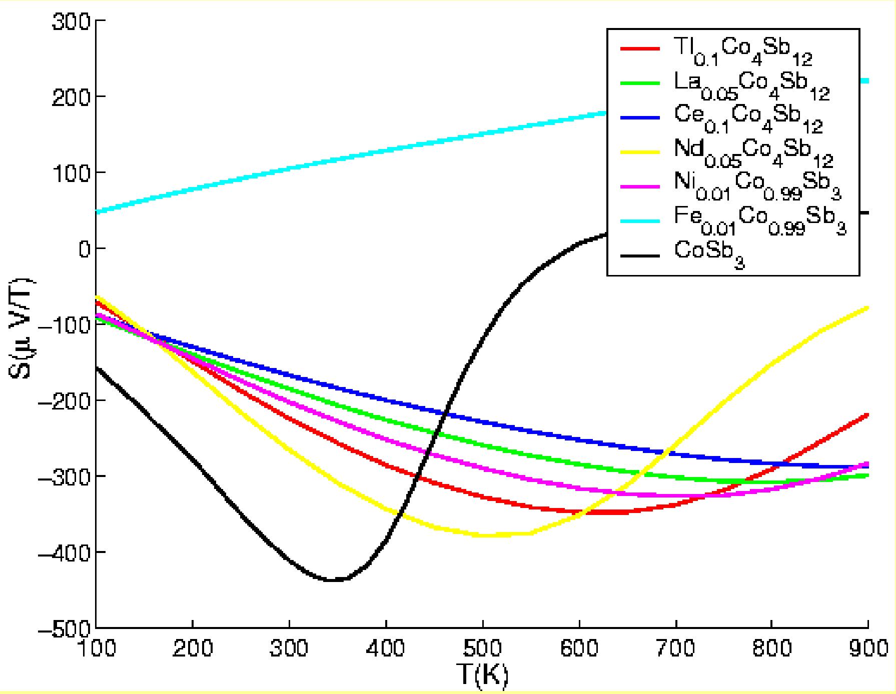
Chaput, ... JT, PRB (2005)

Doped $CoSb_3$: thermopower

Experiment (literature)



FLAPW calculations



Constant relaxation time – NOT important, since Seebeck coefficient Does not depend on this parameter – Excellent test for theory !!

$$S(T) = e(3T\sigma)^{-1} \int dE\, N(E)\, v^2(E)\, E\, \tau(E,T)\, [-\partial f(E)/\partial E\,]$$