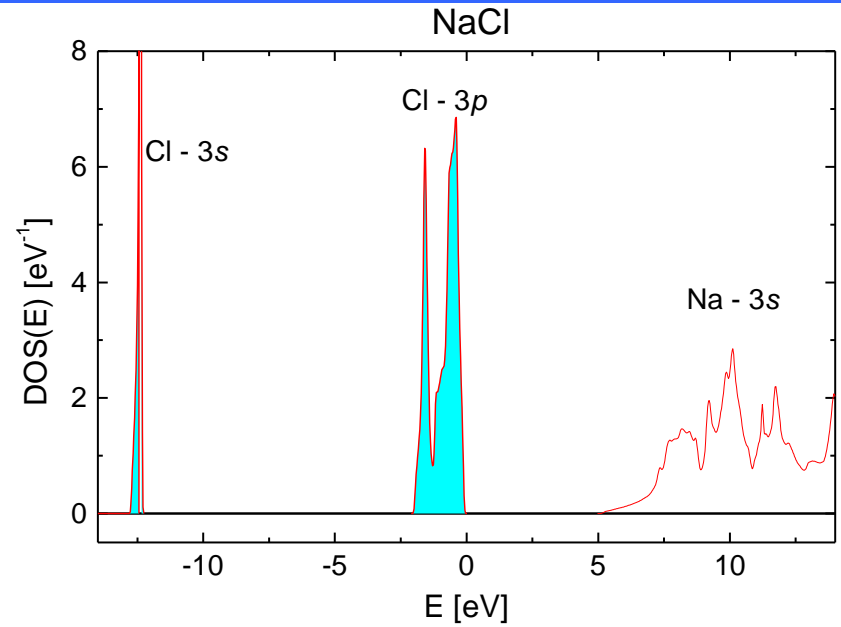
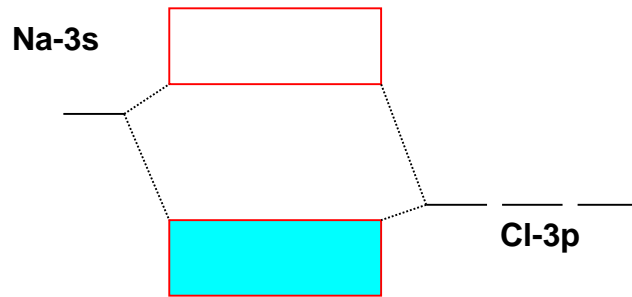
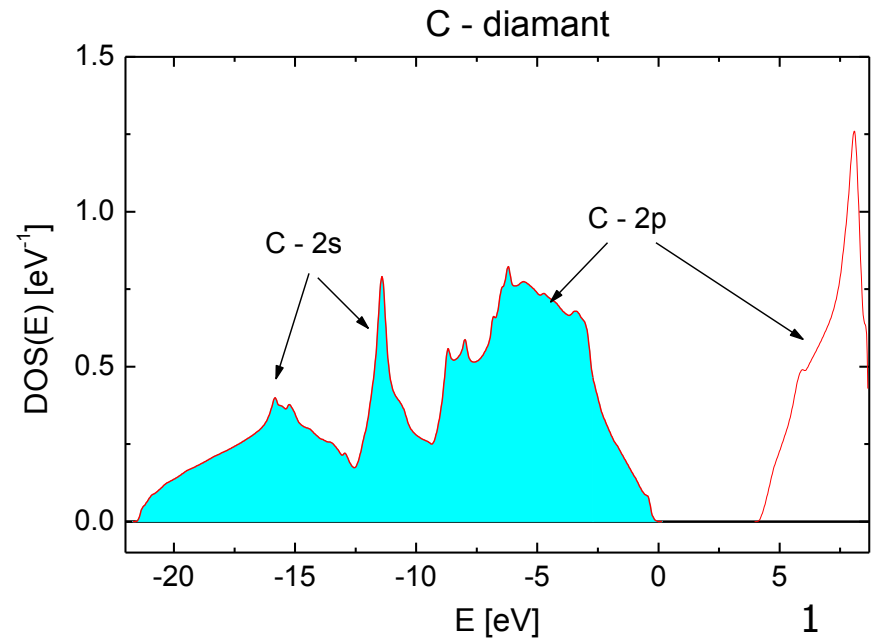
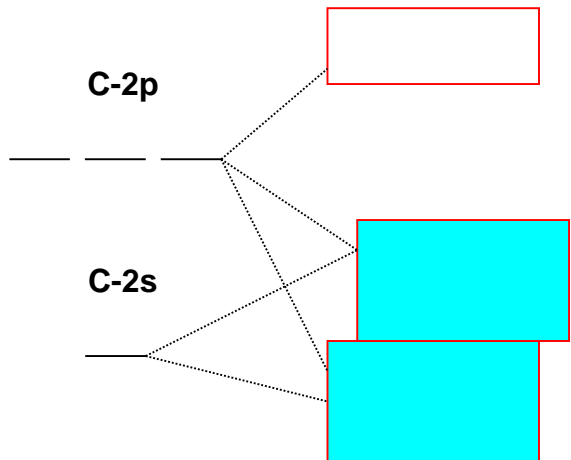


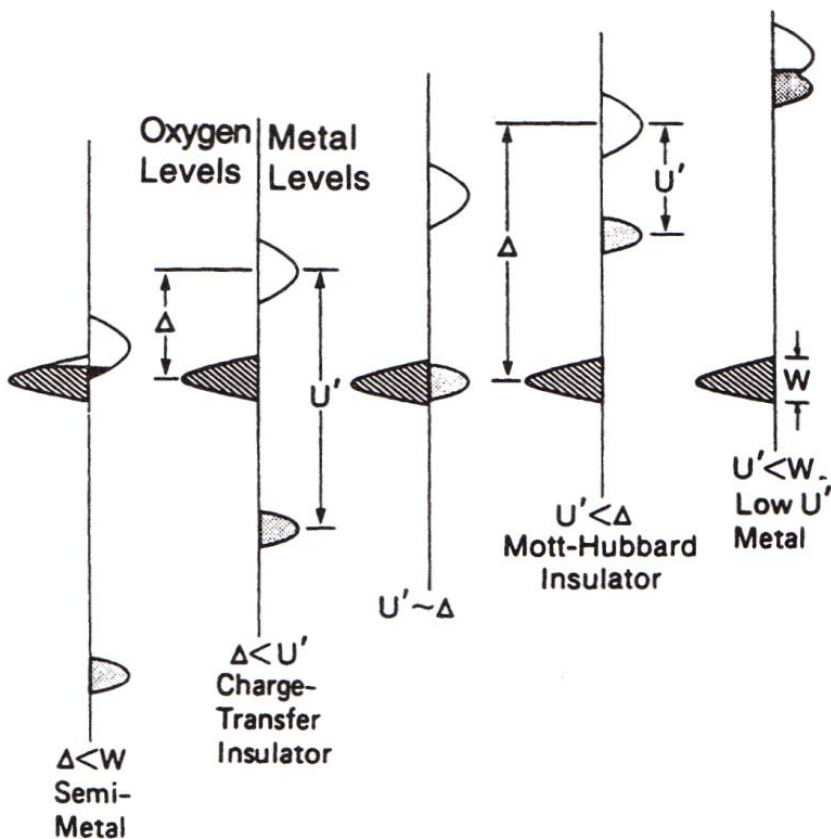
**ionic insulator**



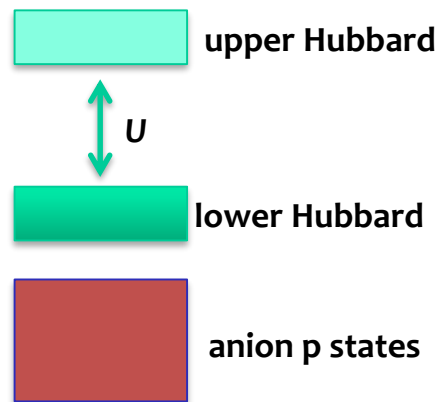
**covalent insulator**



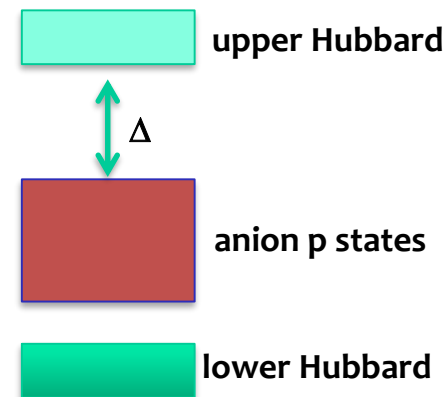
System	Stability .
Semi-Metal	$\Delta < W$
Charge transfer insulator	$\Delta < U$
Mott-Hubbard insulator	$U < \Delta$
Metal	$U < W$



Mott-Hubbard insulators:



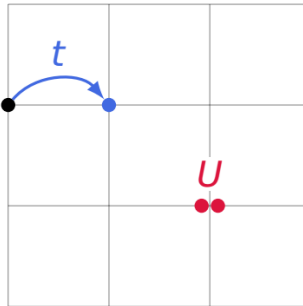
Charge-transfer insulators:



System	Stability.
Semi-Metal	$\Delta < W$
Charge transfer insulator	$\Delta < U$
Mott-Hubbard insulator	$U < \Delta$
Metal	$U < W$

One band:

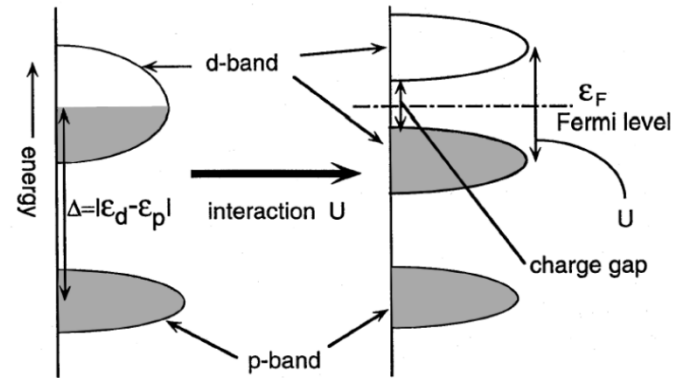
$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^+ c_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$



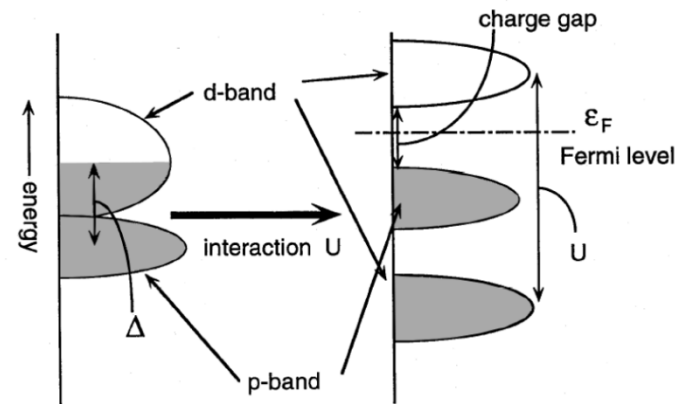
Coulombic interaction  $U$

Generalization for many bands

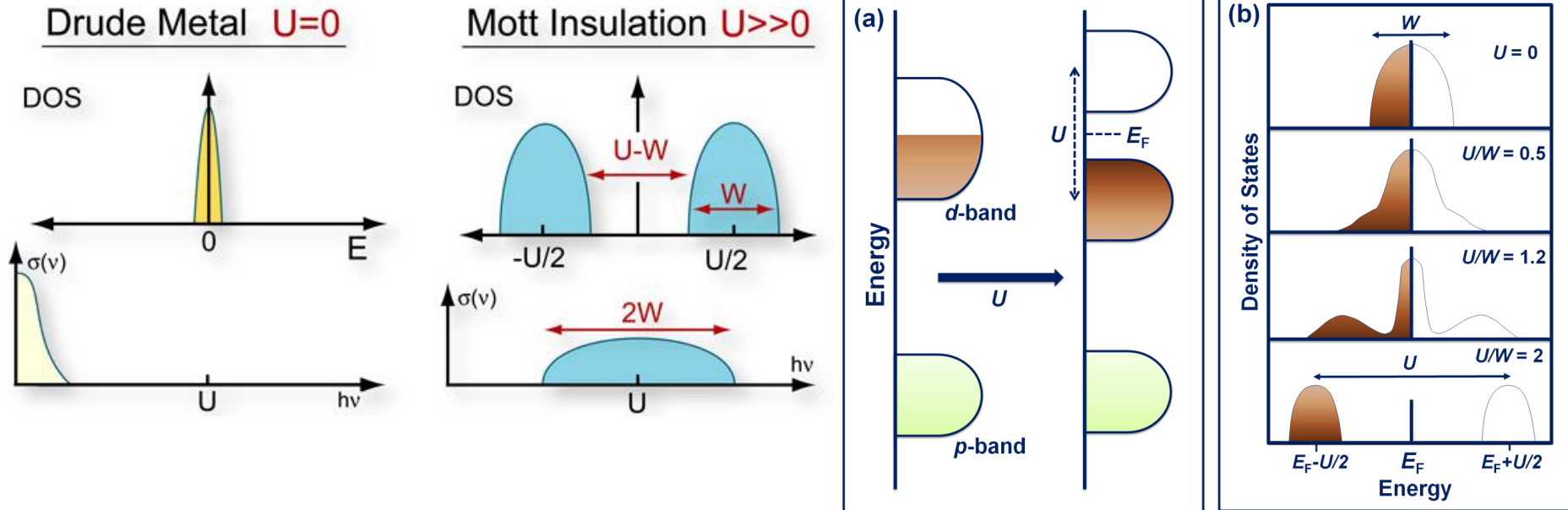
$$U \hat{n}_{\uparrow} \hat{n}_{\downarrow} \rightarrow \sum_{ijkl} U_{ijkl} c_i^+ c_j^+ c_l c_k$$



(a) Mott-Hubbard Insulator



(b) Charge Transfer Insulator



The case of the Mott insulator is due to high electronic correlations competing with the kinetic energy of the conducting electrons. Free electrons in a metal tend to delocalize over the lattice to minimize their energy. However the Coulomb repulsion between them works against that and localizes the electrons on the lattice sites. That reduces the density of states (DOS) at the Fermi energy and the Mott gap opens. The DOS splits into a lower (LHB) and upper (UHB) Hubbard band.

U – Coulombic interaction of electrons (Hubbard parameter)

J – Exchange interaction of electrons with opposite spin  $+\sigma, -\sigma$

(Exchange parameter)

$F^0$  = monopole integral

$F^2$  = dipole like integral

$F^4$  = quadrupole integral

$U = F^0$

$J = (F^2 + F^4)/14$

The dependence of the energy on the orbital occupancy:

Occupied states are stabilized

$$\epsilon_i = \frac{\partial E}{\partial n_i} = \epsilon_i^{\text{LDA}} + U(1/2 - n_i)$$

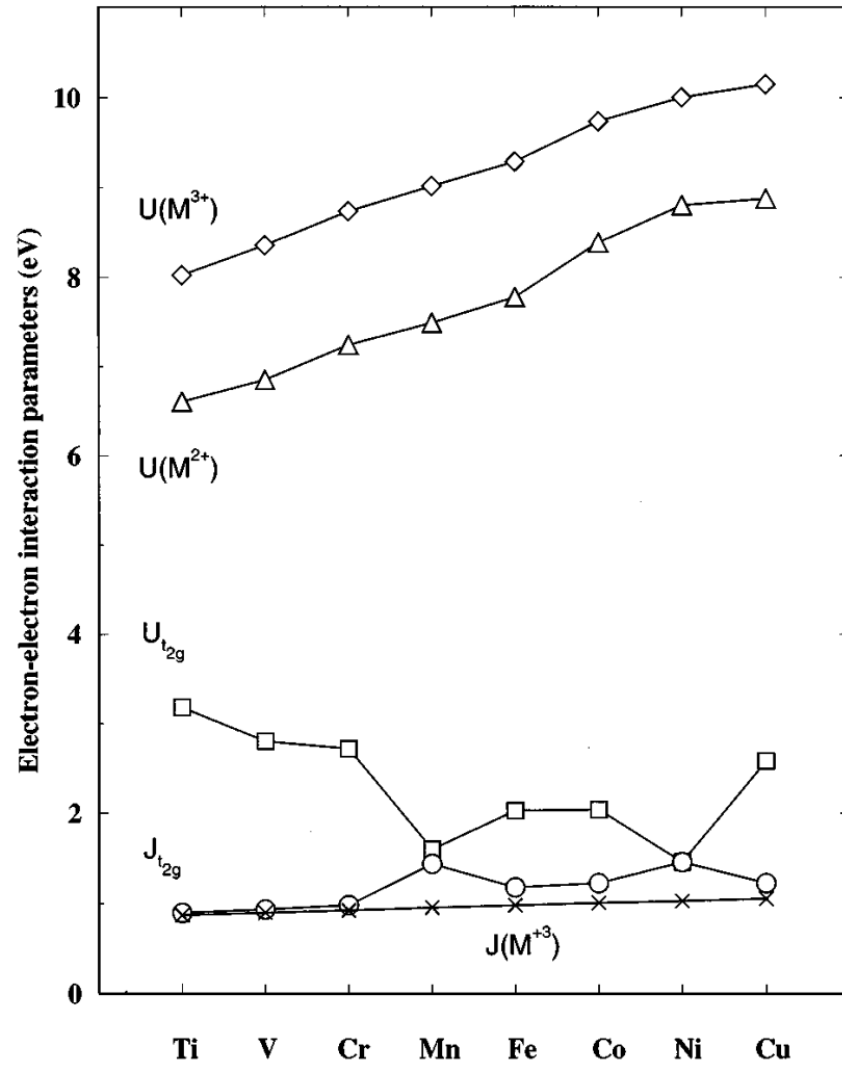
The main idea of our LDA+U method is that the LDA gives a good approximation for the average Coulomb energy of  $d$ - $d$  interactions  $E_{\text{av}}$  as a function of the total number of  $d$  electrons  $N = \sum_{m\sigma} n_{m\sigma}$ , where  $n_{m\sigma}$  is the occupancy of a particular  $d_{m\sigma}$  orbital:

$$E_{\text{av}} = U \frac{N(N-1)}{2} - J \frac{N(N-2)}{4}. \quad (1)$$

But the LDA does not properly describe the full Coulomb and exchange interactions between  $d$  electrons in the same  $d$  shell. So we suggest subtracting  $E_{\text{av}}$  from the LDA total-energy functional, and adding orbital- and spin-dependent contributions to obtain the exact (in the mean-field approximation) formula

$$\begin{aligned} E = E_{\text{LDA}} - & \left( U \frac{N(N-1)}{2} - J \frac{N(N-2)}{4} \right) \\ & + \frac{1}{2} \sum_{m, m', \sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} \\ & + \frac{1}{2} \sum_{m \neq m', m', \sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}. \end{aligned} \quad (2)$$

The dependence of U and J on the atomic number for transition metals 3d



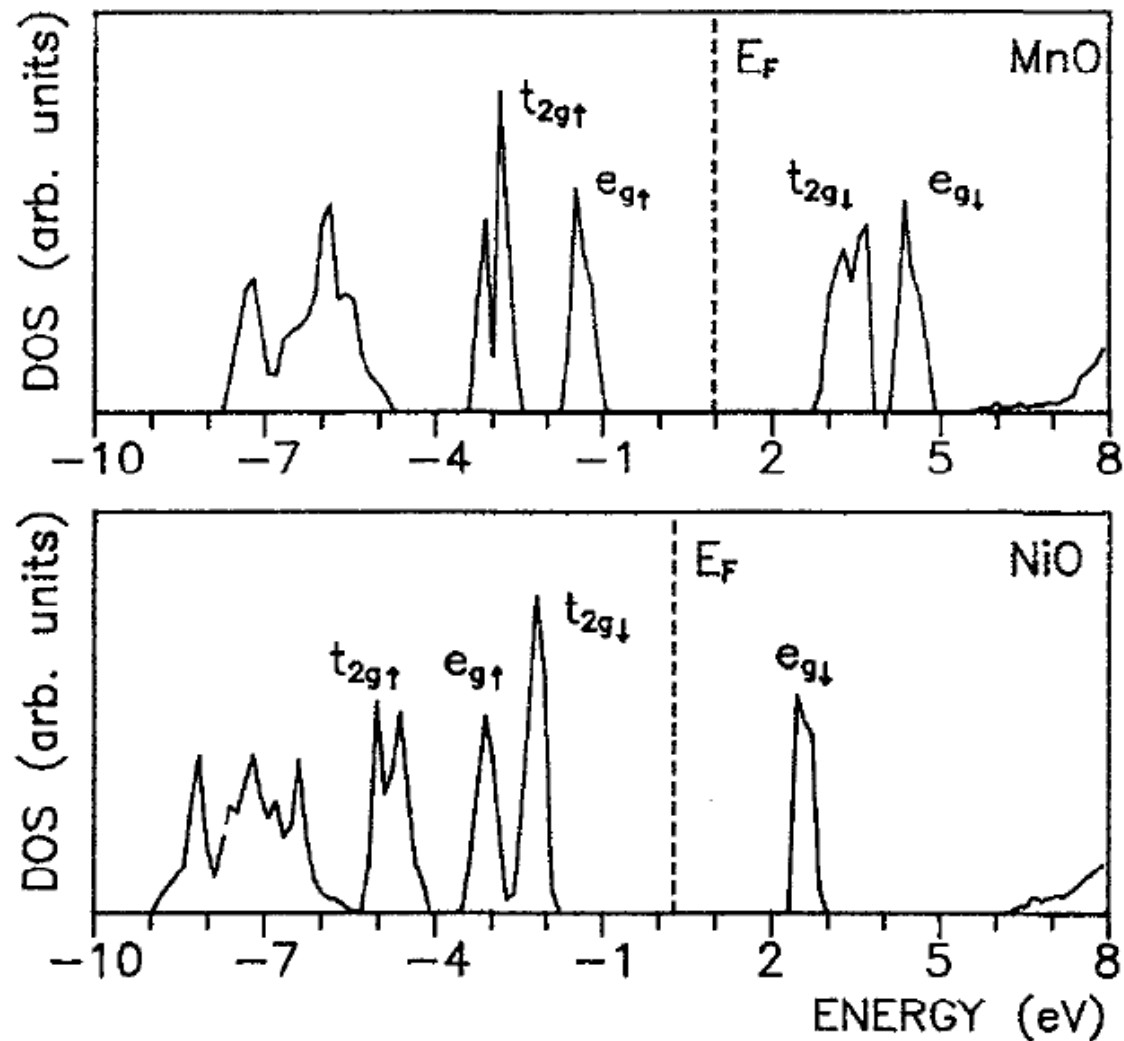
MnO:  $\text{Mn}^{2+} d^5$ NiO:  $\text{Ni}^{2+} d^8$ 

Fig. 1. Ground state densities for MnO and NiO.

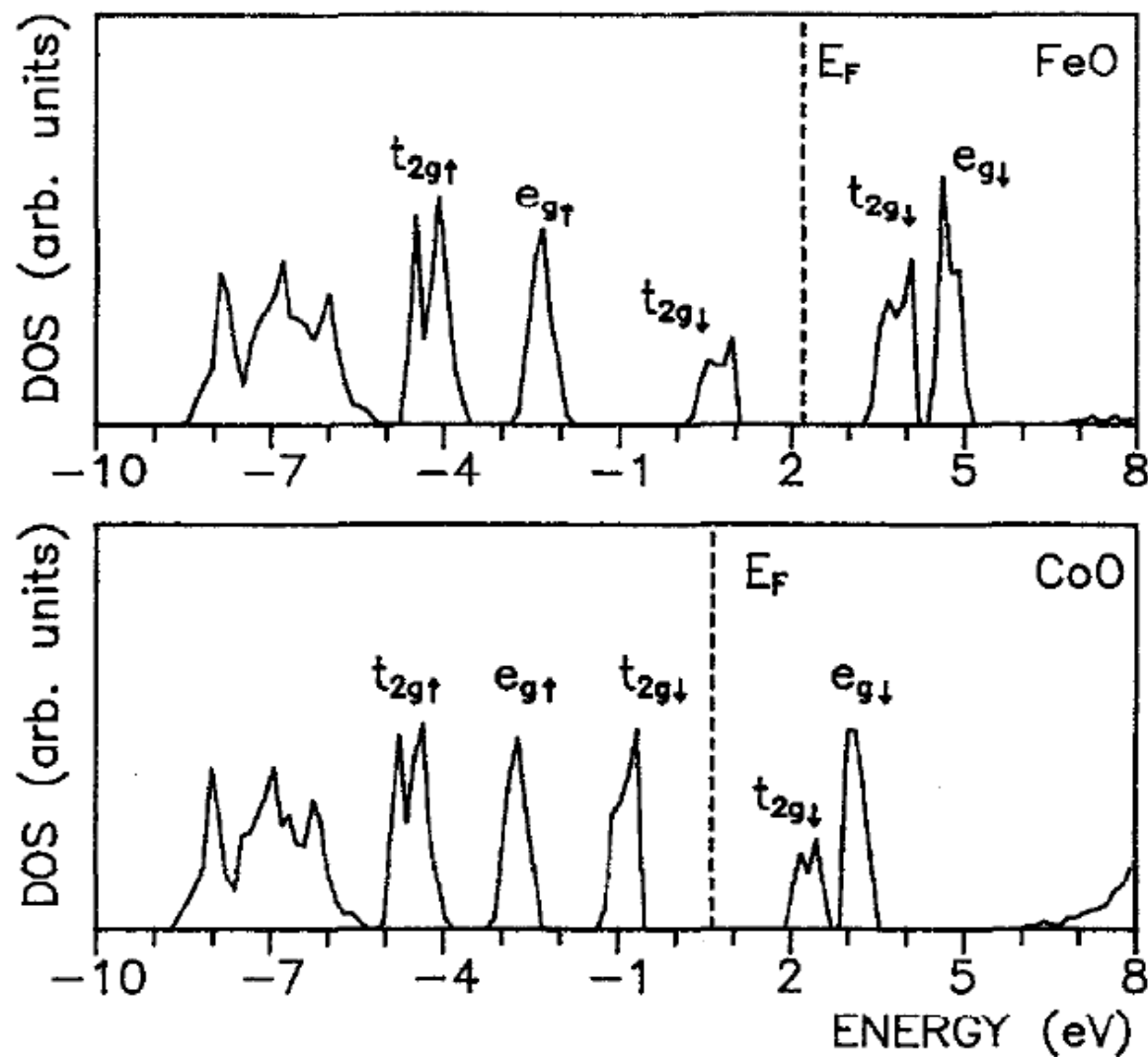
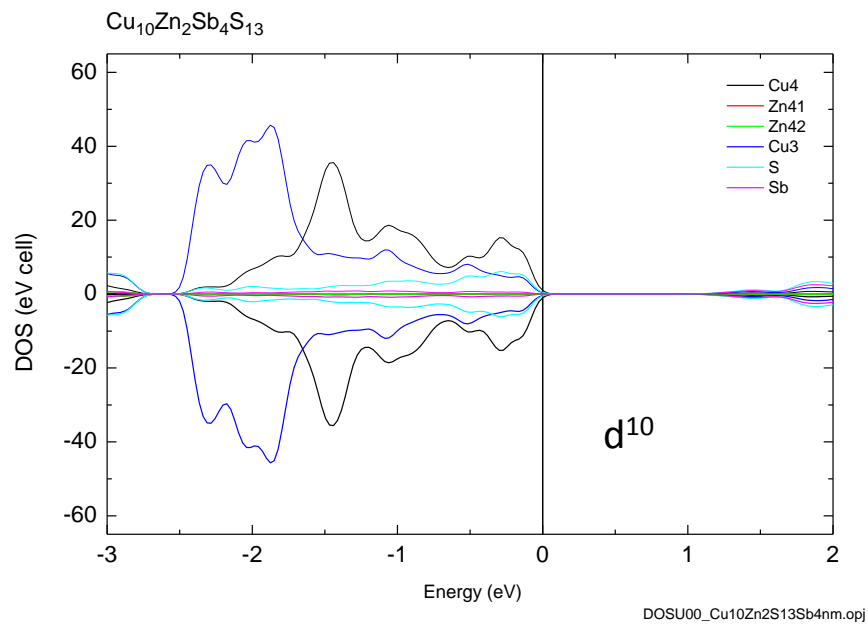
FeO: Fe<sup>2+</sup> d<sup>6</sup>CoO: Co<sup>2+</sup> d<sup>7</sup>

Fig. 2. Ground state densities for FeO and CoO.



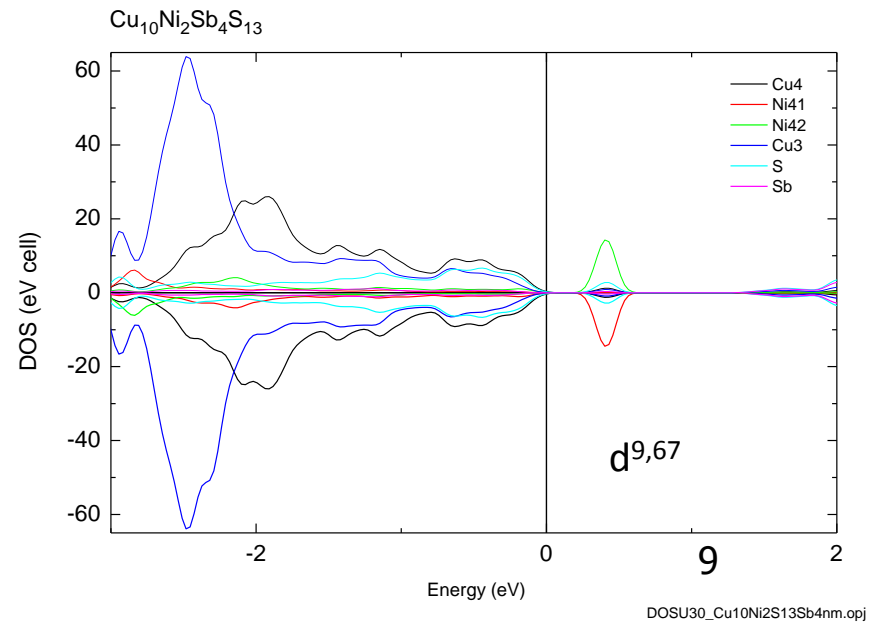
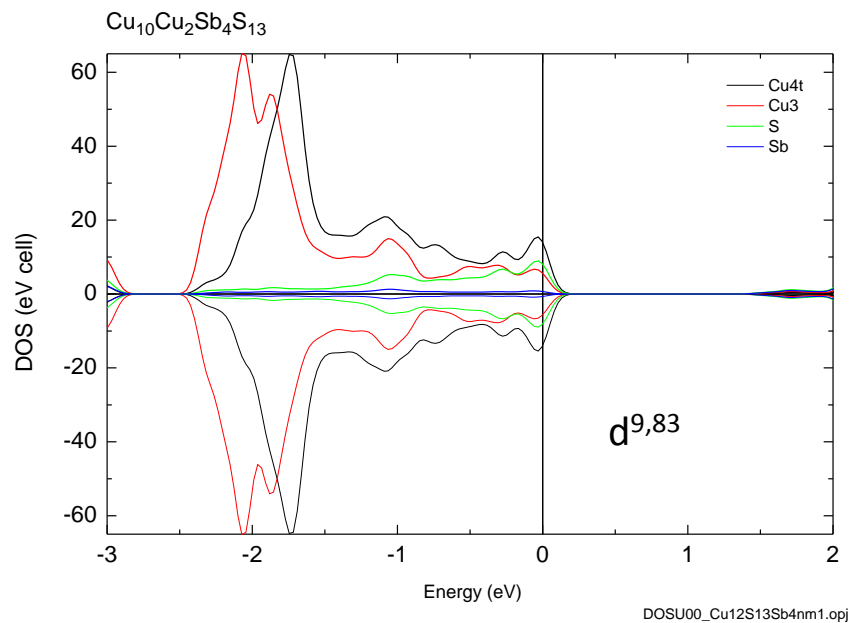
## Tetrahedrite

10×Cu<sup>1+</sup> – d<sup>10</sup>

2×Zn<sup>2+</sup> – d<sup>10</sup>

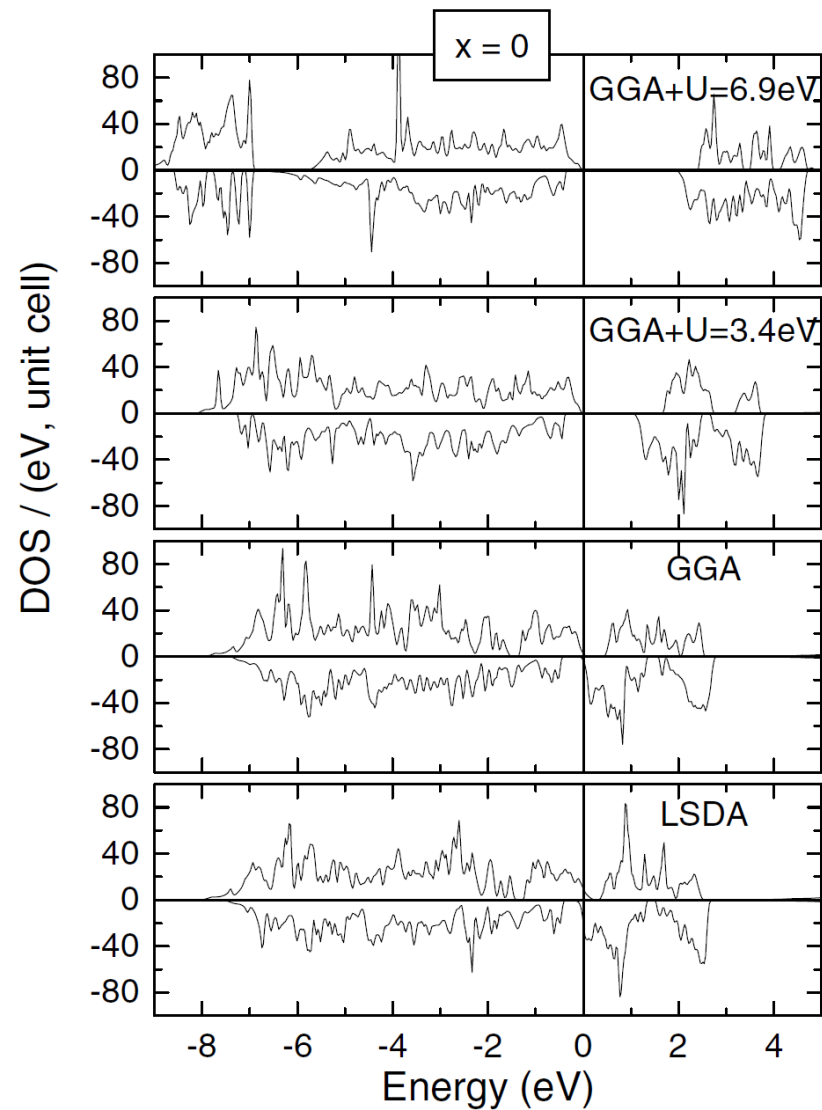
4×Sb<sup>3+</sup>

13×S<sup>2-</sup>



$U (F^0)$  is strongly reduced in the presence of a polarizable medium since it involves a change in the local charge i.e. ionization potential minus electron affinity.

However the other higher order multipole integrals involve simply a dependence on the way the orbitals are occupied keeping the electron count fixed. The surroundings hardly notices such changes and so these integrals remain close to the atomic values.



**Fig. 2.** Total DOS for majority (positive) and minority (negative) states in SrFe<sub>12</sub>O<sub>19</sub> calculated by LSDA, GGA and GGA+U methods with  $U = 3.4$  eV and  $U = 6.9$  eV.

Localization due to the disorder.

**Weak localization:**

for  $T \rightarrow 0$  K, small degree of disorder.

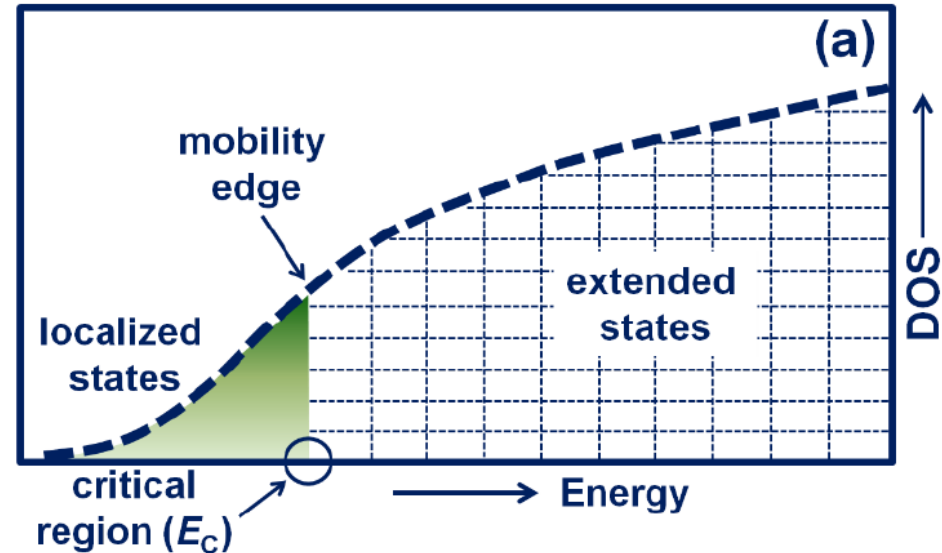
**Andersonova localization:**

higher degree of disorder

$E_C$  – mobility edge

$E_F < E_C$  : insulator

$E_F > E_C$  : metal



Electrons in metals are generally found in asymptotically free wave states, and the probability of finding them is the same in the whole volume. However, P. W. Anderson has shown that with a sufficiently large degree of disorder, all the electron states of the solid may be located in different small parts of the sample volume, and that no electron will be able to move to longer distance even after applying a weak electric field. The originally conductive metal becomes an insulator and electron diffusion completely disappears. Asymptotically free electron states becomes localized (bound) states restricted in some volume by impurities. At this metal-insulating transition, it is unusual that it occurs at a selected energy only by changing the concentration of the impurities in the sample. This means that the same energy can have both scattered and bound states depending on how strong the disorder is in the crystal.

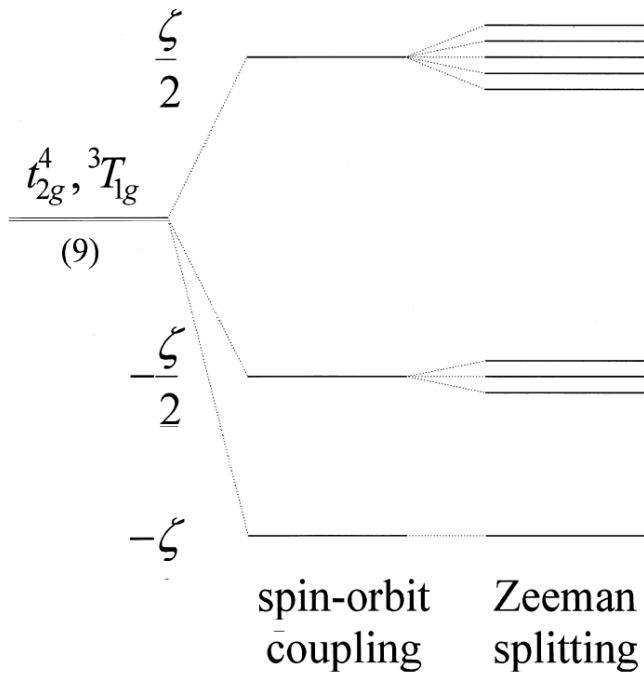


Fig. 5. Energy level diagram for  $t_{2g}^4$  configurations.

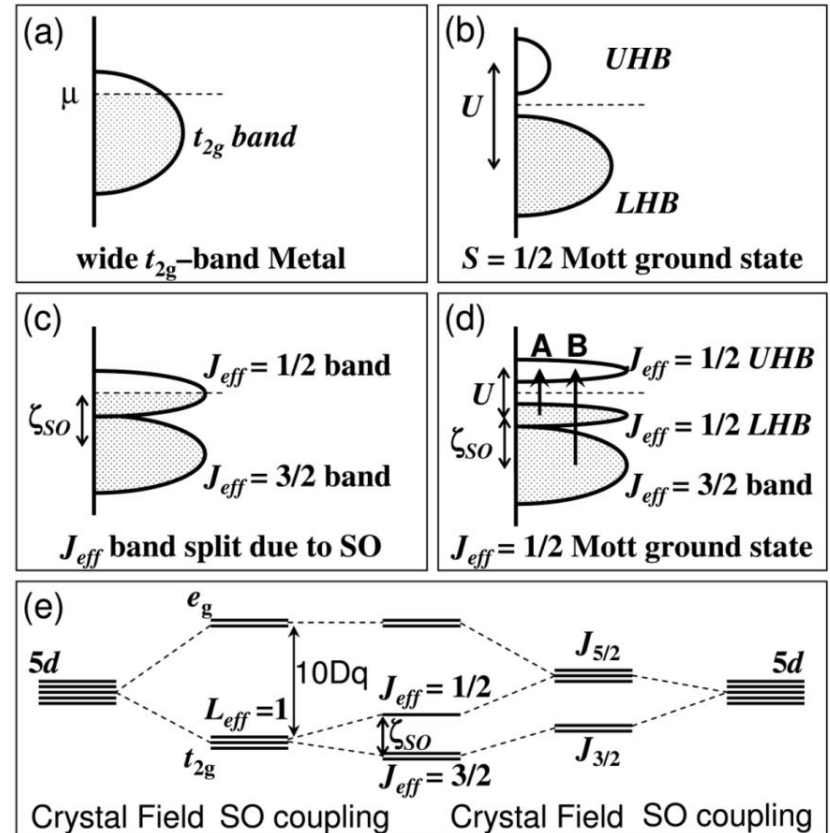
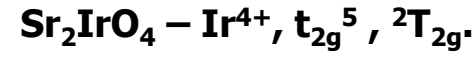
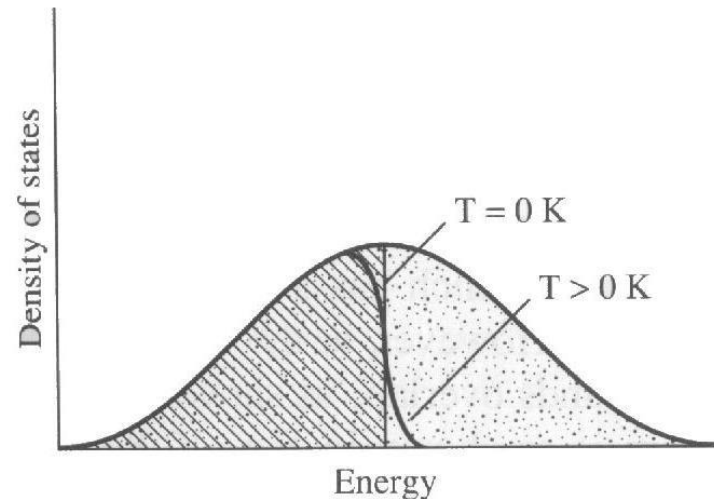
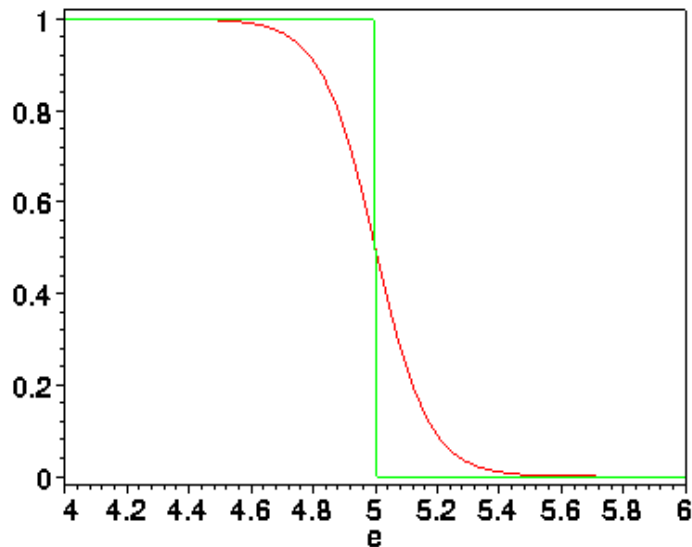


FIG. 1. Schematic energy diagrams for the  $5d^5$  ( $t_{2g}^5$ ) configuration (a) without SO and  $U$ , (b) with an unrealistically large  $U$  but no SO, (c) with SO but no  $U$ , and (d) with SO and  $U$ . Possible optical transitions A and B are indicated by arrows. (e)  $5d$  level splittings by the crystal field and SO coupling.

Fermi level – the highest occupied energy level at  $T=0$  K

$T > 0$  K: Fermi-Dirac statistics is valid  
occupied states  $\text{DOS}(E) \cdot f(E)$

$$f(E) = \frac{1}{\exp((E - E_F)/k_B T) + 1}$$



**Fermi surface – set of  $k$  in  $k$ -space, for which it applies that  $E(k) = E_F$**

$$E = \frac{mv^2}{2}$$

$$p = mv = \hbar k$$

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \text{energy / } k$$

$$\frac{\partial E}{\partial k} = \frac{\hbar^2 k}{m}$$

$$\frac{\partial^2 E}{\partial k^2} = \frac{\hbar^2}{m}$$

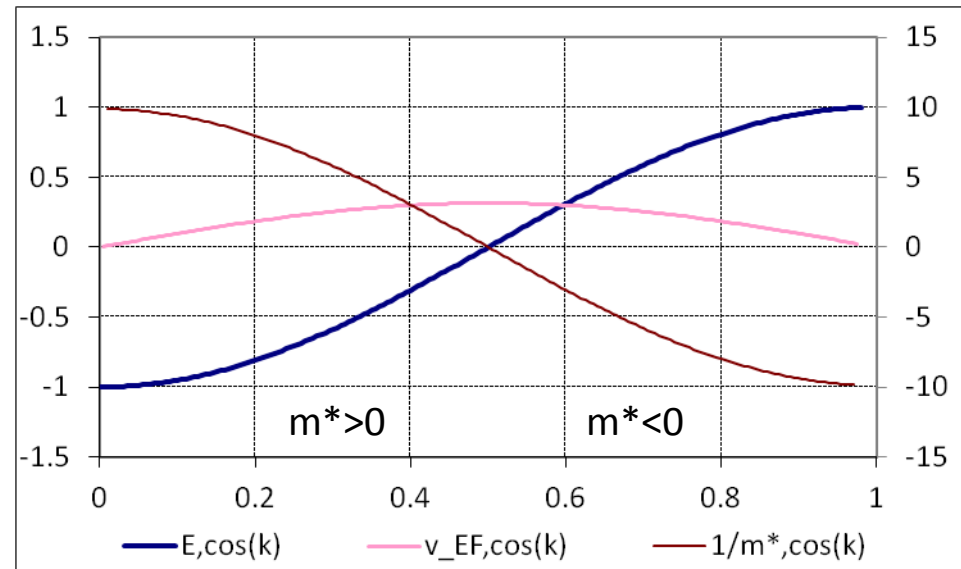
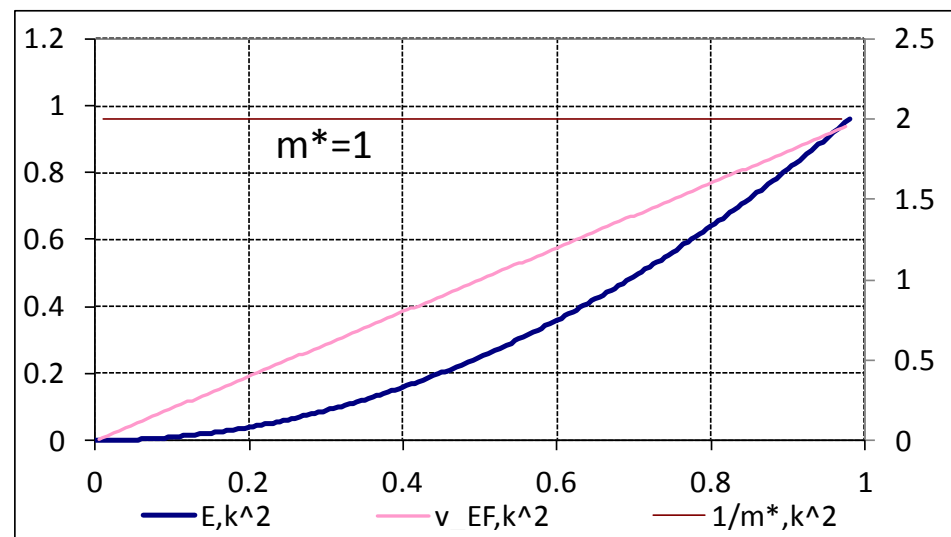
$$v = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$

$$\frac{1}{m} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \quad \text{effective mass}$$

$$DOS^{-1} = \frac{\partial E}{\partial k} = \hbar v$$

$$Fermi - Dirac = \left[ e^{\frac{E}{kT}} + 1 \right]^{-1}$$

E = cos(kπ/a) Tight binding method

E = k<sup>2</sup> Free electron

Drude equation:

$J$  – electrical current

$n$  – number of electrons

$q$  – charge of electron

$\tau$  – relaxation time (time between collisions), for good metals it is

$\tau \sim 10^{-14}\text{s}$

$m$  – mass of electron

$E$  – electric field

$$\mathbf{J} = \left( \frac{nq^2\tau}{m} \right) \mathbf{E}.$$

Boltzmann transport equation

$$\left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{\text{diff}} + \left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{\text{field}} + \left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{\text{scatt}} = 0$$

$$J_e = \sigma E - \sigma S \nabla T \quad [\text{Am}^{-2}] \quad \text{density of the electrical current}$$

$$J_Q = T \sigma S E - \kappa_0 \nabla T \quad [\text{Wm}^{-2}] \quad \text{density of the heat flow}$$

$E$  – electric field [ $\text{Vm}^{-1}$ ]

$\nabla T$  – temperature gradient [ $\text{Km}^{-1}$ ]

$\sigma$  – specific electrical conductivity [ $\text{V}^{-1}\text{Am}^{-1} = \Omega^{-1}\text{m}^{-1}$ ]

$S$  – Seebeck coefficient [ $\text{VK}^{-1}$ ]

$\kappa_0$  – Specific electron thermal conductivity [ $\text{WK}^{-1}\text{m}^{-1}$ ]

$$J_e = \mathbf{K}^{(0)} E - \mathbf{K}^{(1)} \nabla T \quad \mathbf{K}^{(0)} = \sigma \quad \mathbf{K}^{(1)} = \sigma S$$

$$J_Q = T \mathbf{K}^{(1)} E - \mathbf{K}^{(2)} \nabla T \quad \mathbf{K}^{(2)} = \kappa_0$$

Coefficients  $\mathbf{K}^{(n)}$  could be calculated with the help of Boltzmann transport equation from the band structure.

specific electrical conductivity  $\sigma = \mathbf{K}^{(0)}$

Seebeck coefficient for  $J_e = 0$ :  $S = E/\nabla T = \mathbf{K}^{(1)} / \mathbf{K}^{(0)}$

Specific electron thermal conductivity for  $J_e = 0$ :

$$J_Q = T S J_e + (T \sigma S^2 - \kappa_0) \nabla T; \quad \text{pro } J_e = 0 \rightarrow \kappa_e = \kappa_0 - T \sigma S^2 = \mathbf{K}^{(2)} - T \mathbf{K}^{(1)} \mathbf{K}^{(1)} / \mathbf{K}^{(0)}$$

$f(\vec{k}, \vec{r}, t)$  – local density of the charge carriers

$\vec{k}$  – wave vector (momentum)

$\vec{r}$  – position

$t$  – time

$$\frac{\partial f(\vec{k}, \vec{r}, t)}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{drift} + \left( \frac{\partial f}{\partial t} \right)_{scatt}$$

External field (e.g. electrical)  
Temperature gradient

Scattering:  
– electron-electron  
– electron-phonon  
– electron-defect, impurity

In the equilibrium the density of electrons is described by the Fermi-Dirac distribution:

$$f(\vec{k}) = \left[ e^{\frac{\epsilon}{k_B T}} + 1 \right]^{-1}$$

Approximation of the scattering by the relaxation time:

$$df(\vec{k}, \vec{r}, t) = \frac{dt}{\tau} f^0(\vec{k}, \vec{r})$$

$f(\vec{k}, \vec{r}, t)$  – local density of the charge carriers

$\vec{k}$  – wave vector (momentum)

$\vec{r}$  – position

$t$  – time

$$\frac{\partial f(\vec{k}, \vec{r}, t)}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{drift} + \left( \frac{\partial f}{\partial t} \right)_{scatt}$$

External field (e.g. electrical)  
Temperature gradient

Scattering:  
– electron-electron  
– electron-phonon  
– electron-defect/impurity

Taylor series  $f(\vec{k} - \Delta\vec{k}, \vec{r} - \Delta\vec{r}, t - \Delta t)$

$$f(\vec{k} - \Delta\vec{k}, \vec{r} - \Delta\vec{r}, t - \Delta t) - f(\vec{k}, \vec{r}, t) = -\nabla_{\vec{k}} f \Delta\vec{k} - \nabla_{\vec{r}} f \Delta\vec{r} - \frac{\partial f}{\partial t} \Delta t$$

Liouville's theorem

$$\left( \frac{\partial f}{\partial t} \right)_{drift} = -\nabla_{\vec{k}} f \frac{\partial \vec{k}}{\partial t} - \nabla_{\vec{r}} f \frac{\partial \vec{r}}{\partial t}$$

$$\vec{p} = \hbar \vec{k} \quad \frac{\partial \vec{k}}{\partial t} = \frac{1}{\hbar} \vec{F} \quad \frac{\partial \vec{r}}{\partial t} = \vec{v}(\vec{k})$$

$$\left( \frac{\partial f}{\partial t} \right)_{drift} = -\nabla_{\vec{k}} f \cdot \frac{e}{\hbar} \left( \vec{E} + \frac{\vec{v}}{c} \times \vec{H} \right) - \nabla_{\vec{r}} f \cdot \vec{v}(\vec{k})$$

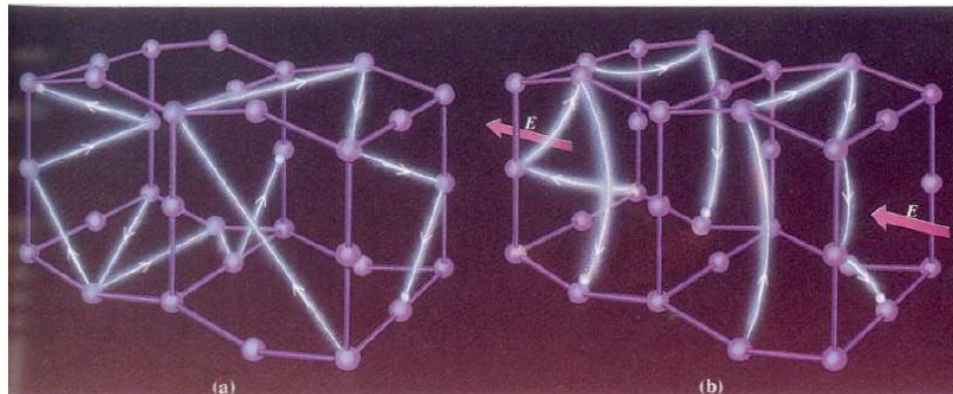
Approximation of the scattering by the relaxation time:  $df(\vec{k}, \vec{r}, t) = \frac{dt}{\tau} f^0(\vec{k}, \vec{r})$

## Scattering

Elastic scattering

$$\left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{\mathbf{k} \rightarrow \mathbf{k}'}^{\text{scatt}} = \int (f_{\mathbf{k}'}(1 - f_{\mathbf{k}}) - f_{\mathbf{k}}(1 - f_{\mathbf{k}'})) Q(\mathbf{k}, \mathbf{k}') d\mathbf{k}'$$

where  $Q(\mathbf{k}, \mathbf{k}')$  is the transition probability from  $\mathbf{k}$  to  $\mathbf{k}'$

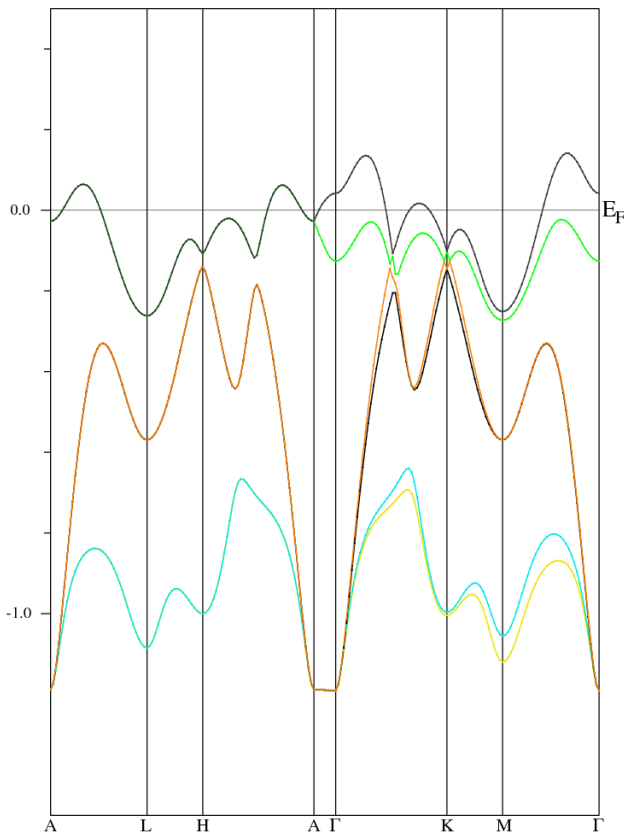


The drift velocity is the average electron *speed*.

Boltzmann theory [10,15,16] is a useful tool for gaining insight into the transport properties of real materials. In the presence of an electric and magnetic field and a thermal gradient the electric current,  $j$ , can be written in terms of the conductivity tensors

$$j_i = \sigma_{ij} E_j + \sigma_{ijk} E_j B_k + v_{ij} \nabla_j T + \dots$$

na66 BAND atom 0 size 0.50



$$v_\alpha(i, \vec{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_{i, \vec{k}}}{\partial k_\alpha}$$

group velocity in the  $\alpha$  direction  
 $k$ : vector,  $i$ : band number

$$\sigma_{\alpha, \beta}(i, \vec{k}) = e^2 \tau_{i, \vec{k}} v_\alpha(i, \vec{k}) v_\beta(i, \vec{k})$$

conductivity tensor  
 ( $i$ : energy,  $k$ : vector)

$$\sigma_{\alpha, \beta}(\varepsilon) = \frac{1}{N} \sum_{i, \vec{k}} \sigma_{\alpha, \beta}(i, \vec{k}) \frac{\partial(\varepsilon - \varepsilon_{i, \vec{k}})}{\partial \varepsilon}$$

conductivity tensor ( $\varepsilon$ )

$$\sigma_{\alpha, \beta}(T, \mu) = \frac{1}{V} \int \sigma_{\alpha, \beta}(\varepsilon) \left( -\frac{\partial f(T, \varepsilon)}{\partial \varepsilon} \right) d\varepsilon$$

conductivity tensor ( $T, \mu$ )

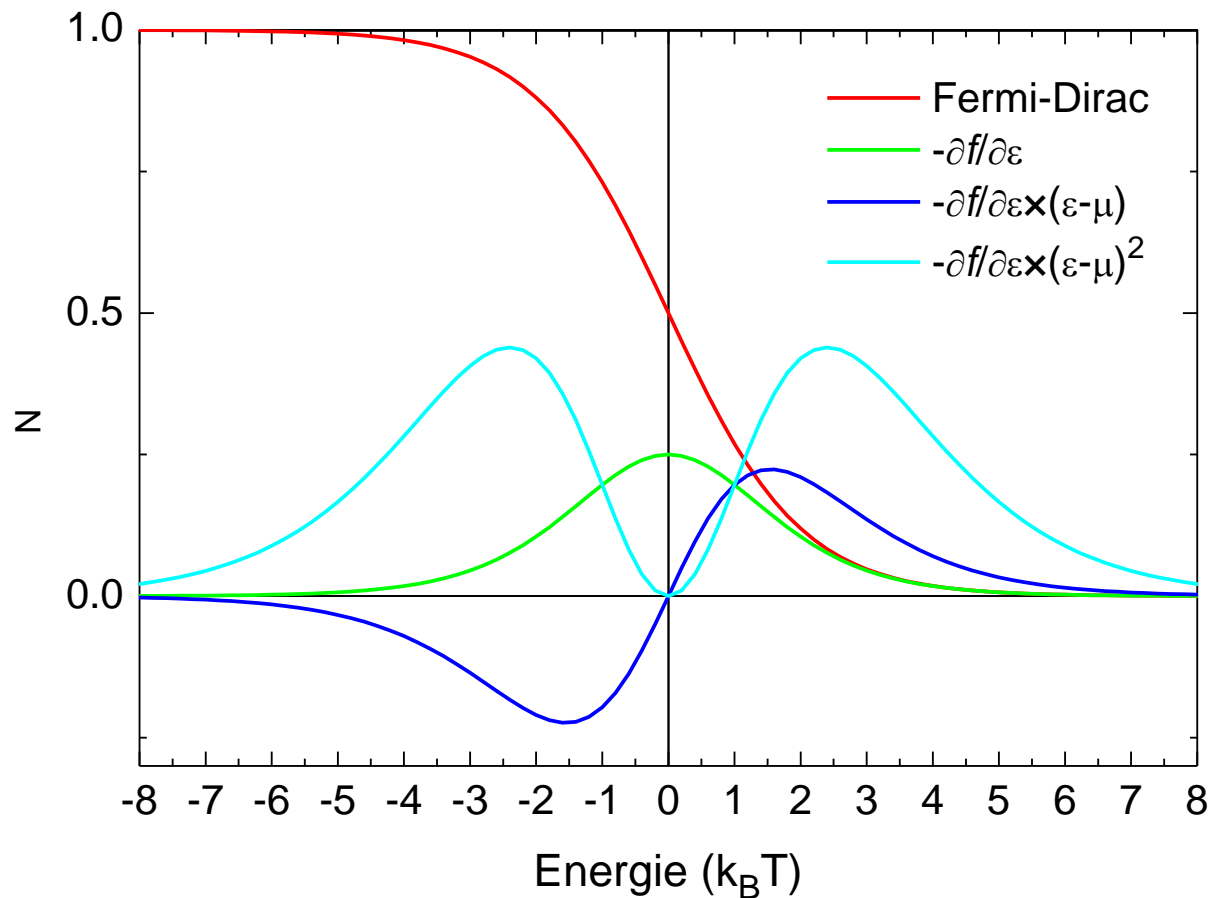
$$\sigma_{ij} = K_{ij}^0$$

where  $K_{\alpha\beta}^n(T, \mu)$  is

$$S_{ij} = \frac{1}{eT} K_{\alpha j}^1 / K_{\alpha i}^0$$

$$K_{\alpha\beta}^n = \int \frac{\tau e^2}{\hbar^2} \frac{\partial \epsilon}{\partial \mathbf{k}_\alpha} \frac{\partial \epsilon}{\partial \mathbf{k}_\beta} (\epsilon - \mu)^n \left[ -\frac{\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon$$

$$\kappa_{ij}^e = \frac{1}{e^2 T} K_{ij}^2$$



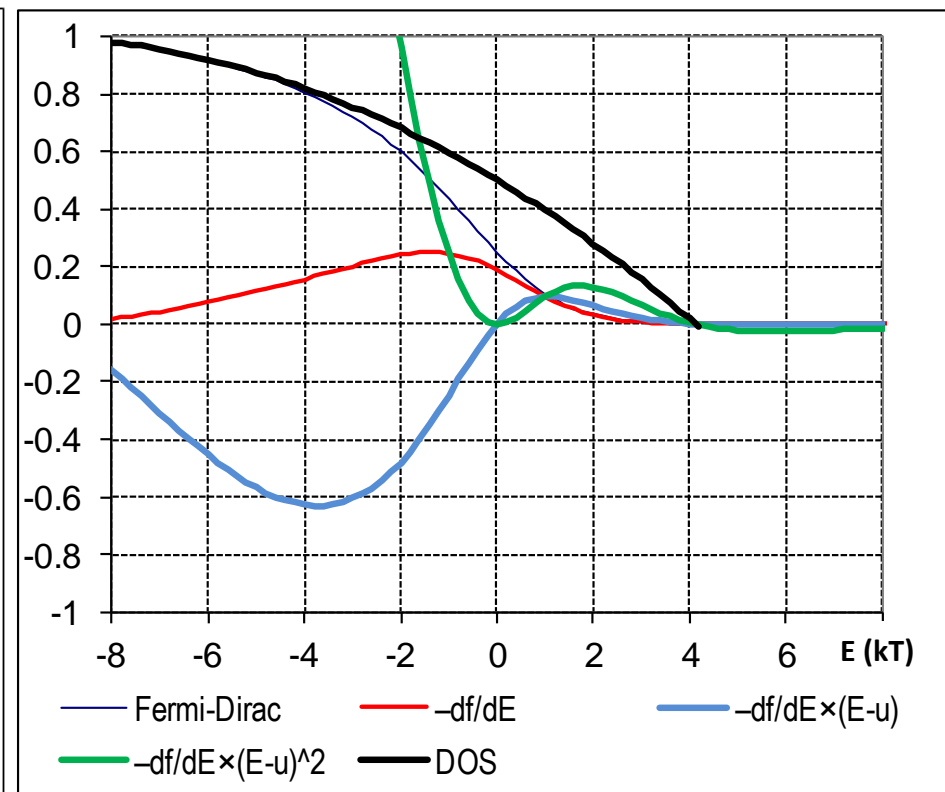
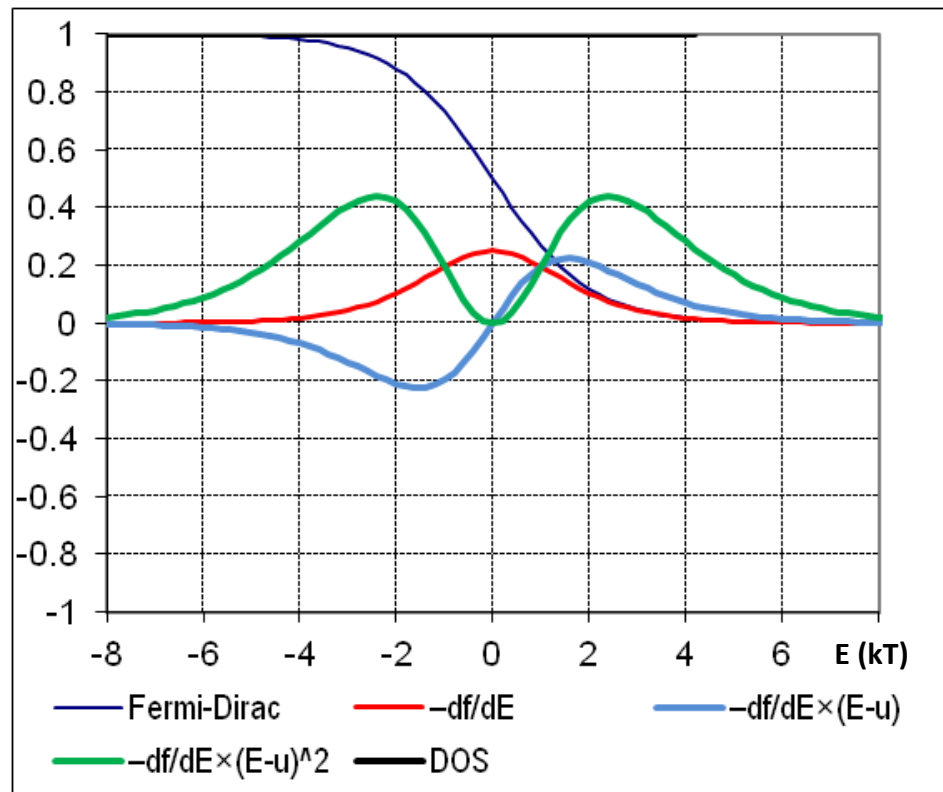
$$\sigma_{ij} = K_{ij}^0$$

$$S_{ij} = \frac{1}{eT} K_{\alpha j}^1 / K_{\alpha i}^0$$

$$\kappa_{ij}^e = \frac{1}{e^2 T} K_{ij}^2$$

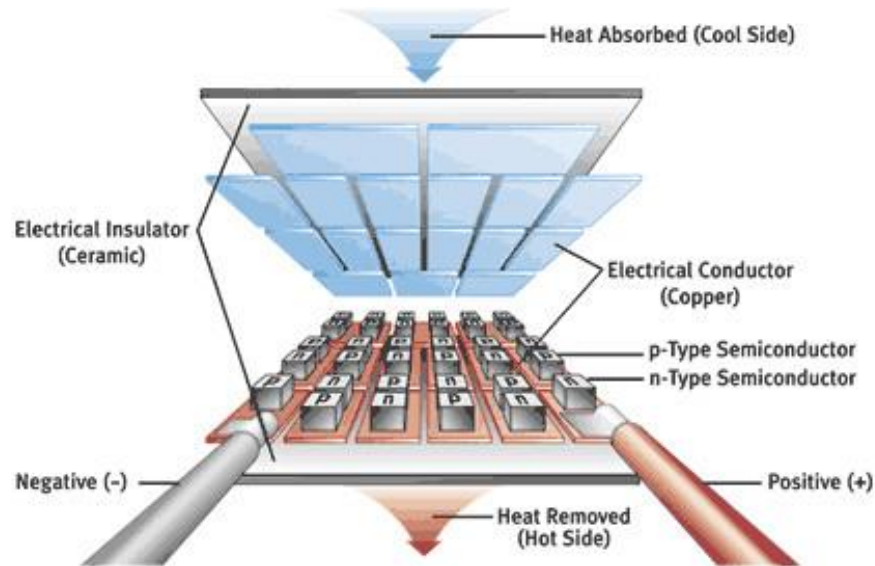
where  $K_{\alpha\beta}^n(T, \mu)$  is

$$K_{\alpha\beta}^n = \int \frac{\tau e^2}{\hbar^2} \frac{\partial \epsilon}{\partial \mathbf{k}_\alpha} \frac{\partial \epsilon}{\partial \mathbf{k}_\beta} (\epsilon - \mu)^n \left[ -\frac{\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon$$



# Thermoelectric generator

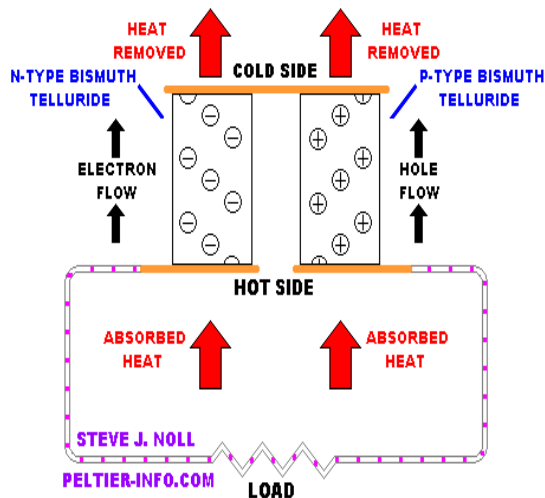
**Electricity source** – conversion of the temperature gradient to electric power



# Peltier module

**Cooling** – conversion of electric power to temperature gradient

ONE SEEBECK DEVICE "COUPLE" CONSISTS OF ONE N-TYPE AND ONE P-TYPE SEMICONDUCTOR PELLETT

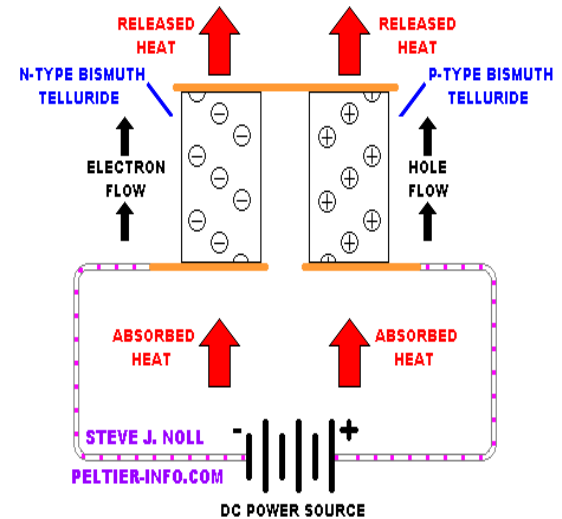


THERE MUST BE A TEMPERATURE DIFFERENCE BETWEEN THE HOT AND COLD SIDES FOR POWER TO BE GENERATED

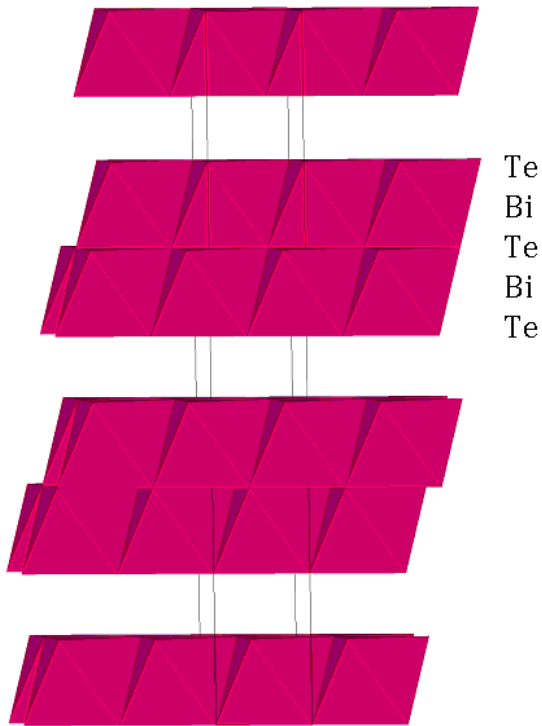
# Thermoelectric module



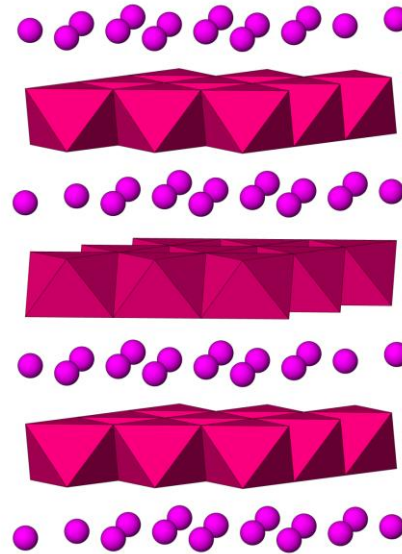
ONE PELTIER DEVICE "COUPLE" CONSISTS OF ONE N-TYPE AND ONE P-TYPE SEMICONDUCTOR PELLETT



THE CHARGE CARRIERS, NEGATIVE ELECTRONS AND POSITIVE HOLES, TRANSPORT THE HEAT.

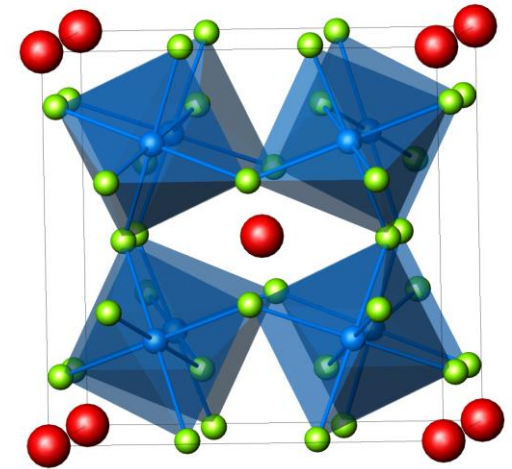


Layered structure of  $\text{Bi}_2\text{Te}_3$  formed by two connected layers of  $\text{BiTe}_6$  octahedra.



Layered structure of  $\text{Na}_x\text{CoO}_2$ .

◆  $\text{CoO}_6$  octahedra    ● Na;



Structure of skutterudite of general formula  $\text{A}_y\text{MX}_3$  with partially filled cavities.

◆  $\text{MX}_6$  octahedra    ● X    ● A

Figure of merit:  $ZT = T \frac{S^2 \sigma}{\kappa_e + \kappa_p}$

$$ZT = T \frac{S^2 \sigma / \tau}{\kappa_e / \tau} \cdot \frac{\kappa_e}{\kappa_e + \kappa_p}$$

$$\kappa_e = LT\sigma \quad L = \text{Lorenz number}$$

$$ZT_{el} = T \frac{S^2 \sigma / \tau}{\kappa_e / \tau} = \frac{S^2}{L}$$

$$\kappa_p = 0:$$

$$ZT_{el} = 1 \rightarrow S = 157 \mu\text{V/K}$$

$$ZT_{el} = 2 \rightarrow S = 222 \mu\text{V/K}$$

$$ZT_{el} = 3 \rightarrow S = 271 \mu\text{V/K}$$

$$ZT_{el} = 10 \rightarrow S = 497 \mu\text{V/K}$$

Wiedemann–Franz

$$L = \frac{\kappa_e}{T\sigma} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$$

$$L = 2.44 \times 10^{-8} \text{ (V}^2\text{K}^{-2}\text{)}$$

Figure of merit:  $ZT = T \frac{S^2 \sigma}{\kappa_e + \kappa_p}$

$S$  – Seebeck coefficient

$\sigma$  – Electrical conductivity

$\kappa_e$  – Electron part of thermal conductivity

$\kappa_p$  – Lattice (phonon) part of thermal conductivity

$$S = -\frac{\Delta U}{\Delta T} \quad (\text{V/K})$$

$U$  – Voltage,

$T$  – Temperature

$$\phi_{max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$

$T_H$  – temperature of the hot side

$T_C$  – temperature of the cold side

$$T = (T_H + T_C)/2$$

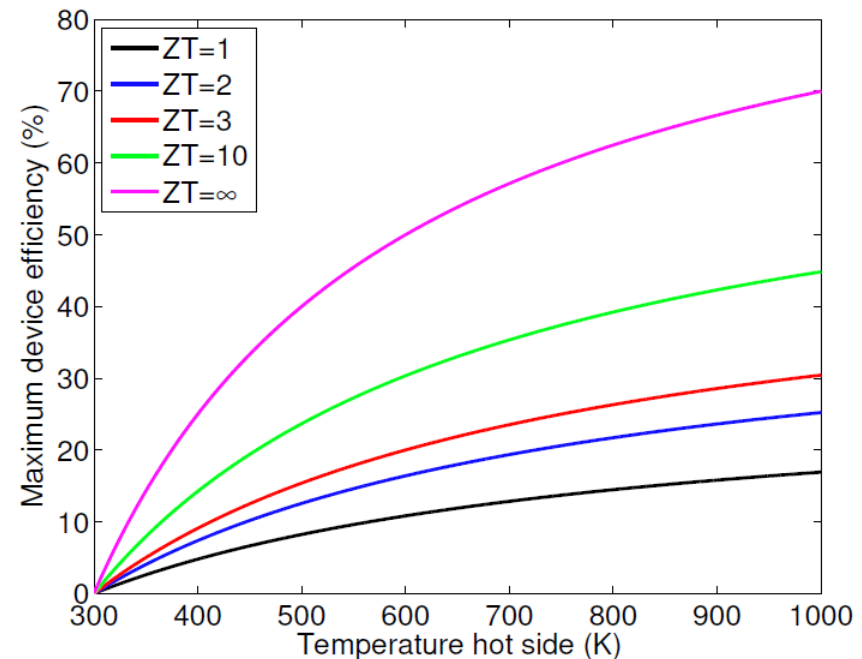


Figure of merit:  $ZT = T \frac{S^2 \sigma}{\kappa_e + \kappa_p}$

$S$  – Seebeck coefficient

$\sigma$  – Electrical conductivity

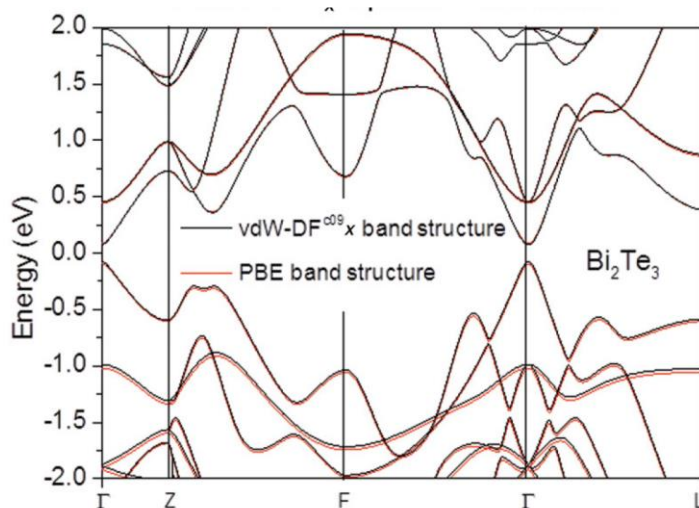
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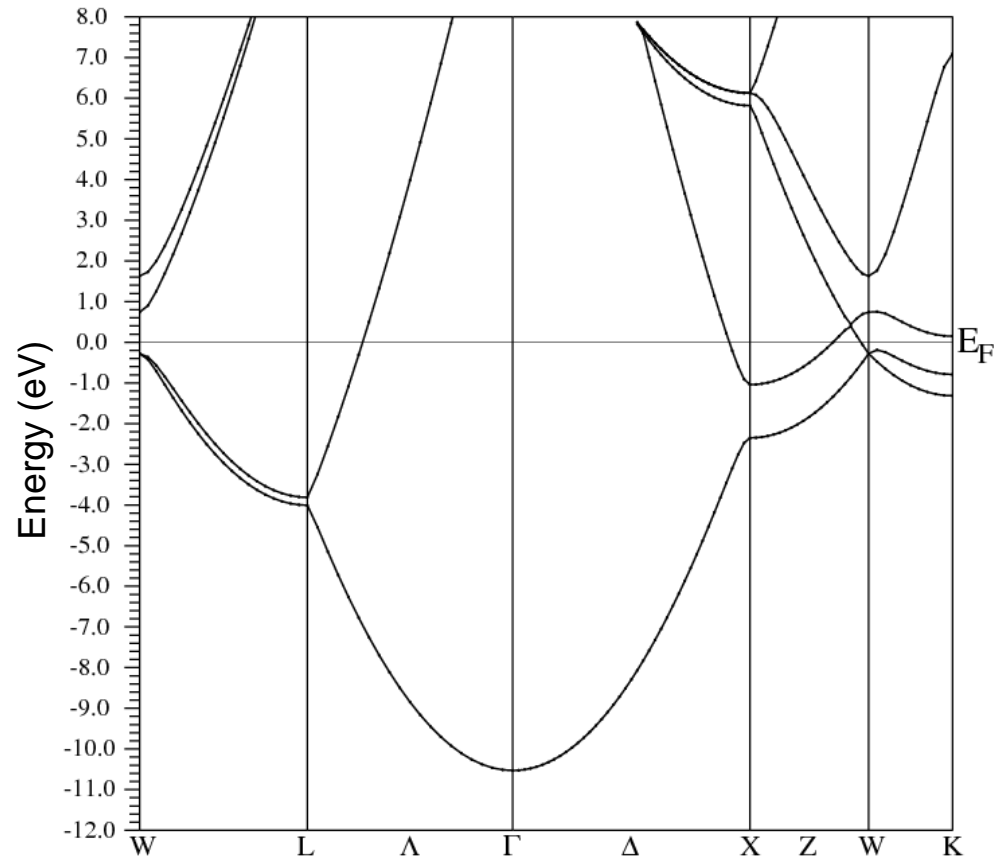
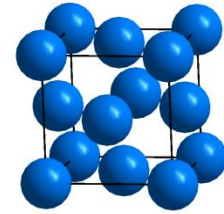
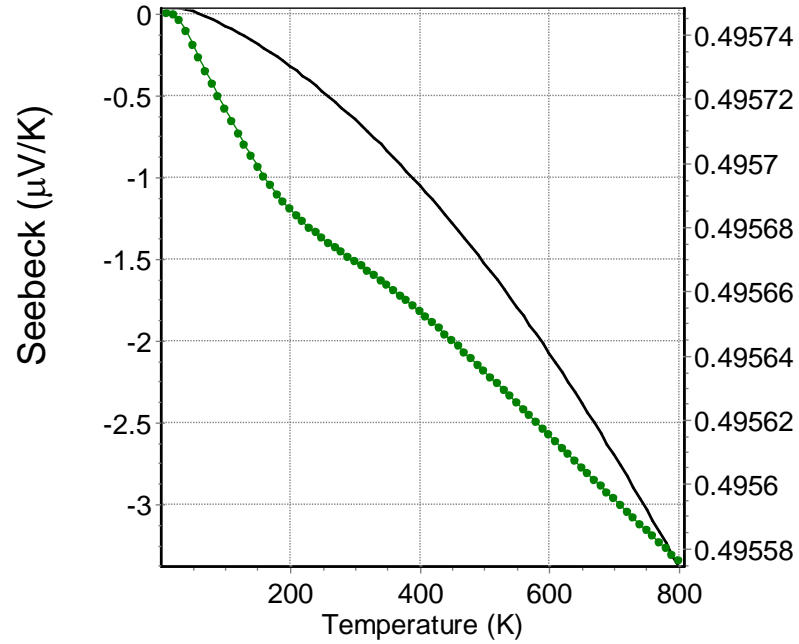
$T$  – Temperature

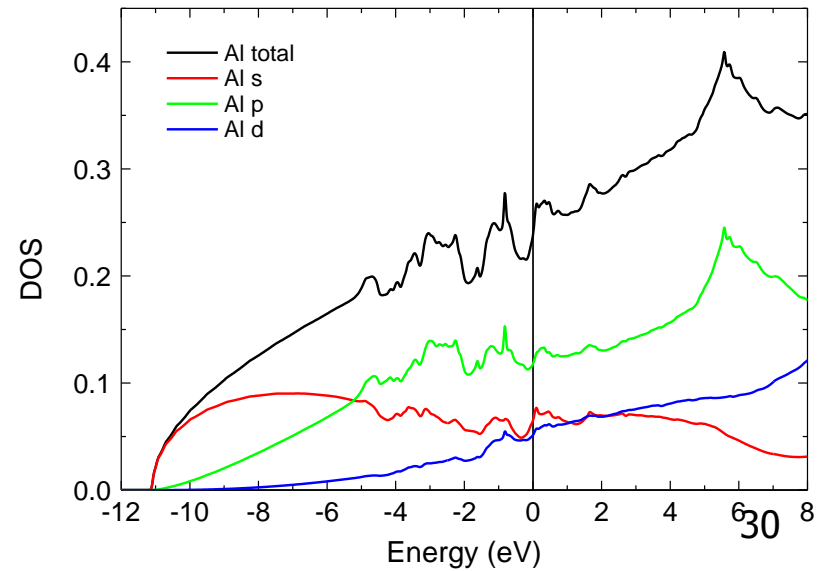
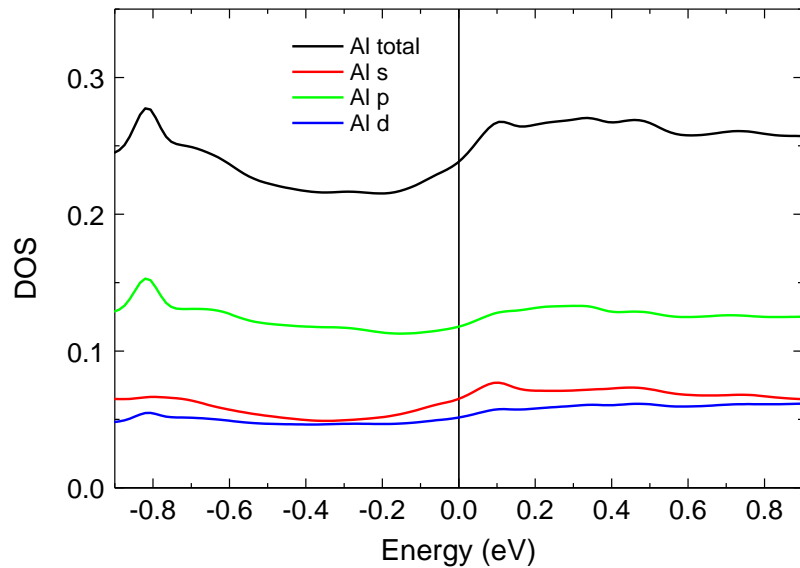
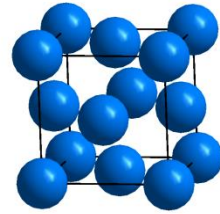
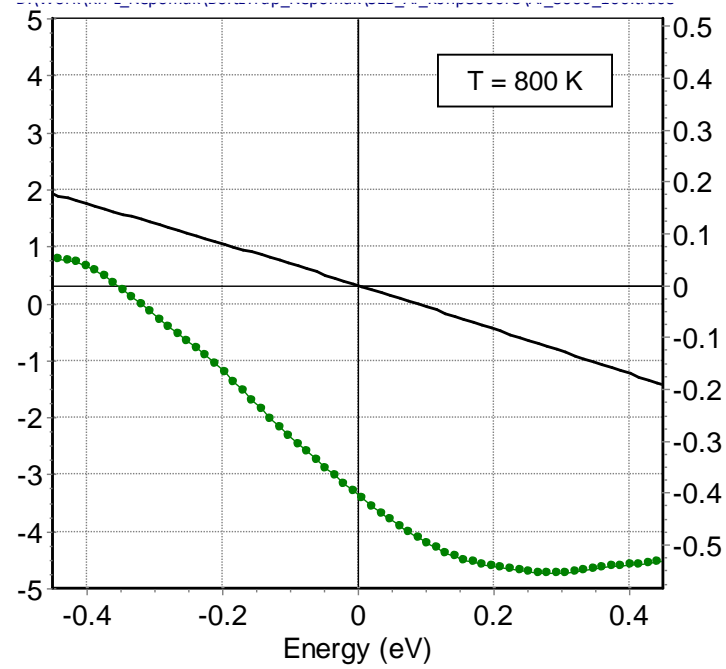
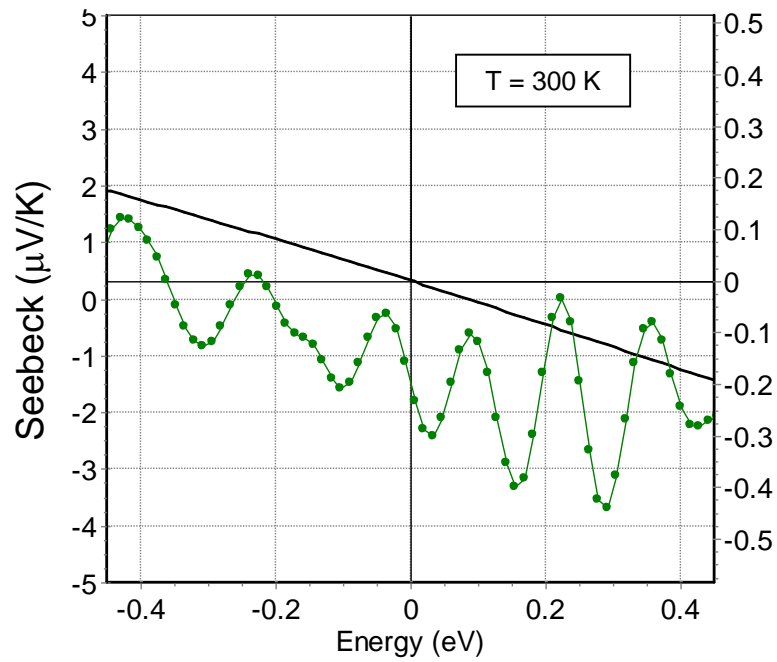


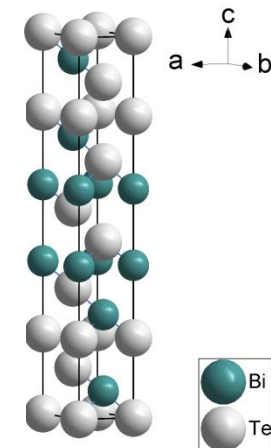
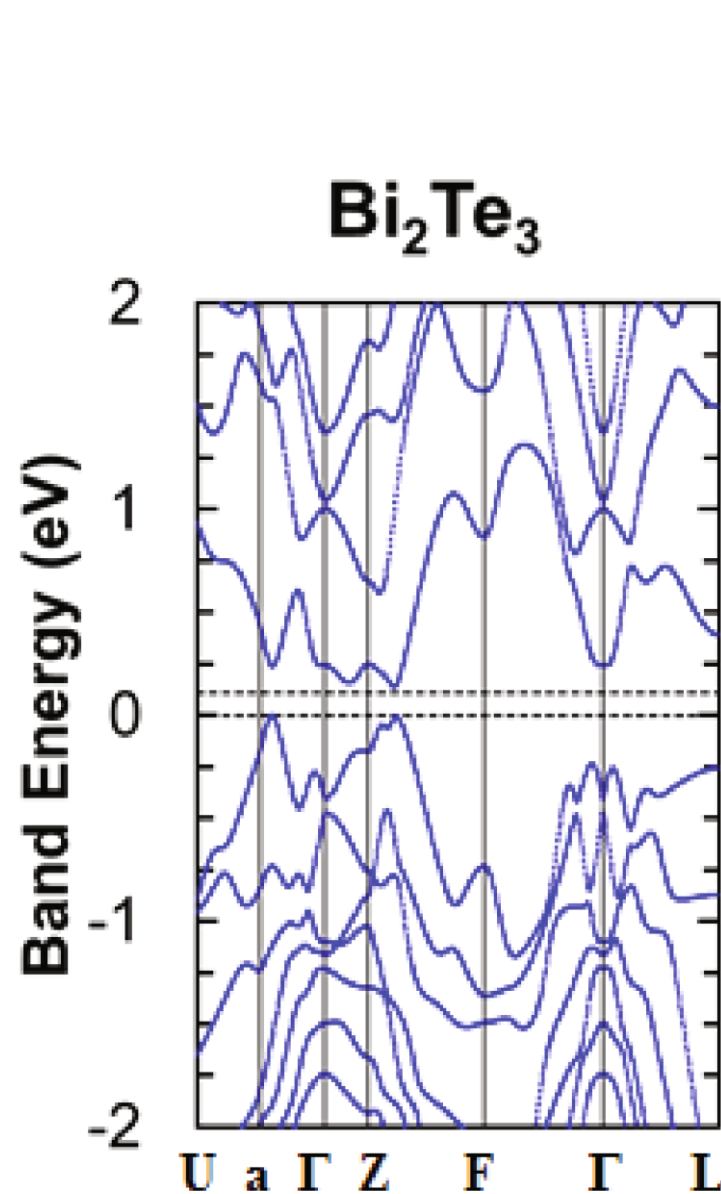
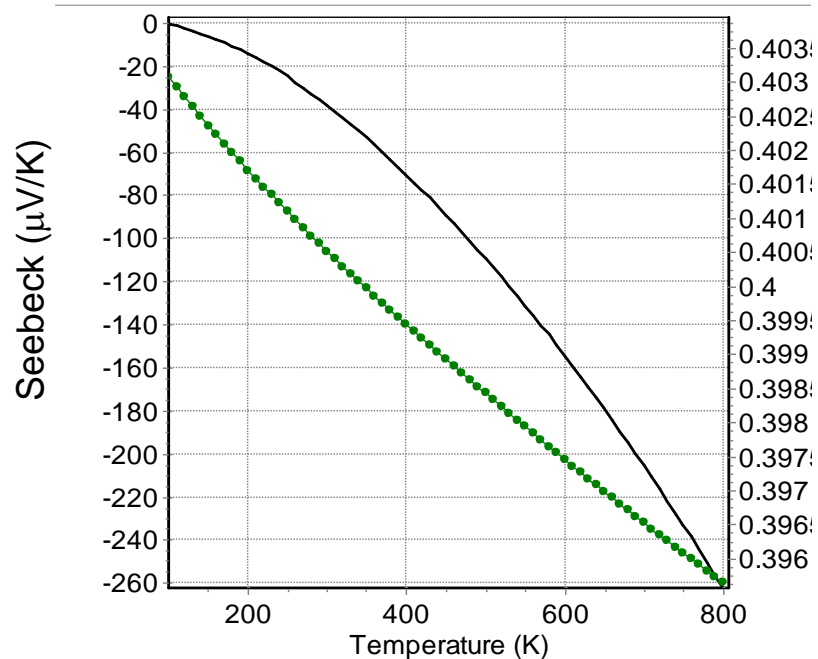
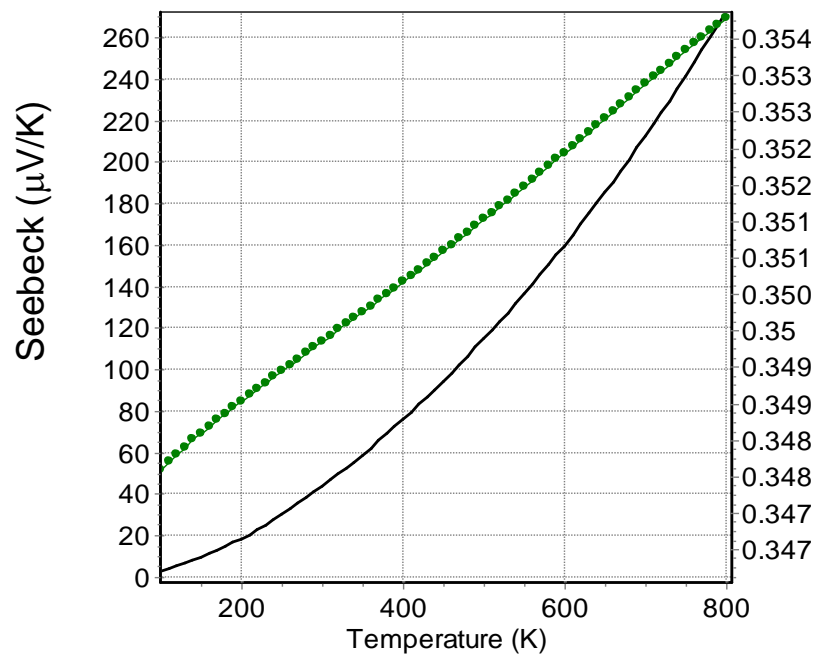
$$ZT = \frac{S^2 \sigma / \tau}{\kappa_e / \tau} \cdot \frac{\kappa_e}{\kappa_e + \kappa_p}$$

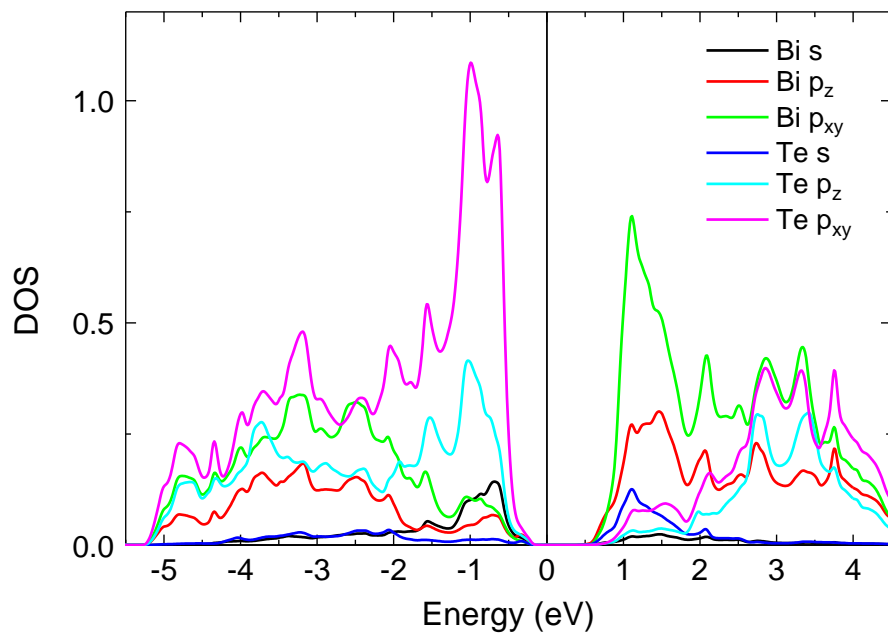
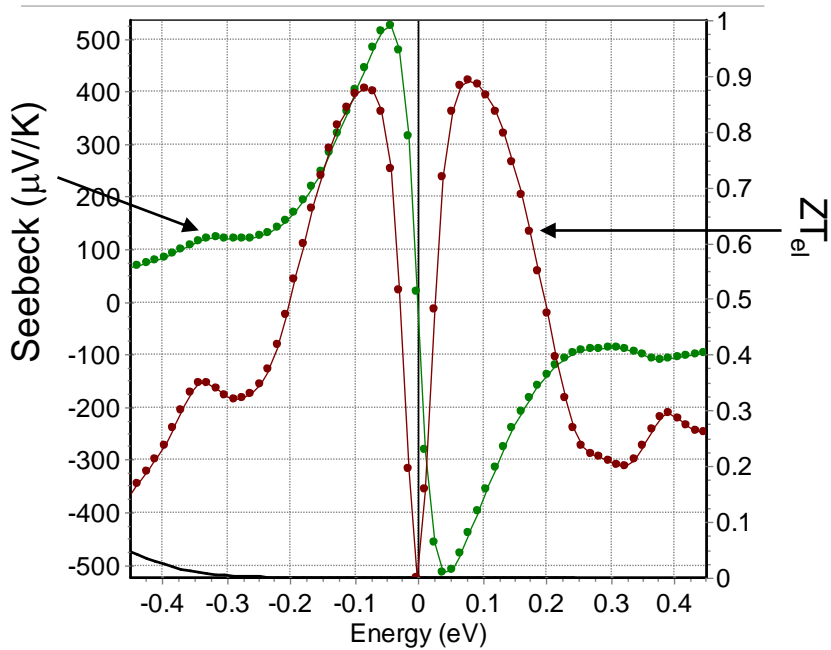
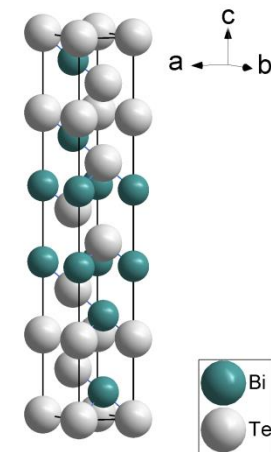
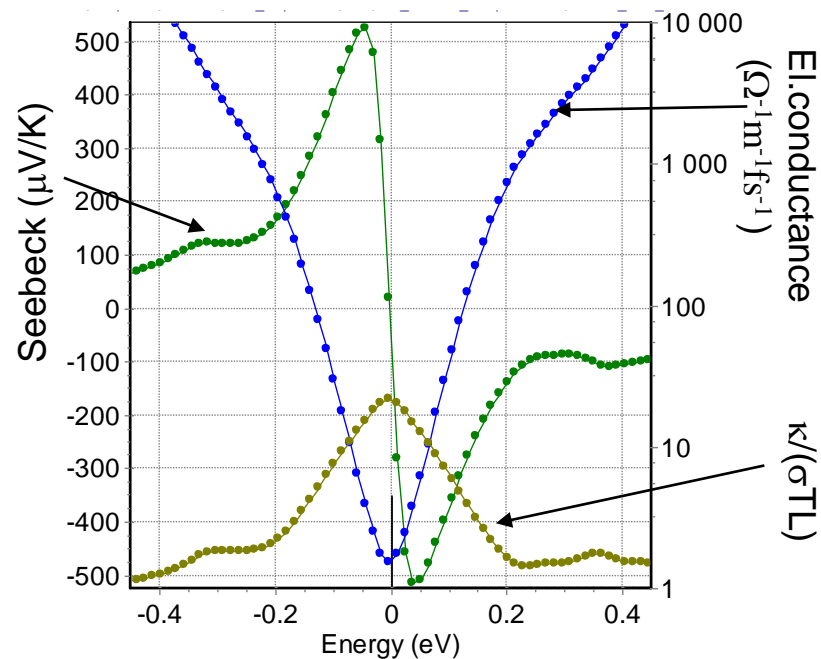
$S, \sigma / \tau, \kappa_e / \tau$  - BoltzTrap

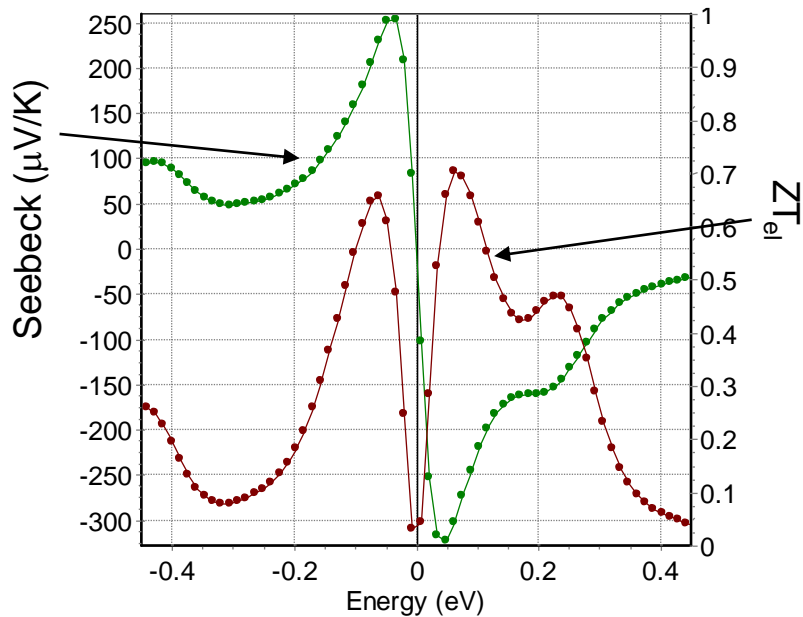
$\kappa_p$  – from the calculation of the phonon band structure  
 $\tau$  – time between collisions



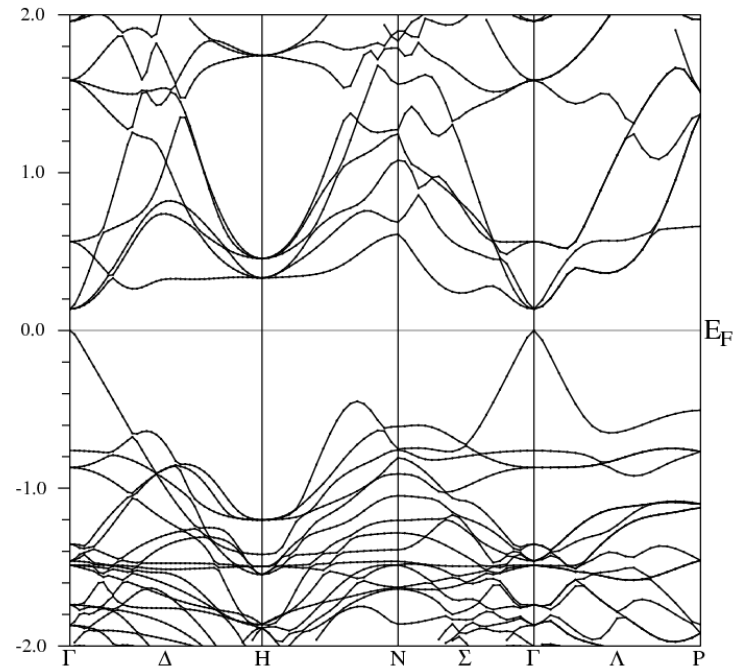
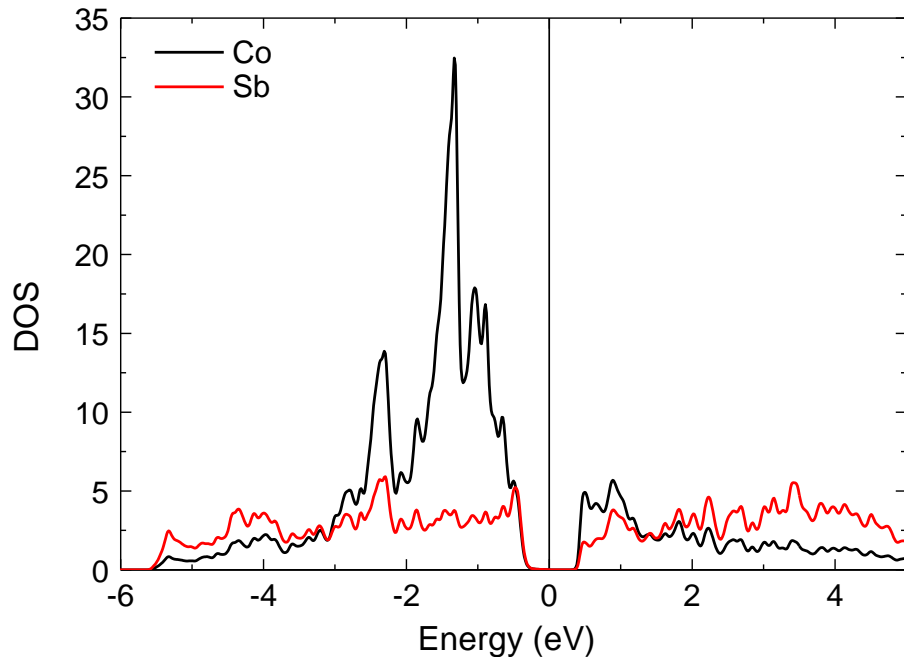
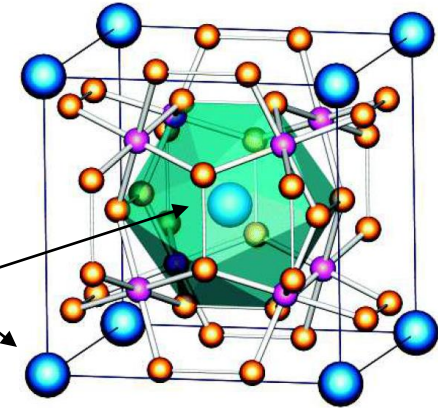






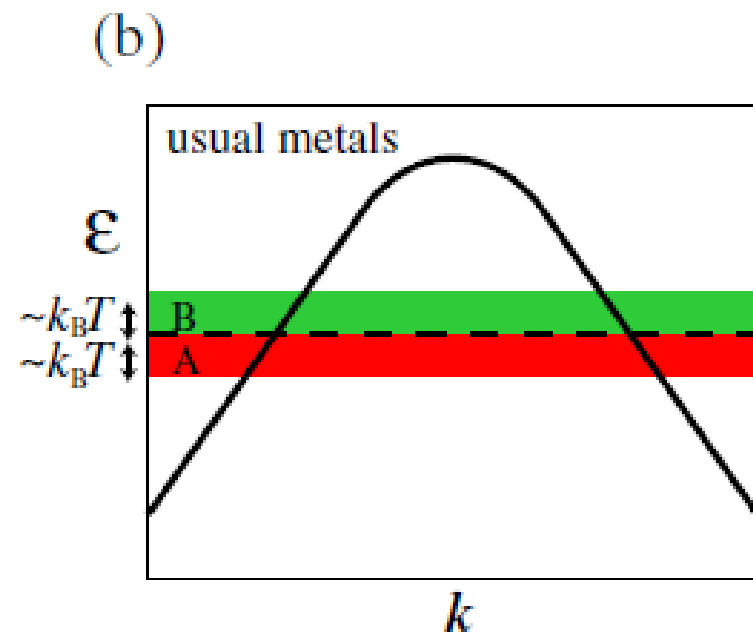
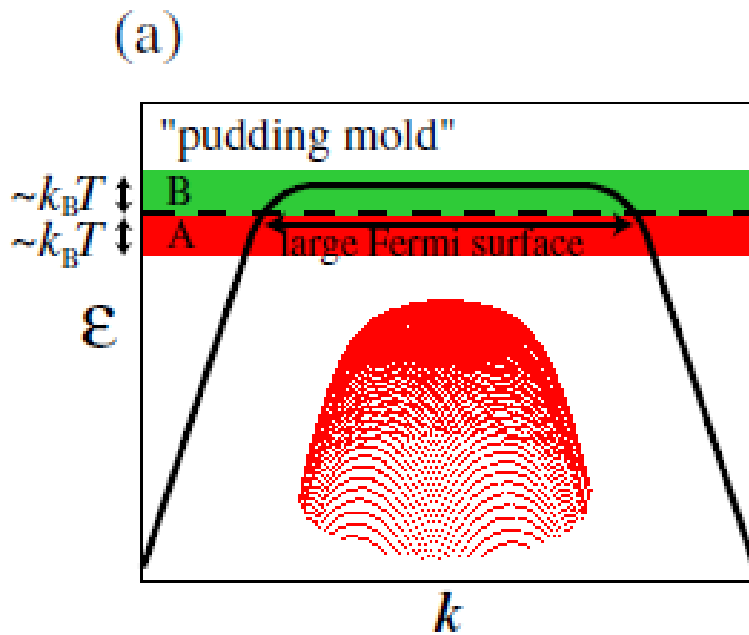


Lowering of the lattice thermal conductivity  $\kappa_p$  by a substitution of an atom into bigger cavity  $\rightarrow$  vibration of the relatively free atom.



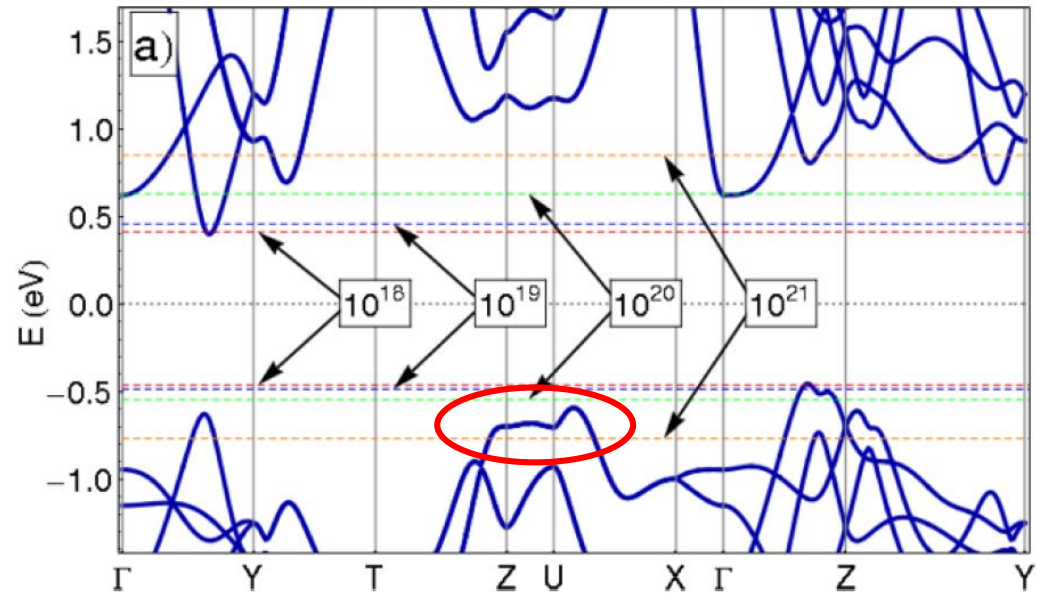
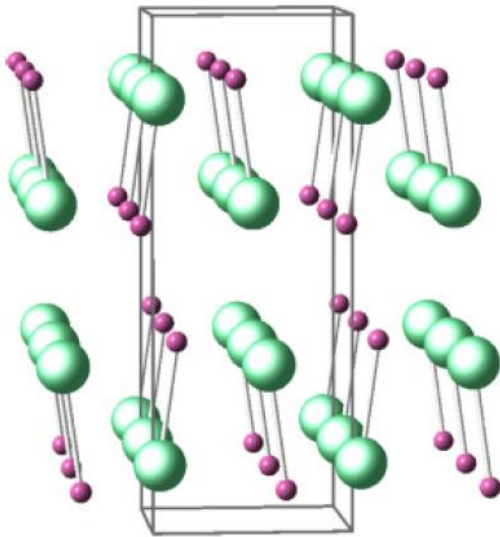
Band shape „pudding-mould“

High Fermi velocity  $v_F$  and Fermi surface  $\rightarrow$  enhancement of both  $S = \kappa^{(1)}/\kappa^{(0)}$  and  $\sigma = \kappa^{(0)}$

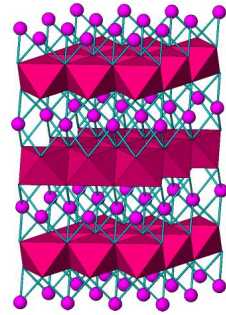
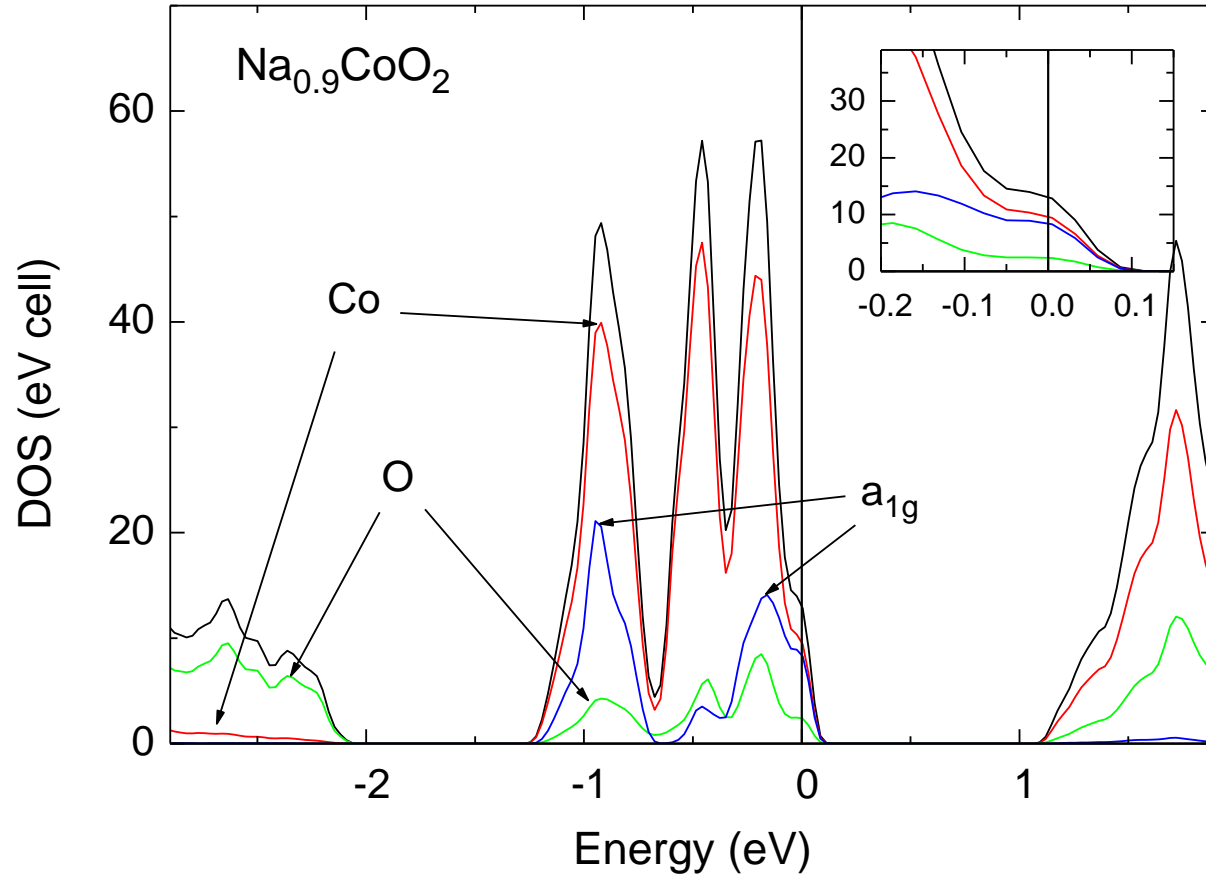


Band shape „pudding-mould“

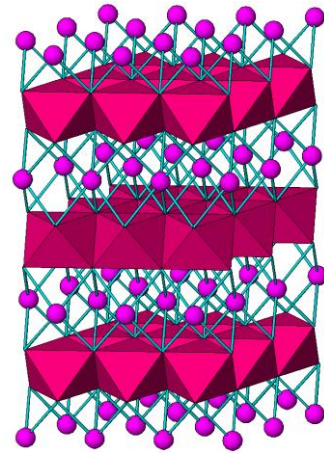
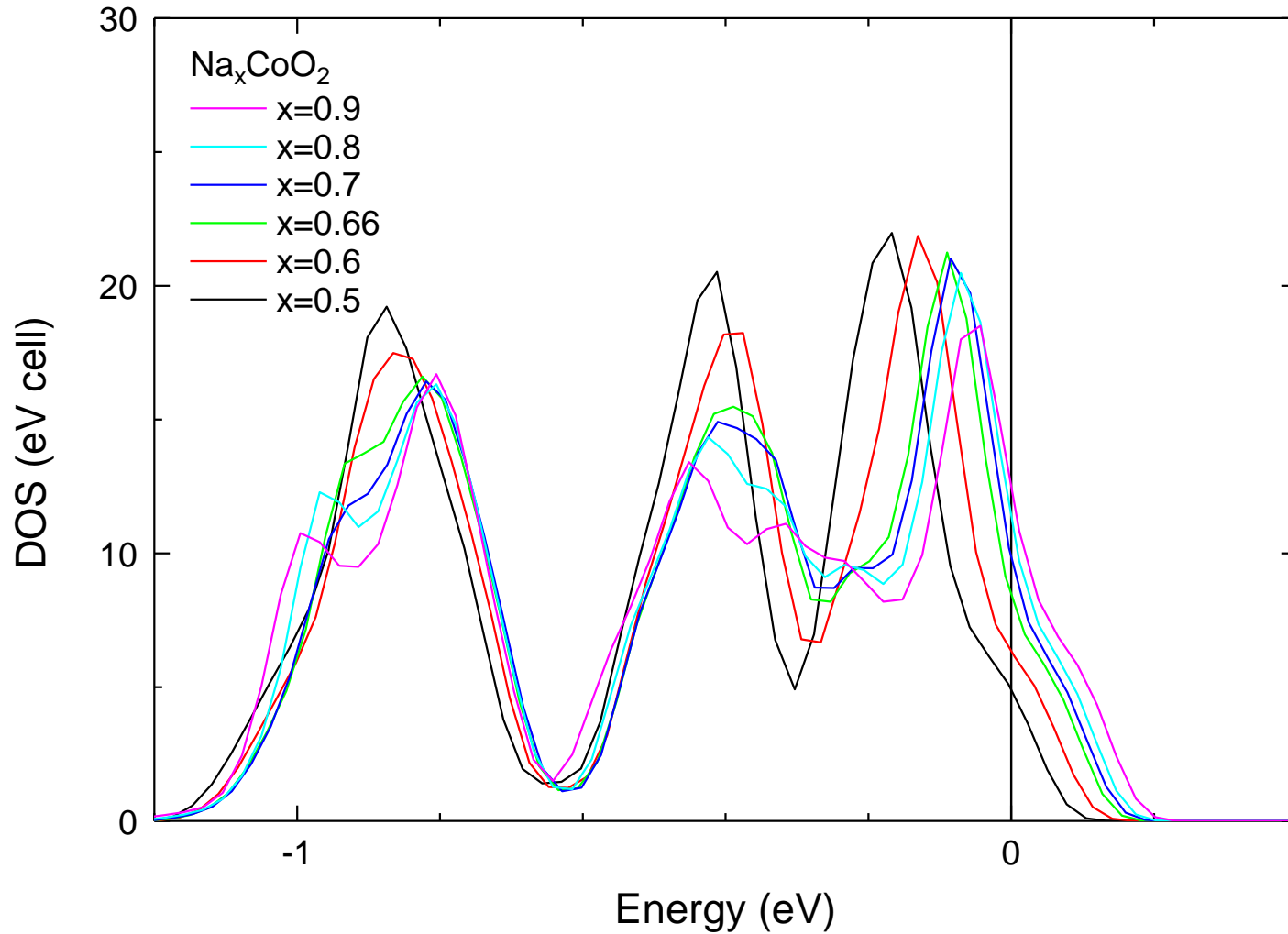
High Fermi velocity  $v_F$  and Fermi surface  $\rightarrow$  enhancement of both  $S = \kappa^{(1)}/\kappa^{(0)}$  and  $\sigma = \kappa^{(0)}$



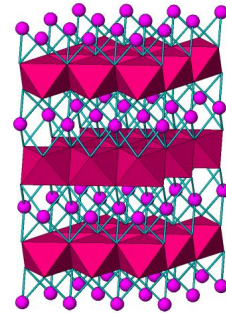
Na<sub>x</sub>CoO<sub>2</sub>, doping by a change of Na concentration: valency Co<sup>(4-x)+</sup>



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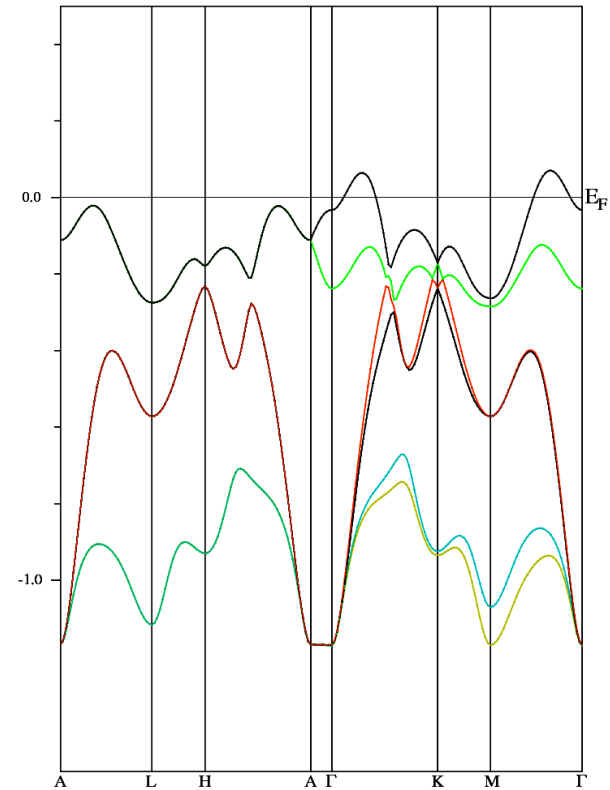
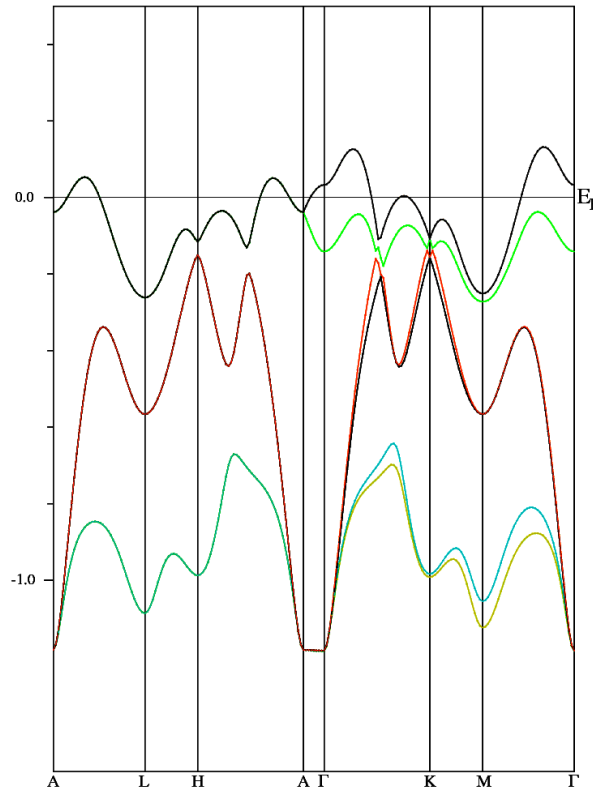
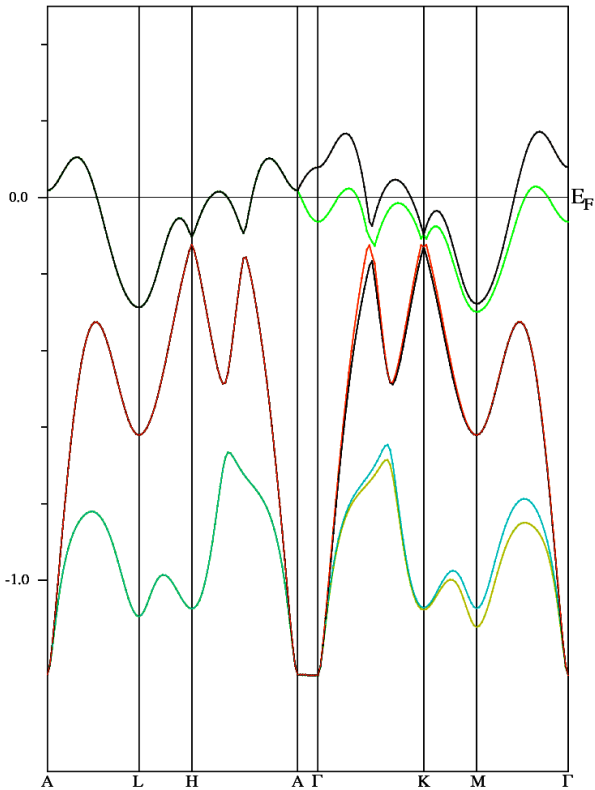
Na<sub>x</sub>CoO<sub>2</sub>, doping by a change of Na concentration: valency Co<sup>(4-x)+</sup>



na50 BAND atom 0 size 0.50

na70 BAND atom 0 size 0.50

na90 BAND atom 0 size 0.50



Na<sub>x</sub>CoO<sub>2</sub>, doping by a change of Na concentration: valency Co<sup>(4-x)+</sup>

