

Charge carrier mobility, quality factor and thermoelectric efficiency

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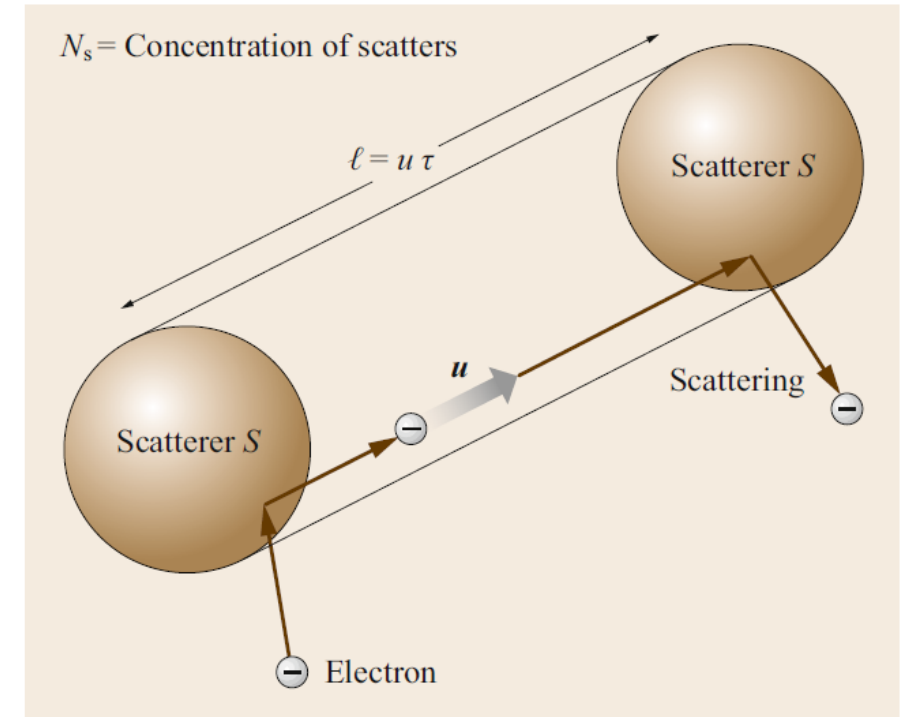
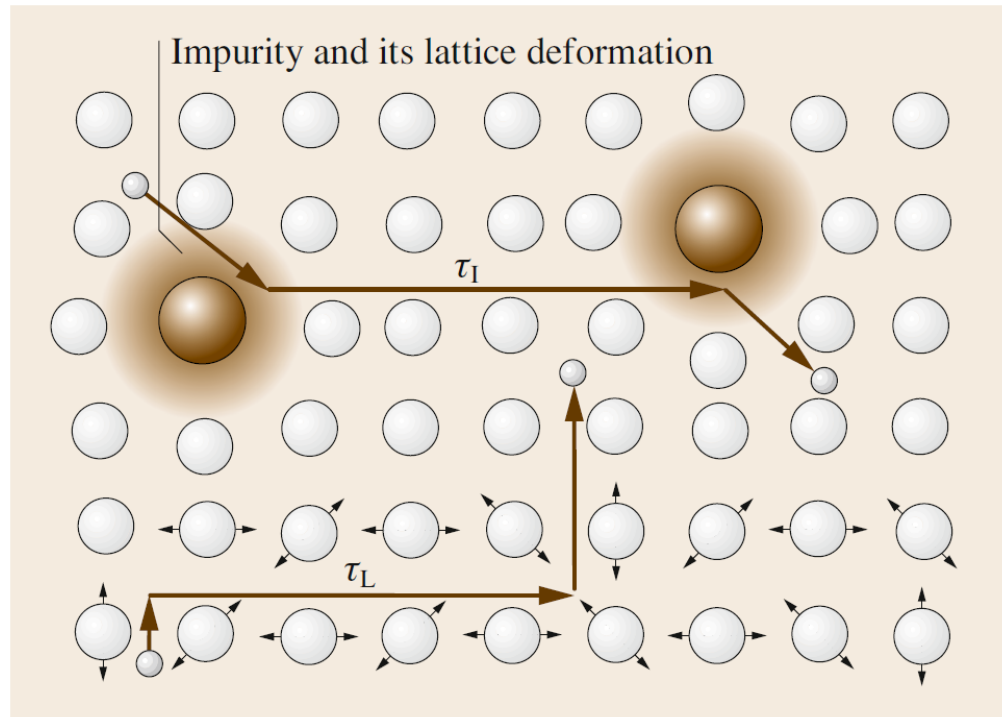
Charge carrier (drift) mobility

Let's remember what is the carrier mobility?^[1]

$$v_d = \frac{e\tau}{m_I^*} E = \mu_d E \text{ and } \sigma = en\mu_d$$

Why is that so important?

scattering

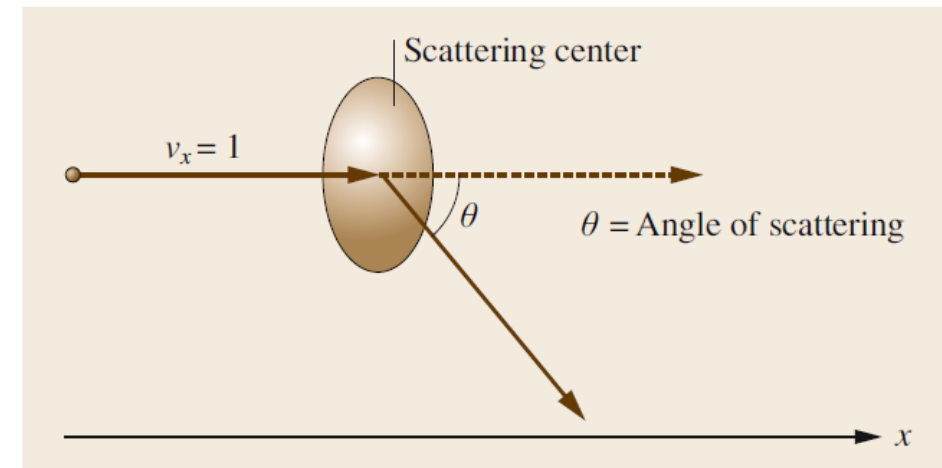


In materials with multiple scattering mechanisms affecting the carrier mean free path, the temperature dependence of charge carrier mobility is complex and total μ can be evaluated by Matthiessen's rule,^[2,3] which assumes scattering channels are independent of each other

$$\mu^{-1} = \sum_i \mu_i^{-1}$$

where μ_i represents the mobility of a specified scattering mechanism.

The dominant scattering mechanism can be determined using log-log plot from the temperature dependence of the Hall mobility fitted by a power-law $\mu \propto T^m$, where m is the scattering factor of the carriers.



Electrical conductivity

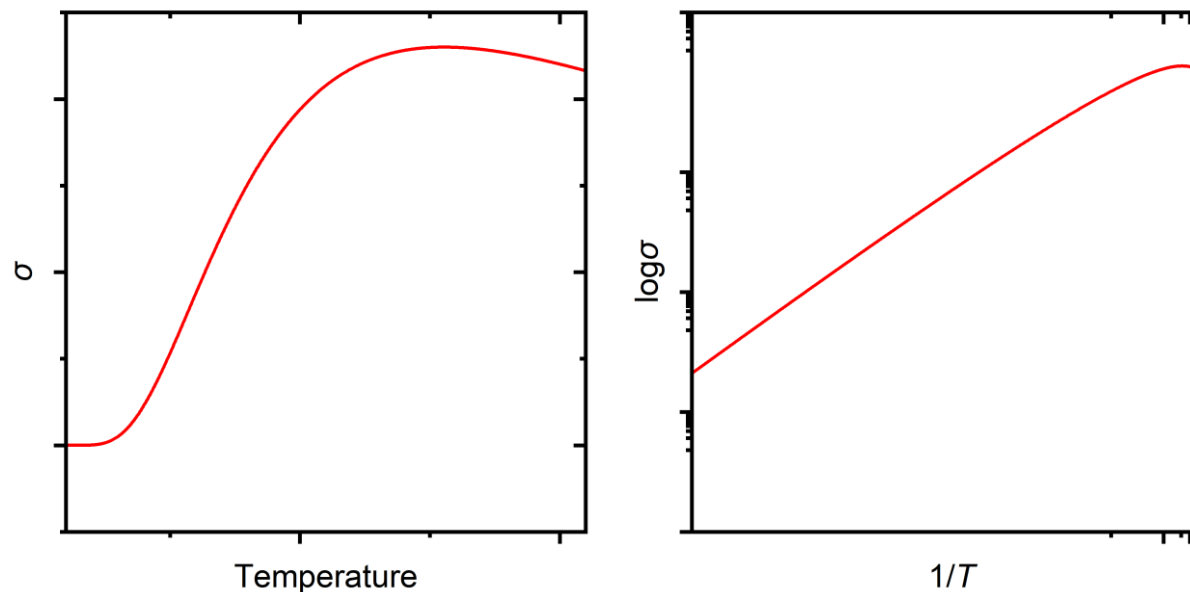
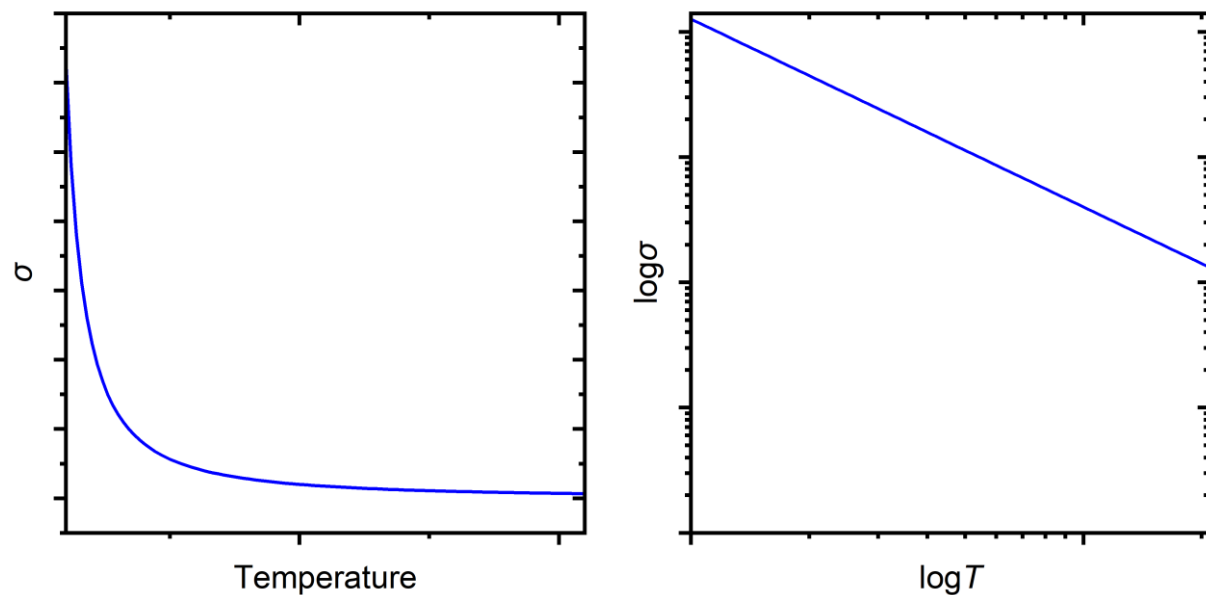
$$\sigma(T) = en(T)\mu(T)$$

For semiconductors:

$$n(T) = N_c e^{-\frac{E_c - F}{k_B T}}, \mu(T) \propto T^m$$

For metals:

$$n = \frac{1}{3\pi^2} \left(\frac{2m_0 E}{\hbar^2} \right)^{3/2}, \mu(T) \propto T^m$$



Charge carrier mobility

For a single parabolic band semiconductor, the Hall mobility can be represented by

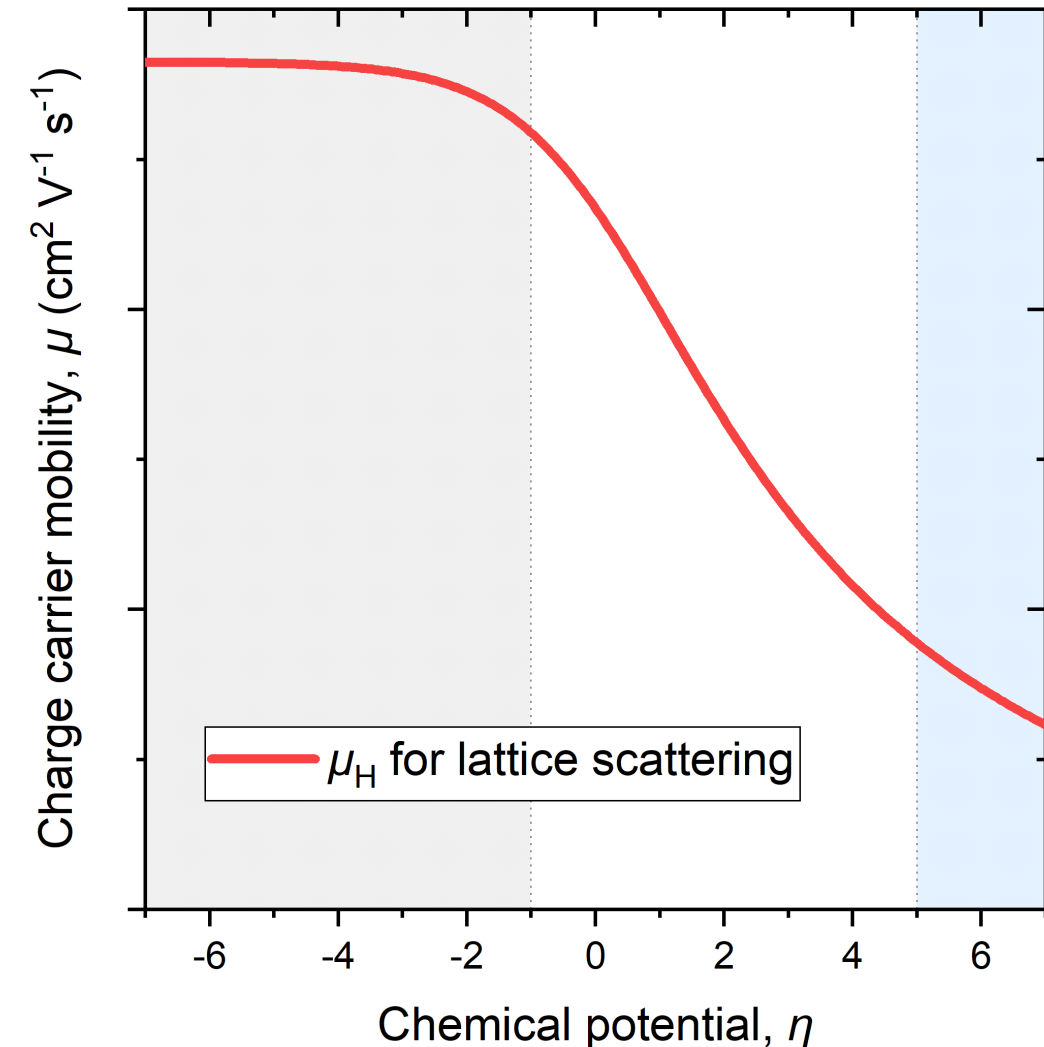
$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

$$F_j(\eta) = \int_0^\infty \frac{\varepsilon^j}{1 + e^{\varepsilon - \eta}} d\varepsilon$$

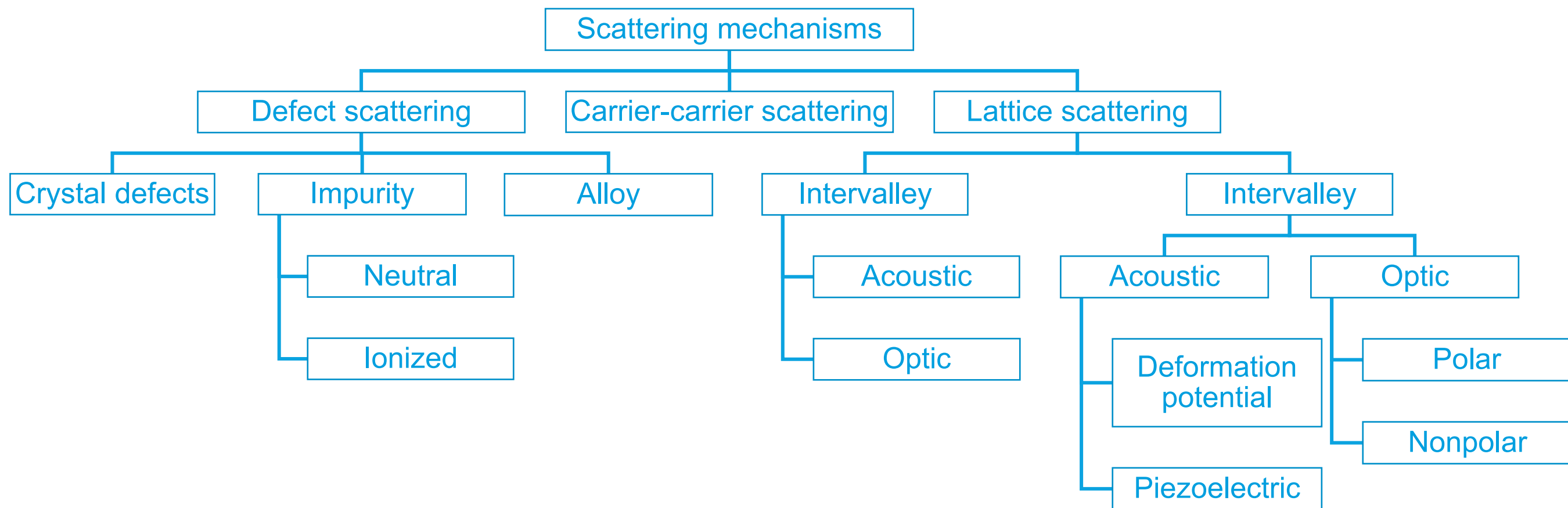
here μ_0 is typically called as the carrier concentration independent mobility parameter or free mobility parameter. μ_0 value can be obtained through the analysis of the Hall mobility data.

Degenerate limit: $\mu_H \propto \frac{\mu_0}{(m^*)^2 T n^{1/3}}$

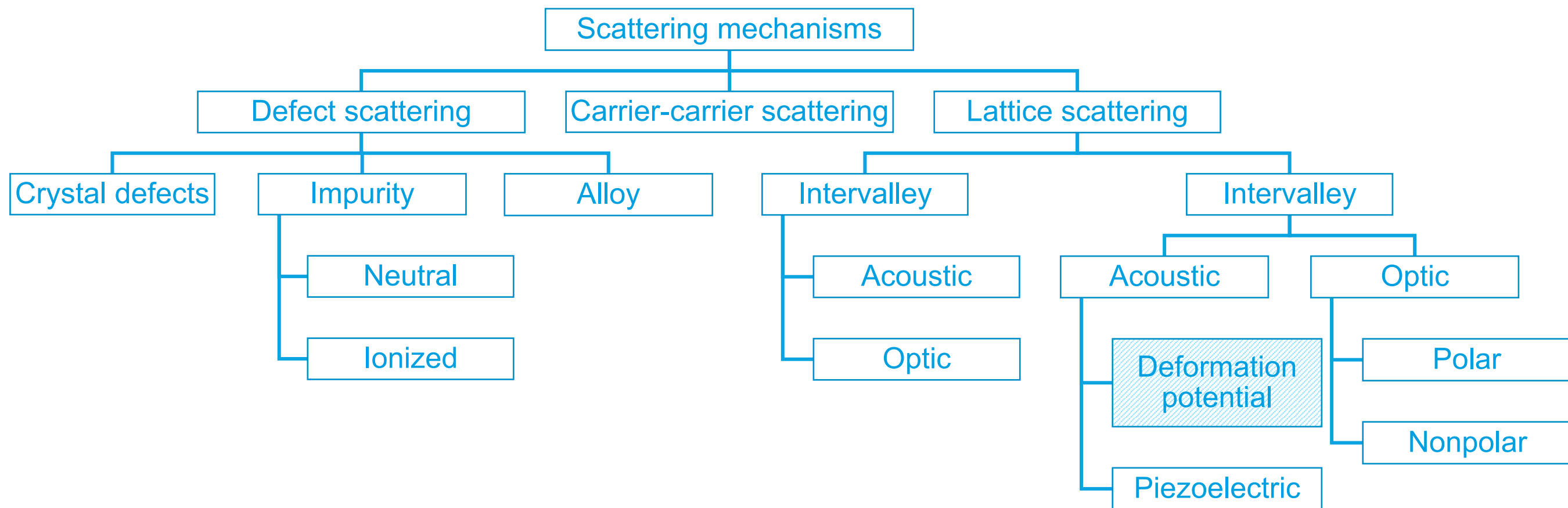
Non-degenerate limit: $\mu_H = \frac{\sqrt{\pi}}{2} \mu_0$



Scattering mechanisms



Scattering mechanisms



$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

For acoustic phonon scattering:

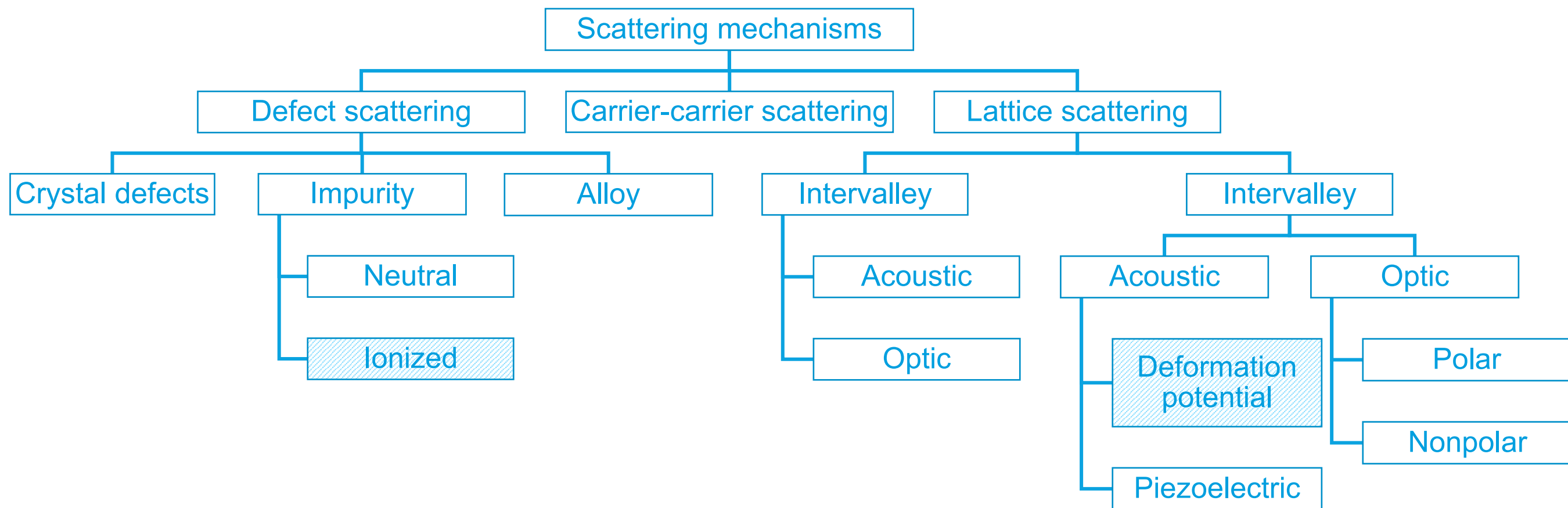
$$\mu_0 = \frac{e\pi\hbar^4 C_{ll}}{\sqrt{2}(k_B T)^{3/2} (m_b^*)^{3/2} m_I^* \Delta_{def}^2}$$

where \hbar is the reduced Planck's constant, C_{ll} is the elastic constant for longitudinal vibrations ($C_{ll} = d v_l^2$, where d is the density, v_l is the longitudinal component of sound velocity), m_b^* is the effective mass of a single valley, m_I^* is the inertial effective mass (for the isotropic spherical case $m_b^* = m_I^*$), and Δ_{def} is the deformation potential characterizing the carrier-phonon interaction.^[2,4]

It should be mentioned, that C_{ll} , m^* and Δ_{def} can also depend on temperature.



Scattering mechanisms



$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

For ionized impurity scattering:

$$\mu_0 = \frac{8\sqrt{2}k_B^{3/2}}{\pi^{3/2}e^3} \frac{(\epsilon\epsilon_0)^2}{N_I(m_d^*)^{1/2}Z^2} \frac{T^{3/2}}{\ln \left[1 + \left(\frac{3\epsilon\epsilon_0 k_B T}{N_I^{1/3} Z e} \right)^2 \right]}$$

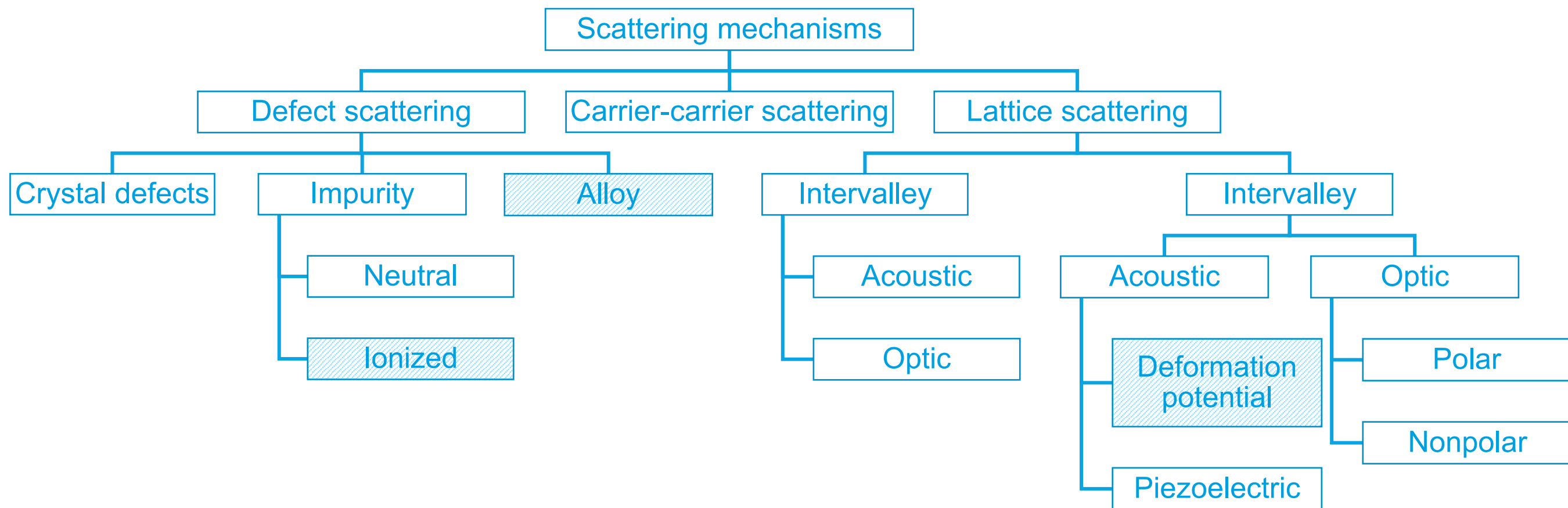
This expression for the mobility encompasses the Conwell-Weisskopf and Brooks-Herring.^[2,4]

It is sufficient when

$$T^2 \ll \frac{N_I^{2/3} Z^2 e^4}{9(\epsilon\epsilon_0)^2 k_B^2}$$



Scattering mechanisms



$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

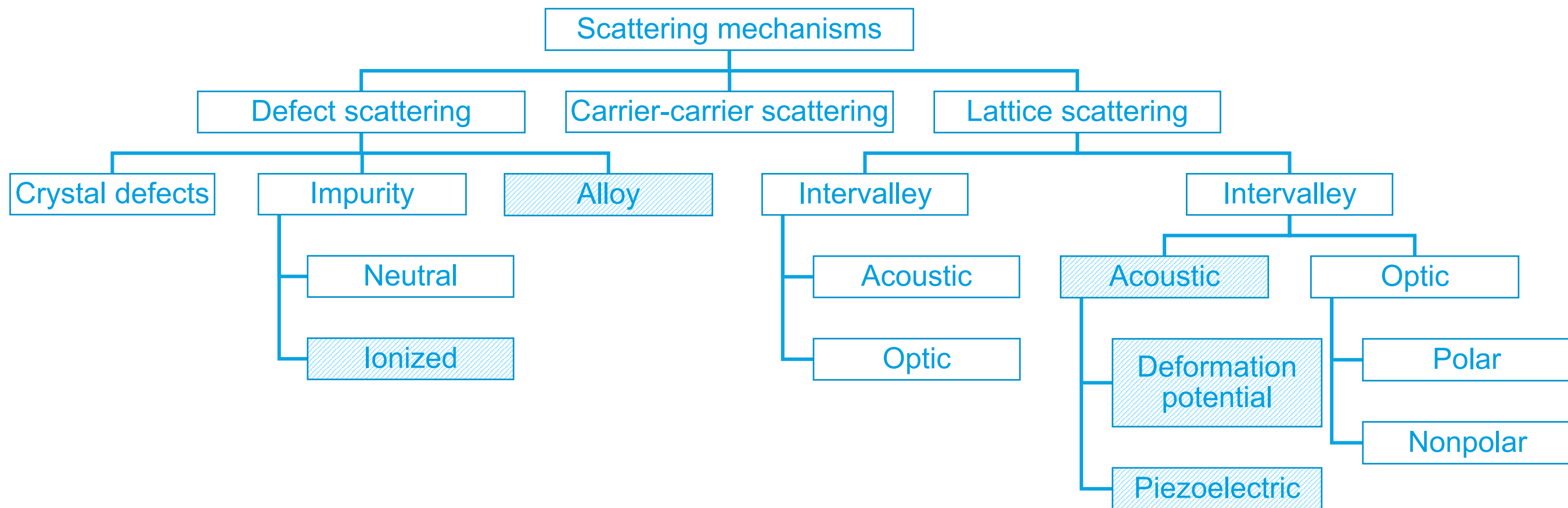
For alloy disorder scattering:

$$\mu_0 = \frac{16e\hbar^4}{9\sqrt{2}z(1-z)(k_B T)^{1/2}} \frac{N_0}{(m_d^*)^{5/2} U^2}$$

where z is fractional concentration of the solid solution and N_0 is the number of atom per unit volume. The potential energy fluctuation caused by alloy disorder is characterized by U , which is analogous the deformation potential Δ_{def} .^[2,5]



Scattering mechanisms



Piezoelectric potential scattering

$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

For piezoelectric potential scattering:

$$\mu_0 = \frac{16\sqrt{2}\pi}{3} \frac{\hbar\epsilon\epsilon_0}{(m^*)^{3/2}eK^2} (k_B T)^{-1/2}$$

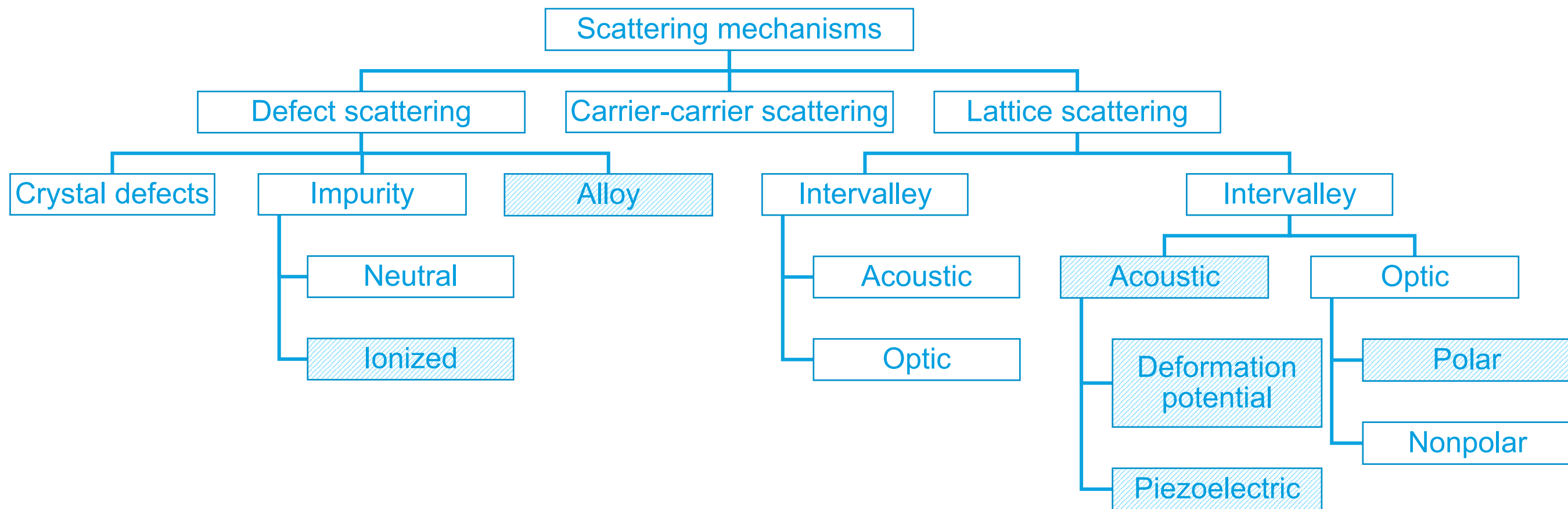
with

$$K = \frac{e_p^2 / C_{11}}{\epsilon\epsilon_0 + e_p^2 / C_{11}}$$

e_p being the piezoelectric coefficient. In strongly ionic crystals, e.g. II–VI semiconductors, the piezoelectric scattering can be stronger than the deformation potential scattering.^[2]



Scattering mechanisms



$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

For polar optical scattering (where $T \ll \theta_D$):

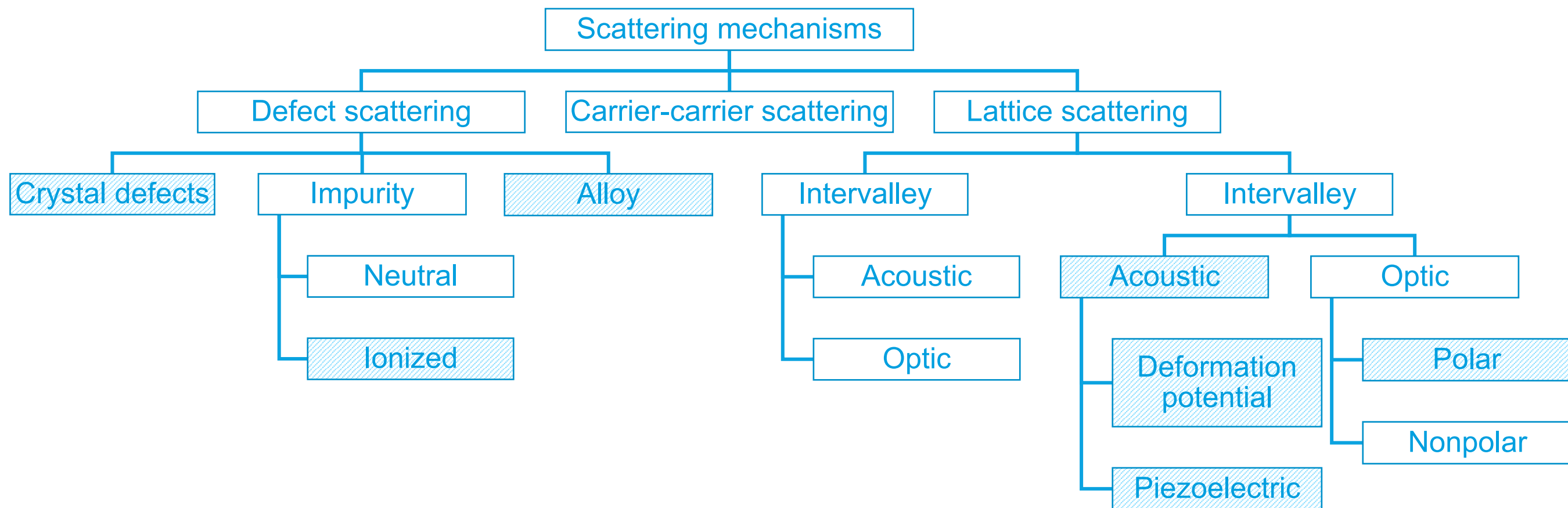
$$\mu_0 = \frac{e}{2m^* \alpha_p \omega_0} e^{\theta_D/T}$$

where in the scattering mechanism the absorbed or emitted phonon energy $\hbar\omega_0$ is comparable to the thermal energy of the carriers,^[2] α_p is the dimensionless polar constant:

$$\alpha_p = \frac{1}{137} \sqrt{\frac{m^* c^2}{2k_B \theta_D}} \left(\frac{1}{\varepsilon(\infty)} - \frac{1}{\varepsilon(0)} \right)$$



Scattering mechanisms



$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

For dislocation scattering (for n -type semiconductor):

$$\mu_0 = \frac{30\sqrt{2\pi}(\epsilon\epsilon_0)^2 d^2}{N_{disl} e^3 f^2 L_D (m^*)^{1/2}} (k_B T)^{3/2}$$

d being the average distance of acceptor centers along the dislocation line, f their occupation rate, N_{disl} the area density of dislocations and $L_D = \sqrt{\epsilon k_B T / (e^2 n)}$ the Debye screening length.

Dislocations can contain charge centers and thus act as scattering centers. The deformation has introduced acceptor-type defects reducing the mobility in particular at low temperatures (similar to ionized impurity scattering).^[2]



Grain boundaries scattering

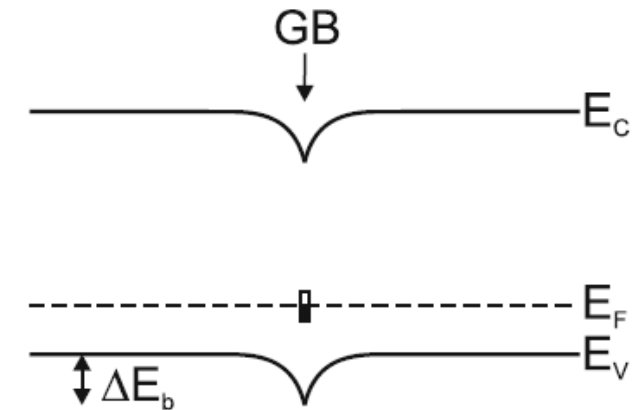
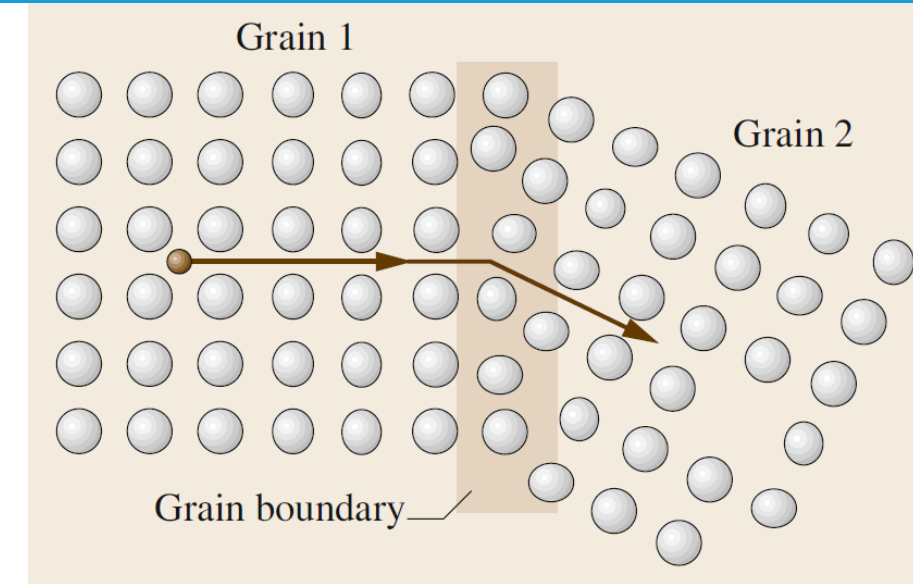
$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

For grain boundaries scattering:

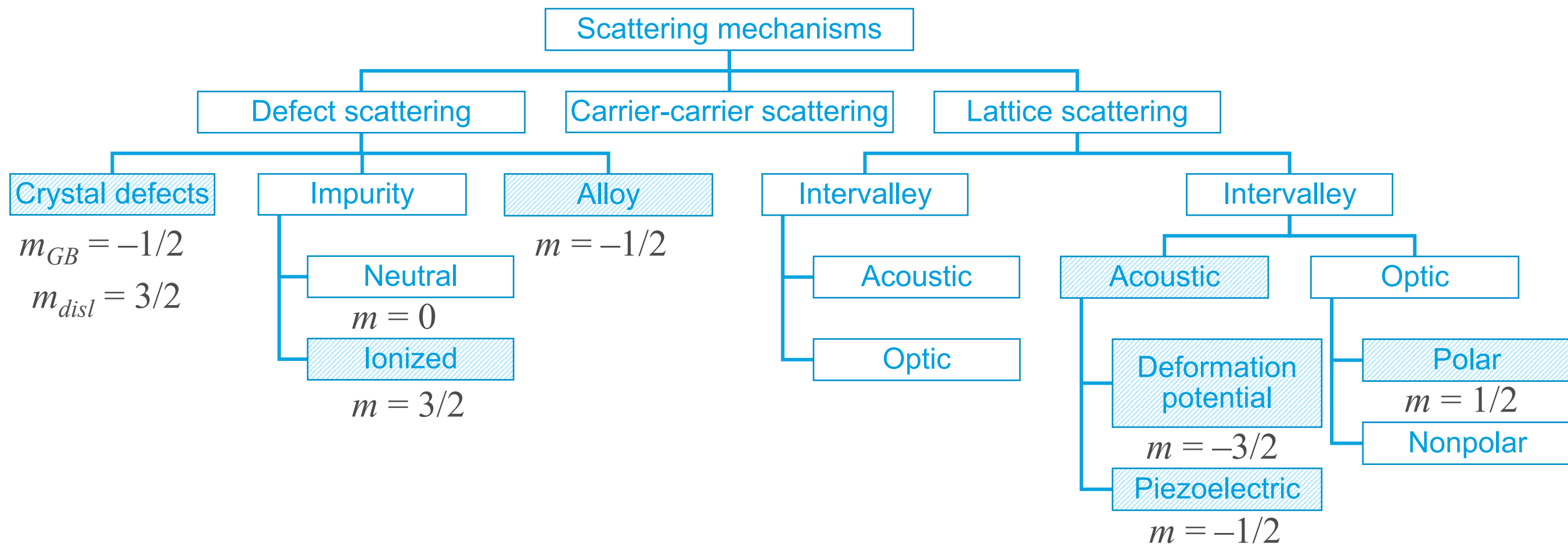
$$\mu_0 = \frac{eL_G}{\sqrt{8m^*\pi k_B}} T^{-1/2} e^{-\Delta E_b/(k_B T)}$$

where L_G is the grain size. Grain boundaries contain electronic traps whose filling depends on the doping of the bulk of the grains. Charges will be trapped in the grain boundaries and a depletion layer will be created.^[2,4]

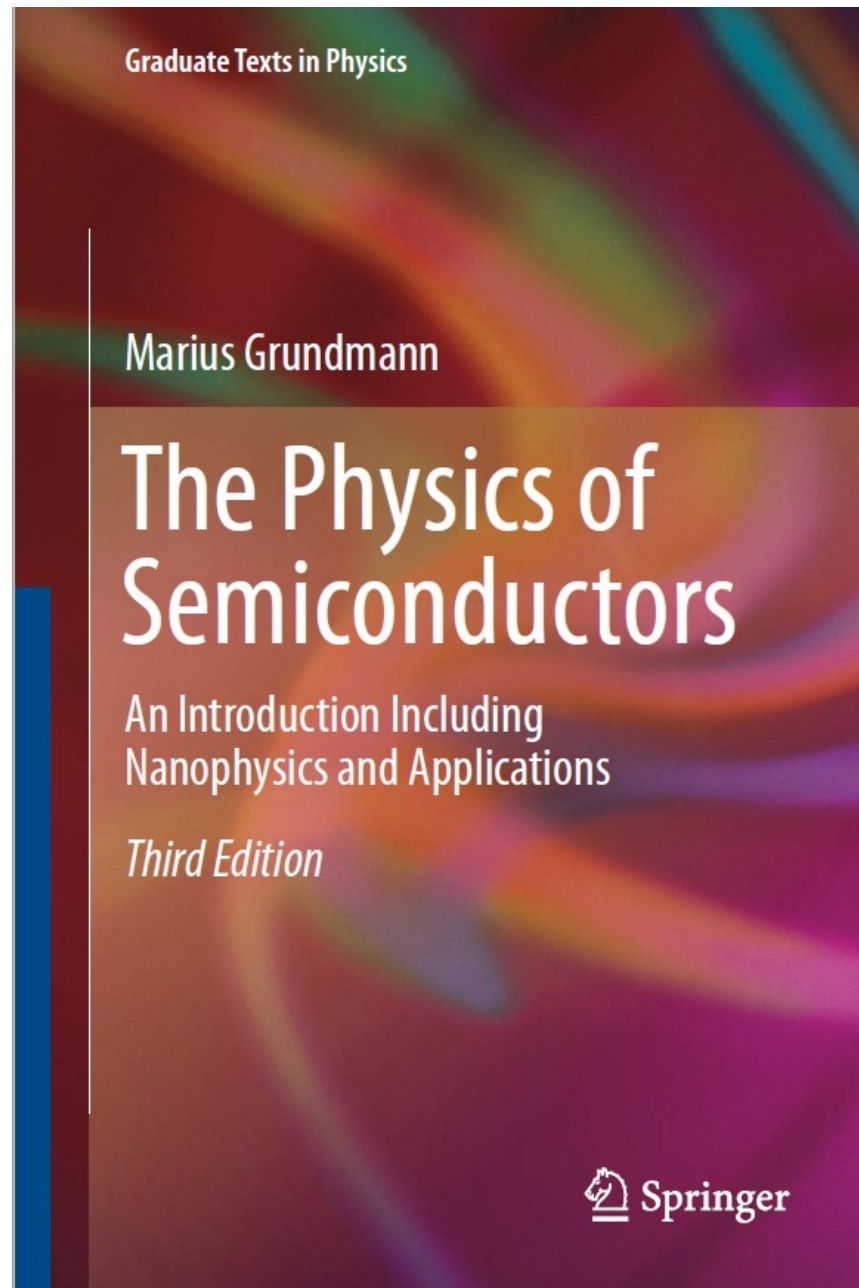
At low doping, the grains are fully depleted and all free carriers are trapped in the grain boundaries. This means low conductivity, however, no electronic barrier to transport exists. At intermediate doping, traps are partially filled and the partial depletion of the grain leads to the creation of an electronic barrier ΔE_b hindering transport since it must be overcome *via* thermionic emission. At high doping the traps are completely filled and the barrier vanishes again.^[4]



Scattering mechanisms



Further reading

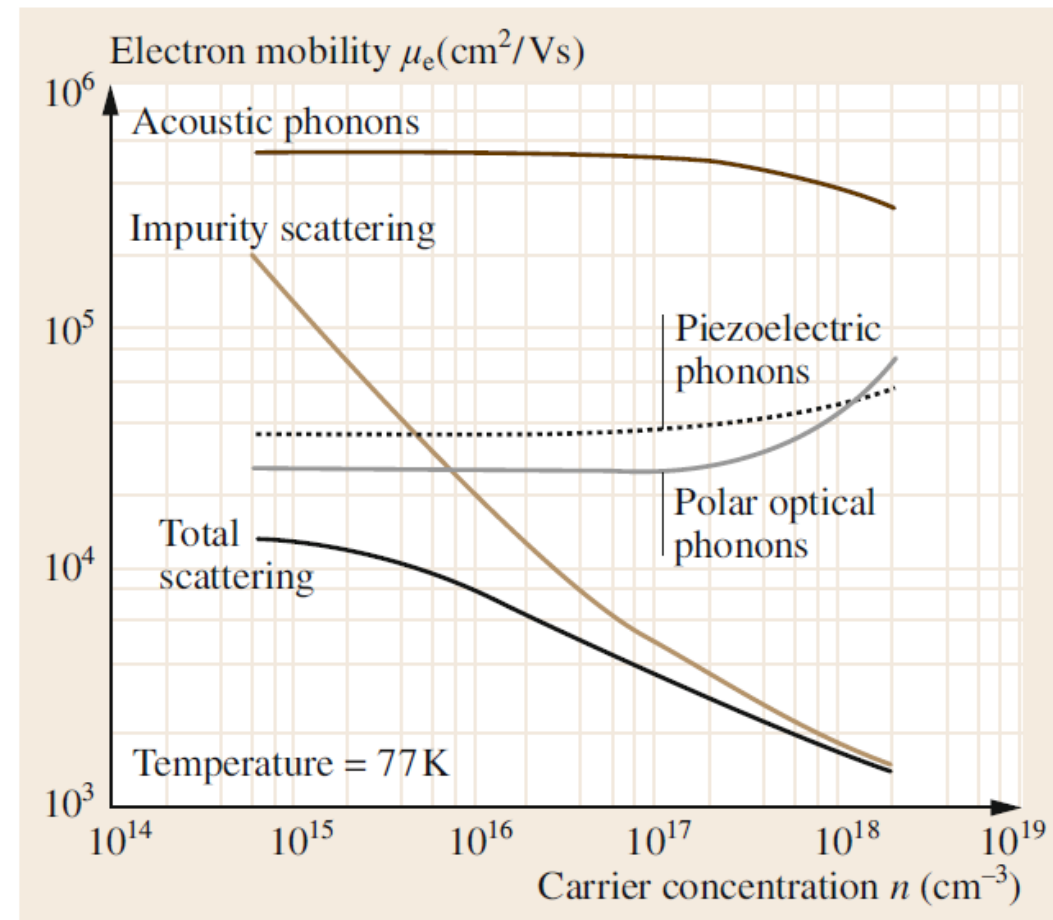


Charge carrier mobility

$$\mu_0^{-1} = \sum_i \mu_{0,i}^{-1} = \frac{1}{\mu_{0,ph}} + \frac{1}{\mu_{0,ion}} + \frac{1}{\mu_{0,gb}} + \dots$$

$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

$$n(\eta) = 4\pi \left(\frac{2m_d^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta)$$

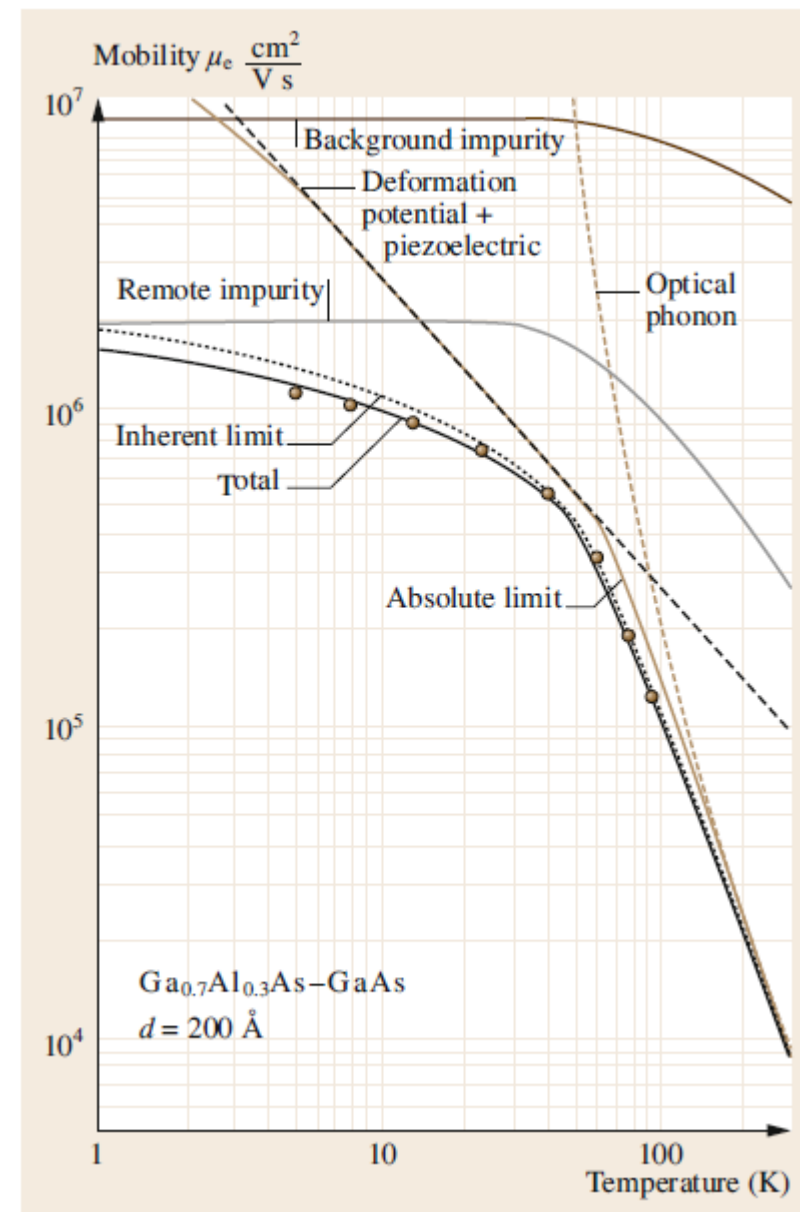


Charge carrier mobility

$$\mu_0^{-1} = \sum_i \mu_{0,i}^{-1} = \frac{1}{\mu_{0,ph}} + \frac{1}{\mu_{0,ion}} + \frac{1}{\mu_{0,gb}} + \dots$$

$$\mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}$$

$$n(\eta) = 4\pi \left(\frac{2m_d^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta)$$



Now it is possible to calculate the electrical conductivity (don't forget that $\mu(\eta) = \mu_H(\eta)/r_H(\eta)$):

$$\sigma(\eta) = en(\eta)\mu(\eta) = \frac{8\pi e(2m_d^*k_B T)^{3/2}}{3h^3} \mu_0 \left(r + \frac{3}{2}\right) F_{r+1/2}(\eta)$$

here σ_{E_0} is the magnitude of conductivity for a given η (describes the conductive “quality” of charge carriers in the material) called transport parameter:

$$\sigma_{E_0} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3} \mu_0 \left(\frac{m_d^*}{m_e}\right)^{3/2} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3} \mu_w$$

$\mu_w = \mu_0 \left(\frac{m_d^*}{m_e}\right)^{3/2}$ is the weighted mobility.

For acoustic phonon scattering:

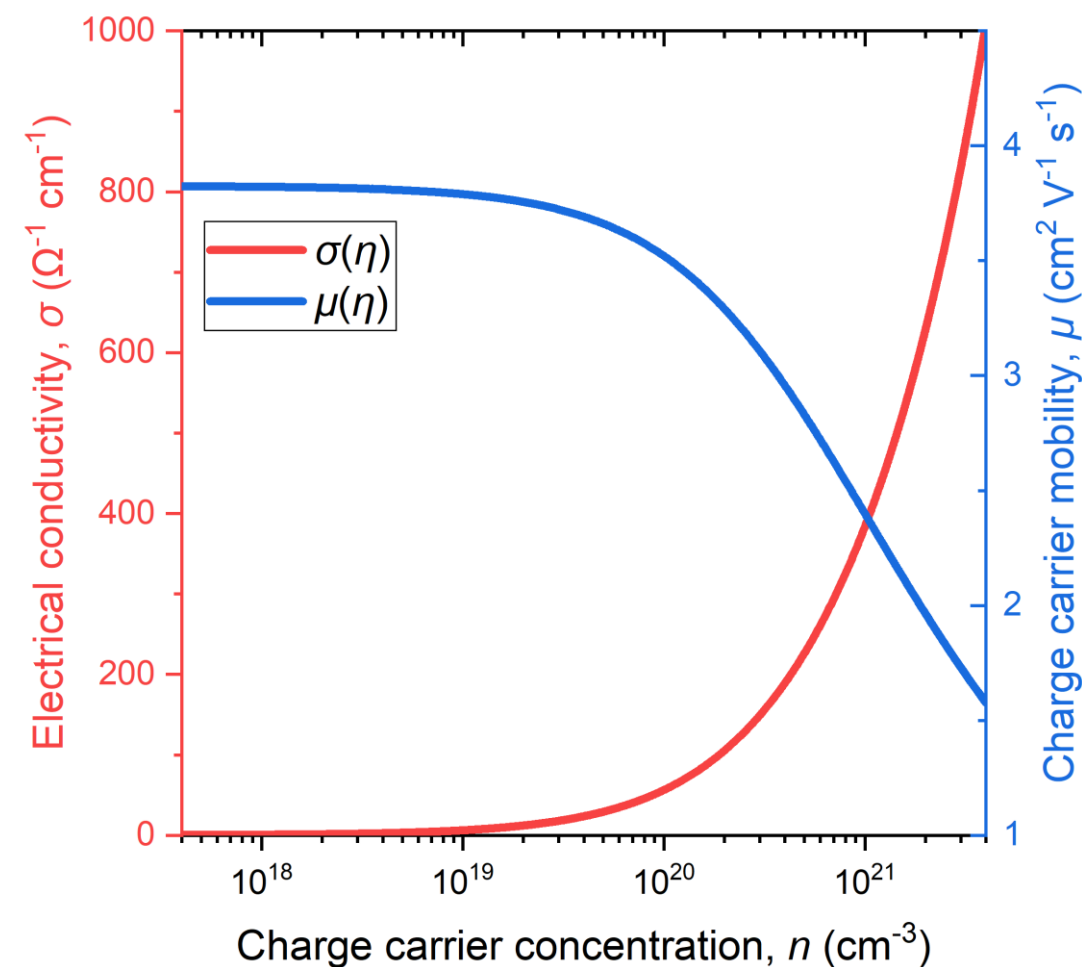
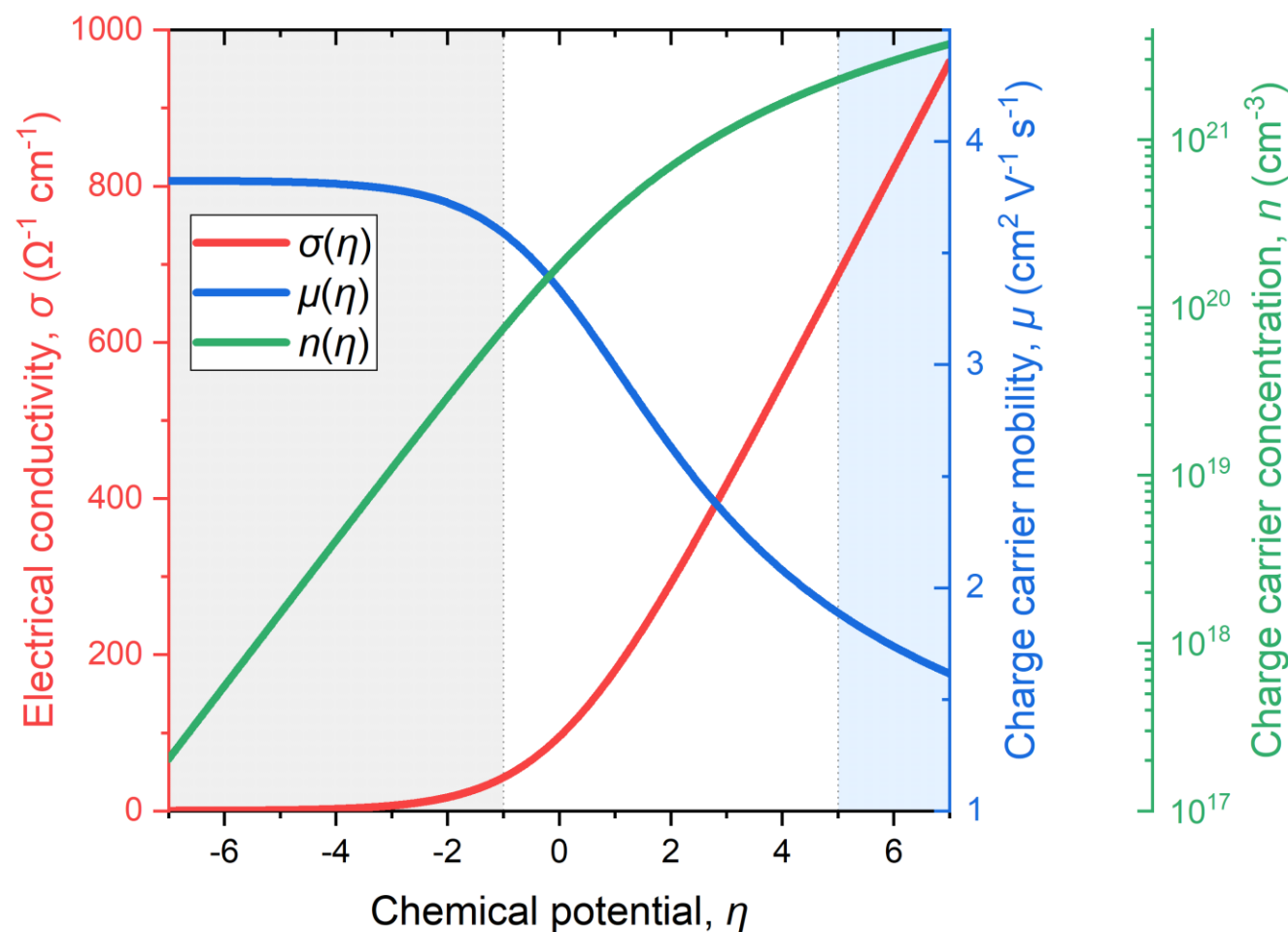
$$\sigma(\eta) = \sigma_{E_0} \ln(1 + e^\eta)$$



Reminder: $\mu_0 = e\tau_0/m_I^*$ and $m_d^* \approx m_s^*$ for acoustic phonon scattering.

Electrical conductivity

$$\sigma(\eta) = \sigma_{E_0} \ln(1 + e^\eta), \quad \sigma_{E_0} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3} \mu_0 \left(\frac{m_d^*}{m_e}\right)^{3/2}, \quad \mu_H(\eta) = \mu_0 \frac{\left(\frac{3}{2} + 2r\right) F_{2r+1/2}(\eta)}{\left(\frac{3}{2} + r\right) F_{r+1/2}(\eta)}, \quad \mu_0 = \frac{e\pi\hbar^4 C_{II}}{\sqrt{2}(k_B T)^{3/2} (m_b^*)^{3/2} m_I^* \Delta_{def}^2}$$



Thermoelectric efficiency

Using calculated m^* , μ_0 , and κ_l it is possible to calculate a 'theoretical' zT to estimate the optimum carrier density at a particular temperature (from the plot of the zT versus n):

$$zT = \frac{\alpha^2 \sigma T}{\kappa_l + \kappa_e} = \frac{\alpha^2}{\frac{\kappa_l}{\sigma T} + L}$$

Considering all that we know:

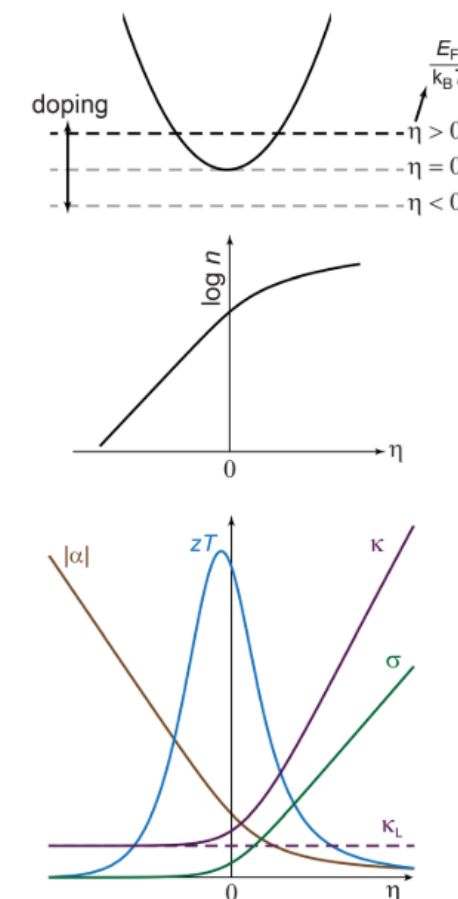
$$zT(\eta) = \frac{\alpha^2(\eta)}{\frac{\kappa_l}{T\sigma_{E_0} \ln(1 + e^\eta)} + L(\eta)} = \frac{\alpha^2(\eta)}{(\psi(\eta)\beta)^{-1} + L(\eta)}$$

here

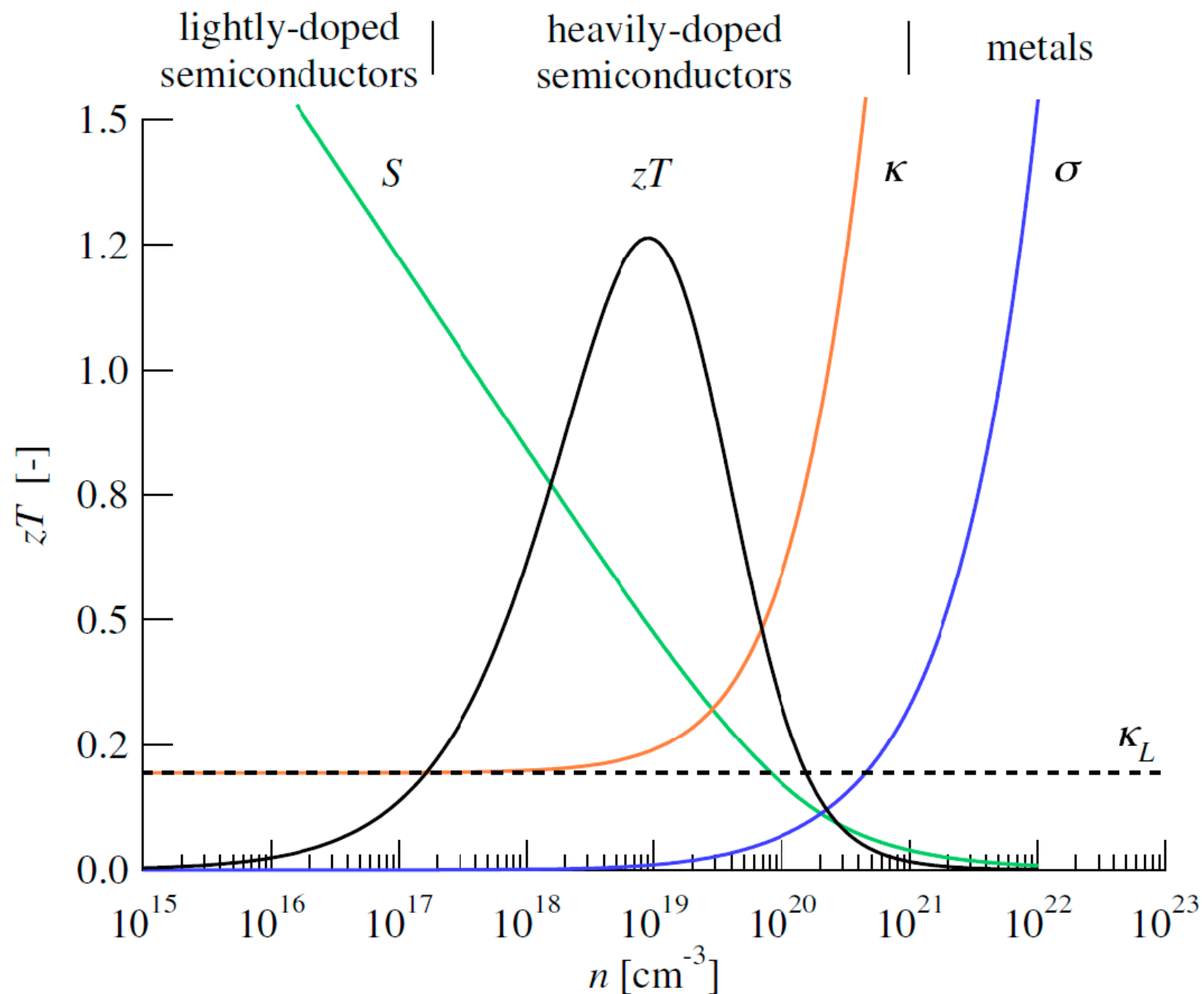
$$\psi(\eta) = \frac{8\pi e}{3} \left(\frac{2m_e k_B}{h^2} \right)^{3/2} F_{r+1/2}(\eta)$$

and

$$\beta = \frac{\mu_0 \left(m^*/m_e \right)^{3/2} T^{5/2}}{\kappa_l}$$



Summary



Again:

$$zT(\eta) = \frac{\alpha^2(\eta)}{\frac{\kappa_l}{T\sigma_{E_0}\ln(1+e^\eta)} + L(\eta)} = \frac{\alpha^2(\eta)}{\frac{(k_B/e)^2}{B\ln(1+e^\eta)} + L(\eta)}$$

$B = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_{E_0}}{\kappa_l} T = \left(\frac{k_B}{e}\right)^2 \frac{8\pi e(2m_e k_B)^{3/2}}{3h^3} \frac{\mu_w}{\kappa_l} T^{5/2}$ is the quality factor.

For example, for acoustic phonon scattering $\tau_0 \propto 1/(m_b^*)^{3/2}$

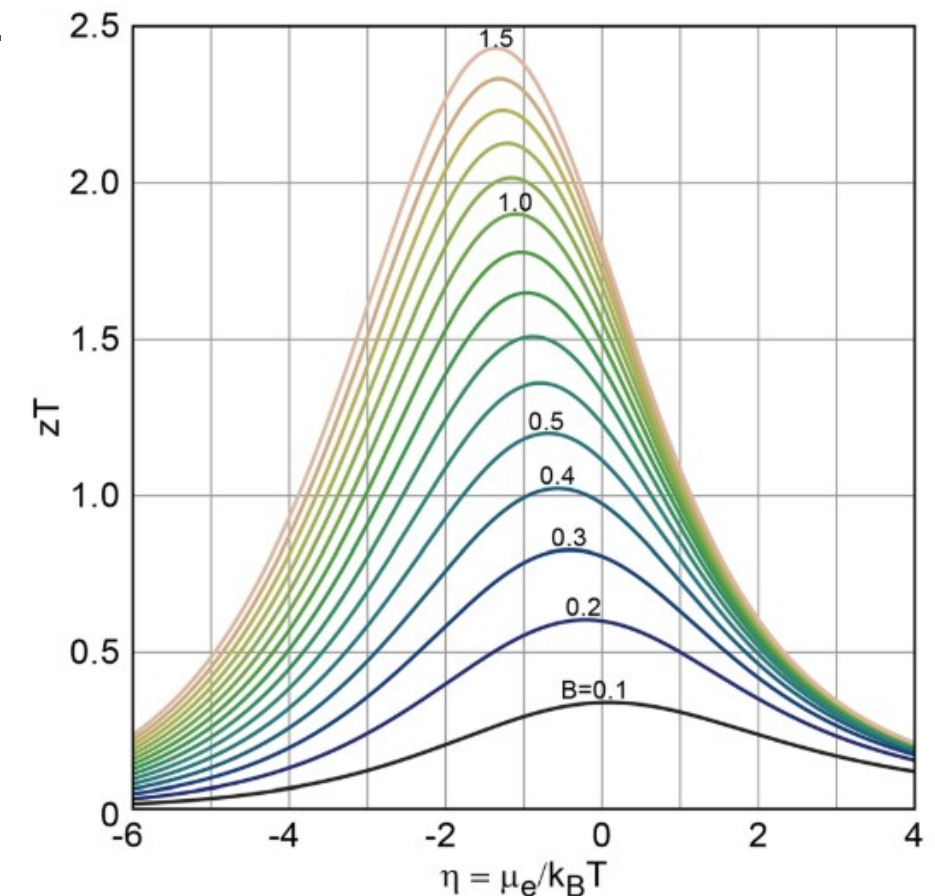
and considering that $m_d^* = N_v^{2/3} m_b^*$, $\mu_0 = \frac{e\tau_0}{m_I^*}$

the quality factor $B \propto N_v/(m_I^* \kappa_l)$



B is materials parameter that might depend on temperature but not doping.

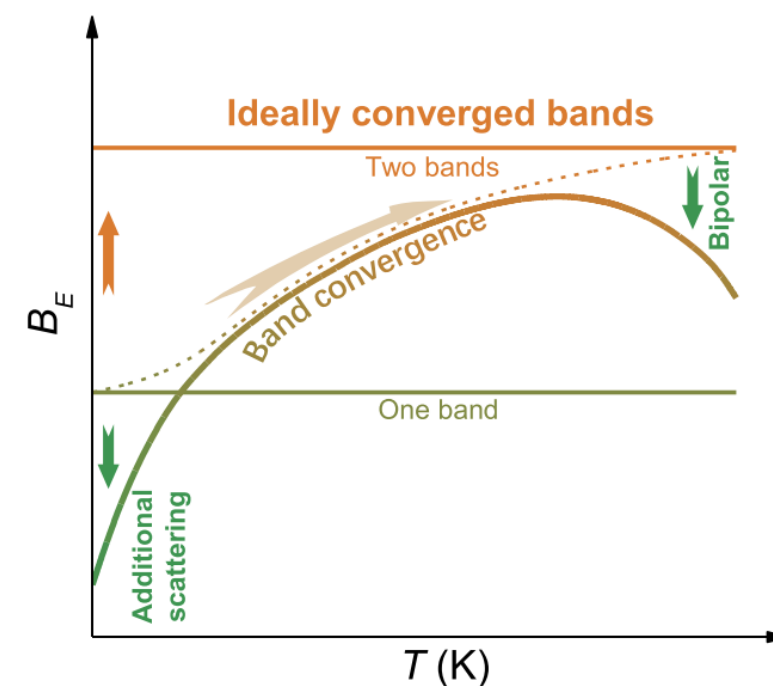
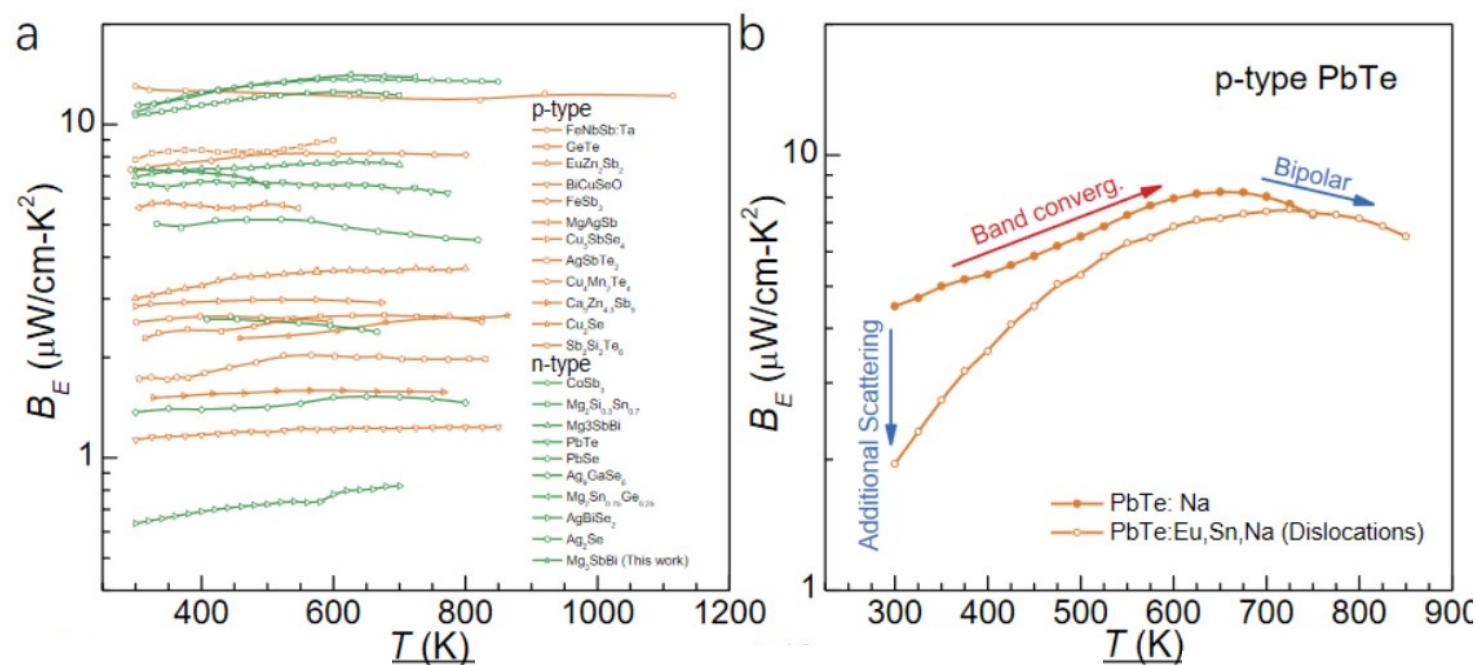
For more details see Ref. [6].



Electronic quality factor

$B_E = \left(\frac{k_B}{e}\right)^2 \sigma_{E_0}$ is the electronic quality factor related to the transport parameter.^[7]

Reminder: $\sigma_{E_0} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3} \mu_0 \left(\frac{m_d^*}{m_e}\right)^{3/2}$ is a material constant for a good thermoelectric because the mobility tends to depend as $T^{-3/2}$, which cancels the temperature dependence here.



Summary

$$zT(\eta) = \frac{\alpha^2(\eta)}{\frac{(k_B/e)^2}{B \ln(1+e^\eta)} + L(\eta)}$$

$$\alpha(\eta) = \pm \frac{k_B}{e} \left(\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta \right)$$

$$B = \left(\frac{k_B}{e} \right)^2 \frac{8\pi e (2m_e k_B)^{3/2} \mu_w}{3h^3 \kappa_l} T^{5/2}$$

$$L(\eta) = \left(\frac{k_B}{e} \right)^2 \left(\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} \right]^2 \right)$$

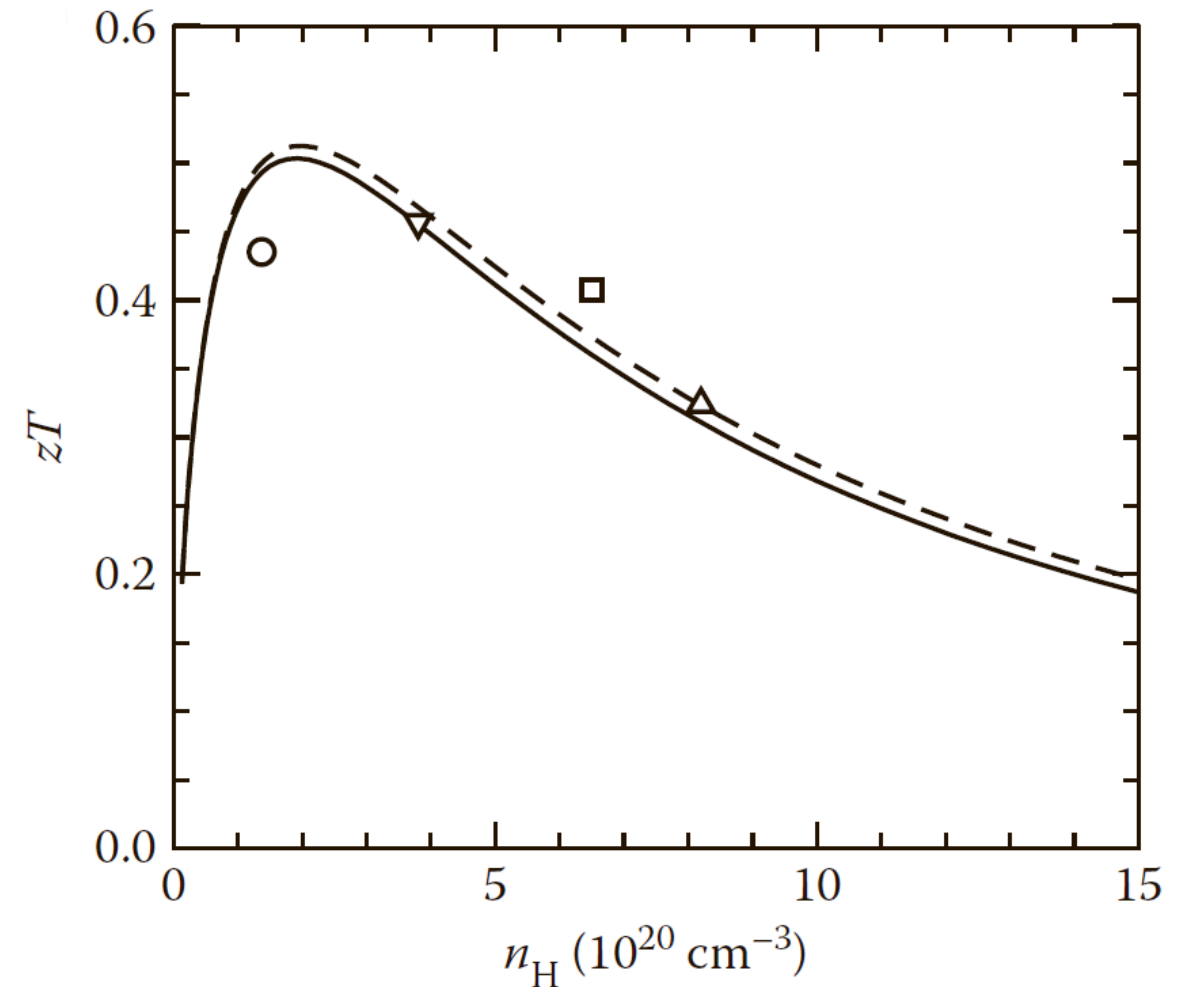
At the same time

$$n(\eta) = 4\pi \left(\frac{2m_d^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta)$$

$$n_H(\eta) = n(\eta)r_H(\eta), \quad r_H(\eta) = \frac{3}{2} F_{1/2}(\eta) \frac{\left(\frac{3}{2}+2r\right)F_{2r+1/2}(\eta)}{\left(\frac{3}{2}+r\right)^2 F_{r+1/2}^2(\eta)}$$

zT as function of doping requires only μ_w and κ_l .

It is enough to measure one sample (α , σ , κ and n_H) to draw the entire $zT = f(n_H)$ curve.



How to calculate?

One way is to use all the formulas that were presented in this and previous lecture as it is (assuming acoustic phonon scattering $r = -1/2$, for example). Thus, the value of η can be found from the experimental value of α considering $\alpha(\eta) = \pm \frac{k_B}{e} \left(\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta \right)$. After this all the transport parameters can be calculated.

Another possible way to perform the SPB calculations is to use approximated sigmoid functions proposed by Snyder's group.^[7–9]

COMMUNICATION

Weighted Mobility

G. Jeffrey Snyder,* Alemayouh H. Snyder, Maxwell Wood, Ramya Gununathan, Berhanu H. Snyder, and Changning Niu

Engineering semiconductor devices requires an understanding of charge carrier mobility. Typically, mobilities are estimated using Hall effect and electrical resistivity measurements, which are routinely performed at room temperature and below, in materials with mobilities greater than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. With the availability of combined Seebeck coefficient and electrical resistivity measurement systems, it is now easy to measure the weighted mobility (electron mobility weighted by the density of electronic states). A simple method to calculate the weighted mobility from Seebeck coefficient and electrical resistivity measurements is introduced, which gives good results at room temperature and above, and for mobilities as low as $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

$$\mu_w = 331 \frac{\text{cm}^2}{\text{Vs}} \left(\frac{\text{mV cm}}{\rho} \right)^{-1/2} \left(\frac{T}{300\text{K}} \right)^{-1/2} \left[\frac{\exp\left[\frac{S}{k_B T}\right] - 2}{1 + \exp\left[-\frac{S}{k_B T}\right]} + \frac{\frac{3}{2} \left[\frac{S}{k_B T} \right]}{1 + \exp\left[\frac{S}{k_B T}\right]} \right]$$

Here, μ_w is the weighted mobility, ρ is the electrical resistivity measured in $\text{m}\Omega \text{ cm}$, T is the absolute temperature in K, S is the Seebeck coefficient, and $k_B/e = 86.3 \mu\text{V K}^{-1}$. Weighted mobility analysis can elucidate the electronic structure and scattering mechanisms in materials and is particularly helpful in understanding and optimizing thermoelectric systems.

Charge carrier mobility is perhaps the most important material parameter to experimentally characterize in order to understand or engineer semiconductor electronic devices. The optimization of carrier mobility is critical to research fields ranging from organic semiconductors to photovoltaics to thermoelectrics.^{1–5} Mobility is usually defined with the Drude–Sommerfeld free electron model ($\mu = \sigma / nq$ where σ is the electrical conductivity, n is the charge carrier concentration, e the electronic charge, and μ the drift mobility. Historically, the easiest way to characterize mobility is through the Hall effect, where the Hall mobility can be defined as $\mu_H = \sigma/\mu_H$ with R_H as the Hall resistance.⁶ In most cases where

the charge transport is dominated by a single band, the Hall mobility is a good estimate (within 10–20%) for the free-drift mobility.¹¹

With the proliferation of Seebeck coefficient measurement systems, particularly in laboratories studying thermoelectric materials,^{6,8} the weighted mobility is an independent measurement giving similar information. This can be particularly helpful when there are other magnetic effects to consider in the Hall measurements, such as the anomalous Hall effect, and the measured Hall resistance does not seem to correlate well with the actual charge carrier concentration ($R_H = 1/nq_0$) or mobility.¹⁰ The weighted mobility measurement is also practicable in regimes where the Hall resistivity measurement is difficult, such as at high temperatures or with low mobility bulk systems.^{12,8}

The weighted mobility like the Hall mobility can be defined as a simple function of two measured properties (Figure 1). Seebeck coefficient S and electrical conductivity σ of the Hall mobility is a function of many parameters (2) including band degeneracy (3), effective mass (4), scattering factor (2), Fermi level (2), and elastic constants (5). None of these parameters can be easily determined or used as a complete descriptor for S/σ . In addition, because S/σ does not include nq_0 , it does not describe all the effects transporting electrons have on S/σ and does not optimize at the same doping as S/σ . This leads the traditional development of thermoelectric materials to involve repeated experiments including synthesis, characterization, and property measurement, which includes some modeling calculations because of the reoptimization of the materials required for each target temperature. The procedure and models will often differ because of the breadth, complexity, and diversity of crystal structures, microstructures, and compositions of materials (7).

To advance thermoelectrics more efficiently, here, we collect thousands of Seebeck coefficient and conductivity datasets from dozens of thermoelectric materials, at various temperatures and degenerate doping, but not necessarily optimized. Such a “big-data” investigation unexpectedly shows that all scaled power factor

$$\mu_w = \frac{30/\sigma}{8\pi(2m_0 k_B T)^{3/2}} \left[\frac{\exp\left[\frac{S}{k_B T}\right] - 2}{1 + \exp\left[-\frac{S}{k_B T}\right]} + \frac{\frac{3}{2} \left[\frac{S}{k_B T} \right]}{1 + \exp\left[\frac{S}{k_B T}\right]} \right]$$

An equivalent form using the electrical resistivity $\rho = 1/\sigma$ is given in the abstract. In the free electron model, the weighted mobility is a (temperature dependent) material property that is independent of doping whereas the drift mobility depends on doping through the free charge carrier concentration n . Generally, the weighted mobility μ_w is related to the drift mobility μ by

$$\mu_w = \mu \left(\frac{m_0}{m} \right)^{1/2}$$

SCIENCE ADVANCES | RESEARCH ARTICLE

MATERIALS SCIENCE

Electronic quality factor for thermoelectrics

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Development of thermoelectrics usually involves trial-and-error investigations, including time-consuming synthesis and measurements. Here, we identify the electronic quality factor B_0 for determining the maximum thermoelectric power factor, which can be conveniently estimated by a single measurement of Seebeck coefficient and electrical conductivity of only one sample, not necessarily optimized, at an arbitrary temperature. We demonstrate that thousands of experimental measurements in dozens of materials can all be described by a universal curve and a single material parameter B_0 for each class of materials. Furthermore, any deviation in B_0 with temperature or doping indicated new effects such as band convergence or additional scattering. This makes B_0 a powerful tool for evaluating and guiding the development of thermoelectrics. We demonstrate the power of B_0 to show both p-type GeTe alloys and n-type Mg_2Sb alloys as highly competitive materials, at near room temperature, to state-of-the-art Bi₂Te₃ alloys used in nearly all commercial applications.

INTRODUCTION

Without any emissions or moving parts, thermoelectricity, which enables a direct conversion between heat and electricity, is considered as a clean and sustainable technology for both power generation and refrigeration (1). Sufficient conversion efficiency requires materials of high thermoelectric figure of merit, $zT = S^2 \sigma T / (\kappa_0 + \kappa_L)$, where S , T , κ_0 , and κ_L are the Seebeck coefficient, the absolute temperature, the electrical conductivity, and the electronic and lattice component of the thermal conductivity, respectively. The thermoelectric power factor ($S^2 \sigma$) is frequently used to describe the primary electronic terms determining zT .

$S^2 \sigma$ depends on the band structure, charge scattering, and the doping level of a material, leading its quantity to be a collection of many parameters (2) including band degeneracy (3), effective mass (4), scattering factor (2), Fermi level (2), and elastic constants (5). None of these parameters can be easily determined or used as a complete descriptor for $S^2 \sigma$. In addition, because $S^2 \sigma$ does not include nq_0 , it does not describe all the effects transporting electrons have on $S^2 \sigma$ and does not optimize at the same doping as $S^2 \sigma$. This leads the traditional development of thermoelectric materials to involve repeated experiments including synthesis, characterization, and property measurement, which includes some modeling calculations because of the reoptimization of the materials required for each target temperature. The procedure and models will often differ because of the breadth, complexity, and diversity of crystal structures, microstructures, and compositions of materials (7).

To advance thermoelectrics more efficiently, here, we collect thousands of Seebeck coefficient and conductivity datasets from dozens of thermoelectric materials, at various temperatures and degenerate doping, but not necessarily optimized. Such a “big-data” investigation unexpectedly shows that all scaled power factor

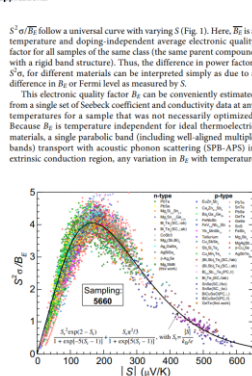


Fig. 1. Scaled power factor versus universal curve for dozens of thermoelectrics. The experimental thermoelectric power factor $S^2 \sigma$ divided by the average electronic quality factor B_0 follows a universal curve for dozens of thermoelectrics with various types of dopants and additives. This represents thousands of measured results at various temperatures and doping concentrations. Data for amorphous materials are collected in white. SC, single crystals; PC, polycrystals. Detailed references are given in Fig. S4.

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RESEARCH ARTICLE

Effective Mass from Seebeck Coefficient

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Engineering semiconductor devices requires an understanding of the effective mass of electrons and holes. Effective masses have historically been determined in metals at cryogenic temperatures estimated using measurements of the electronic specific heat. Instead, by combining measurements of the Seebeck and Hall effects, a density of states effective mass can be determined in doped semiconductors at room temperature and above. Here, a simple method to calculate the electron effective mass using the Seebeck coefficient and an estimate of the free electron or hole concentration, such as that determined from the Hall effect, is introduced by a simple tensor.²⁰ Measurable material properties often probe the average E versus k over a constant energy Fermi surface. Thus, each property is associated with a distinct definition of effective mass, which can change with doping and temperature, even for rigid bands. Despite the complexity, effective mass m^* is the most useful descriptor of the band structure, as it is generally more constant for the relevant electrons than E , p , or n . Additionally, m^* usually has similar values (within an order of magnitude) when comparing the average mass to define or measure it.

The most commonly discussed effective mass is the inertial effective mass tensor usually defined from the second derivative of the E versus k dispersion relation, even though the first derivative is more directly relevant to measurable phenomena such as cyclotron resonance and electron transport.²¹ The anisotropy of the band structure makes any effective mass defined from E versus k anisotropic, even more anisotropic than can be described by a simple tensor.²⁰ Measurable material properties often probe the average E versus k over a constant energy Fermi surface. Thus, each property is associated with a distinct definition of effective mass, which can change with doping and temperature, even for rigid bands. Despite the complexity, effective mass m^* is the most useful descriptor of the band structure, as it is generally more constant for the relevant electrons than E , p , or n . Additionally, m^* usually has similar values (within an order of magnitude) when comparing the average mass to define or measure it.

1. Introduction

The effective mass of the free electrons in metals or semiconductors is perhaps the most fundamental materials parameter needed to understand or engineer electronic devices. Effective mass, usually denoted m^* , is the mass that the electrons appear to have based on analogy with classical physics. For example, in response to a force, an electron will accelerate allowing the deduction of an inertial mass: $F = ma$. As it greatly simplifies the more general theory of electronic mass, the effective mass is an important engineering parameter that influences measurable properties, such as the efficiency of a solar cell or the speed of electronic devices. However, there are other ways of defining mass through analogies to energy, $E = \frac{1}{2}mv^2$, and momentum, $p = mv$, and this leads to numerous possible definitions as well as for effective mass.

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There are two classes of effective masses used in solid state physics: the first describe an inertial effective mass that characterizes the response of an individual electron and the second depend more on the density of electron states (DOS), and are hence called a DOS mass, m_{DOS} . The DOS is another quantity that underpins most electronic properties. For example, the relationship between the electron concentration in a semiconductor and the Fermi level (average electron energy) depends on the available density of electronic states, $g(E)$. In metals, the DOS has historically been measured by the low temperature specific heat. The DOS mass, m_{DOS} , is an important engineering quantity used to characterize the density of states using the free electron (parabolic band) approximation

$$g(E) = \frac{8\pi\sqrt{2}}{h^3} m_{\text{DOS}}^{3/2} \sqrt{E}$$

where h is Planck's constant. When there are multiple bands or multiple valleys (band minima or maxima in E versus k) the density of states is proportionally larger. Silicon, for example, has six equivalent valleys in the conduction band, making the density of states six times that of just one pocket. Because $g(E) \propto m_{\text{DOS}}^{3/2}$, the DOS effective mass will be $6^{2/3}$ times larger than the DOS mass of a single valley in its type.

The next section discusses an effective mass defined using the Seebeck coefficient and an estimate of the charge carrier

Assuming acoustic phonon scattering (which is reasonable for many of thermoelectrics):^[7]

$$\alpha(\eta) = \pm \frac{k_B}{e} \left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right)$$

thus

$$\alpha_r = \frac{|\alpha|}{k_B/e} = \frac{2F_1(\eta)}{F_0(\eta)} - \eta$$

at the same time:

$$\sigma = \sigma_{E_0} F_0(\eta) = B_E \left(\frac{e}{k_B} \right)^2 F_0(\eta)$$

$$\text{while } B_E = \left(\frac{k_B}{e} \right)^2 \sigma_{E_0} = \left(\frac{k_B}{e} \right)^2 \frac{\alpha^2 \sigma \sigma_{E_0}}{\alpha^2 \sigma} = \left(\frac{k_B}{e} \right)^2 \frac{\alpha^2 \sigma \sigma_{E_0}}{\alpha^2 \sigma_{E_0} F_0(\eta)} = \frac{\alpha^2 \sigma}{\left(\frac{k_B}{e} \right)^2 F_0(\eta)} = \frac{\alpha^2 \sigma}{\left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right)^2 F_0(\eta)} = \frac{\alpha^2 \sigma}{\alpha_r^2 F_0(\eta)}$$

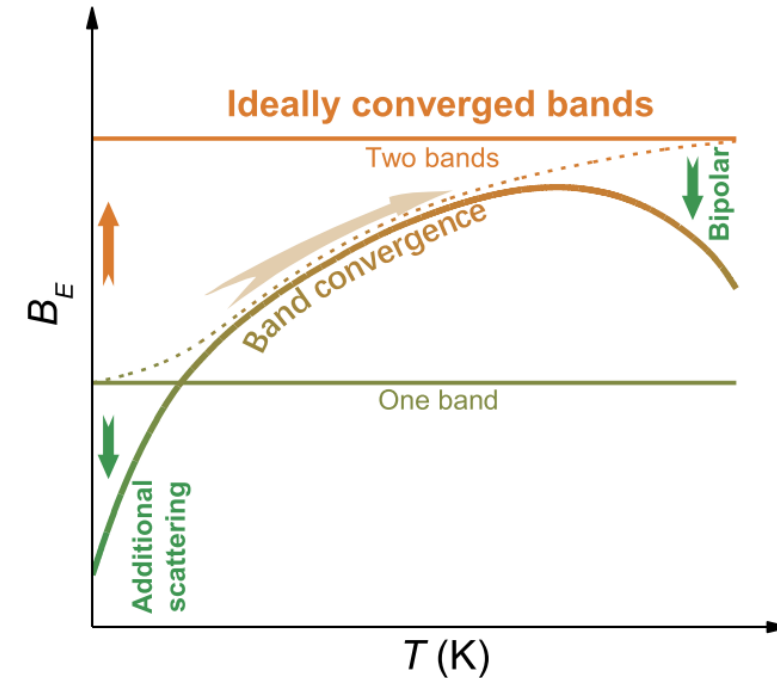
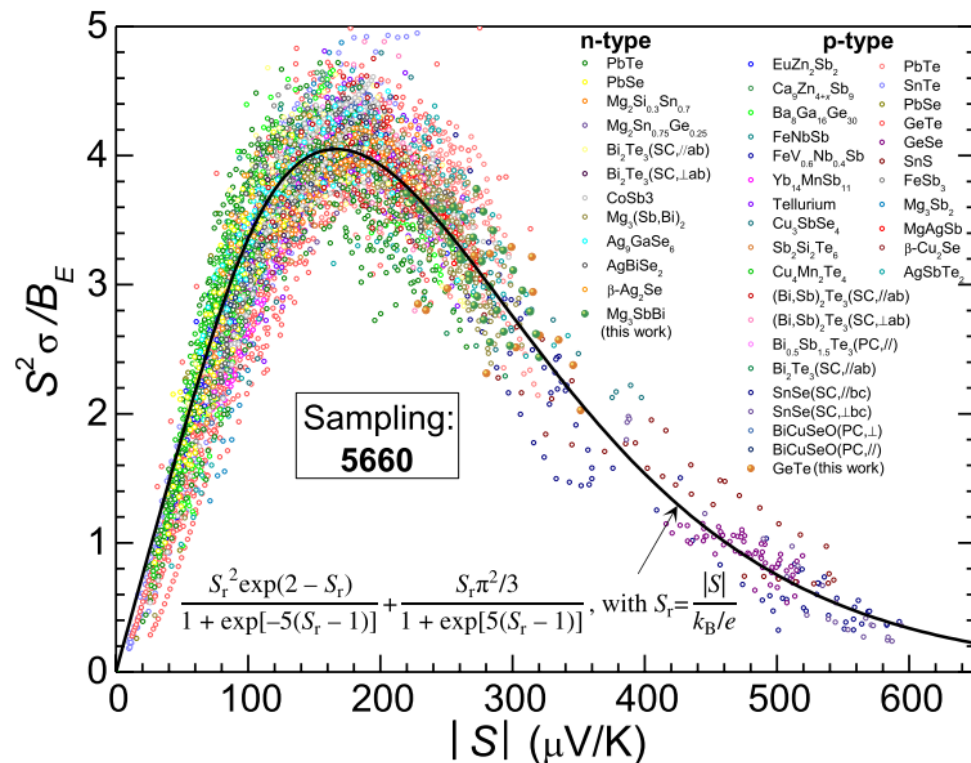
For non-degenerate limit $F_0(\eta)$ reduces to $F_0(\eta) = e^{2-\alpha_r}$

In fully degenerate case $F_0(\eta)$ reduces to $F_0(\eta) = \frac{\pi^2}{3\alpha_r}$

Thus, by using sigmoid selection function that smoothly goes between the degenerate and non-degenerate limits the following relation can be written for B_E :^[7,8]

$$B_E = \alpha^2 \sigma \left[\frac{\alpha_r^2 e^{2-\alpha_r}}{1 + e^{-5(\alpha_r-1)}} + \frac{\alpha_r \pi^2/3}{1 + e^{5(\alpha_r-1)}} \right]^{-1}$$

here $\alpha_r = \frac{|\alpha|}{k_B/e}$, where α is the experimental value of the Seebeck coefficient.

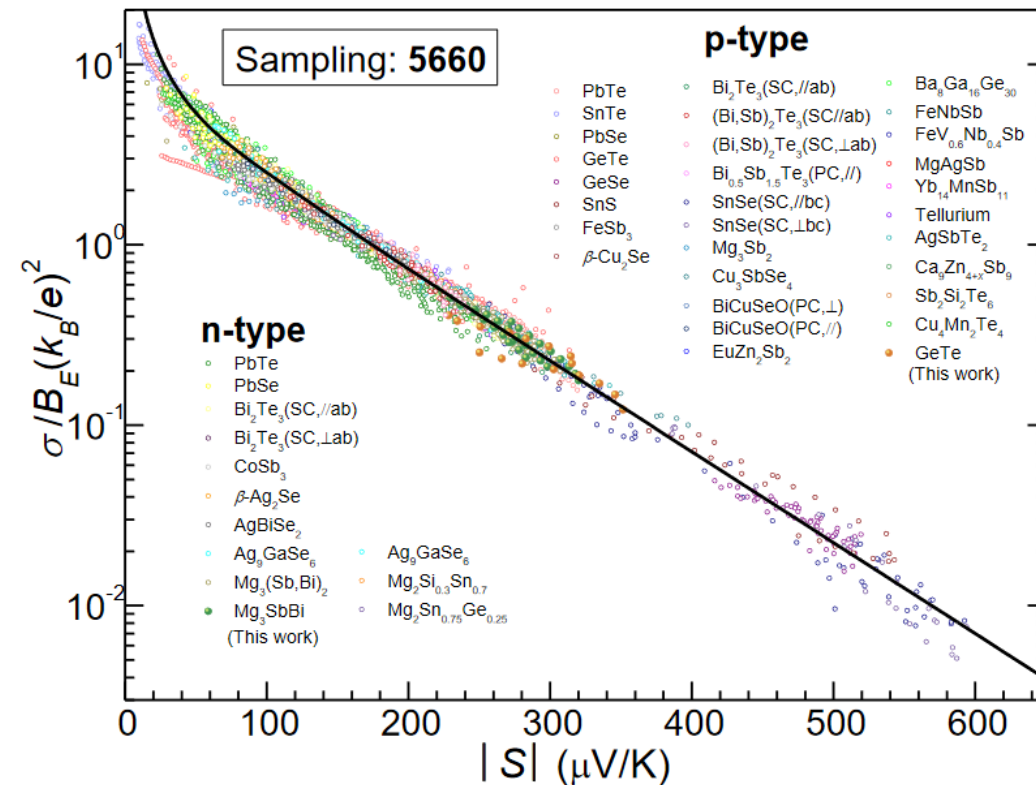


Similarly, the electrical conductivity:[7,8]

$$\sigma = \sigma_{E_0} \left[\frac{e^{2-\alpha_r}}{1 + e^{-5(\alpha_r-1)}} + \frac{\pi^2/3\alpha_r}{1 + e^{5(\alpha_r-1)}} \right]$$

here $\alpha_r = \frac{|\alpha|}{k_B/e}$, where α is the experimental value of the Seebeck coefficient.

In this case the reduced Fermi energy can be calculated from $\sigma = \sigma_{E_0} \ln(1 + e^\eta)$



In the same manner (see details in Refs. [7–9]) such relation can be written for the Seebeck effective mass:

$$m_S^* = \frac{h^2}{2k_B T} \left(\frac{3n_H}{16\sqrt{\pi}} \right)^{2/3} \left[\frac{(e^{\alpha_r - 2} - 0.17)^{2/3}}{1 + e^{-5(\alpha_r - 1)}} + \frac{\frac{3}{\pi^2} \left(\frac{2}{\sqrt{\pi}} \right)^{2/3} \alpha_r}{1 + e^{5(\alpha_r - 1)}} \right]$$

and for the weighted mobility:

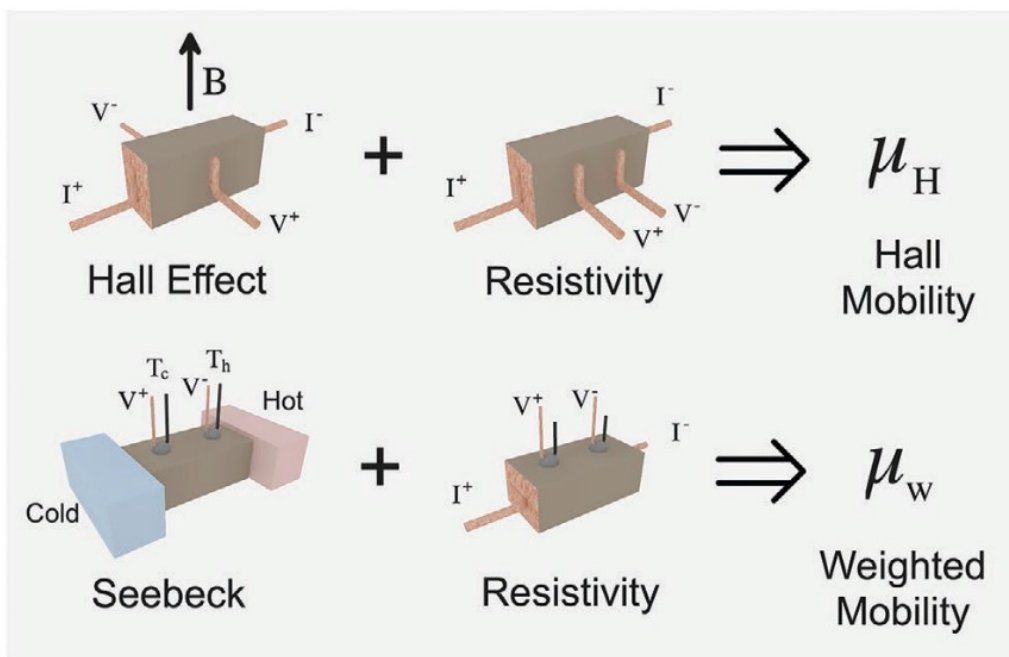
$$\mu_w = \frac{3h^3\sigma}{8\pi e(2m_e k_B T)^{3/2}} \left[\frac{e^{\alpha_r - 2}}{1 + e^{-5(\alpha_r - 1)}} + \frac{\frac{3}{\pi^2} \alpha_r}{1 + e^{5(\alpha_r - 1)}} \right]$$

here $\alpha_r = \frac{|\alpha|}{k_B/e}$, where α is the experimental value of the Seebeck coefficient.



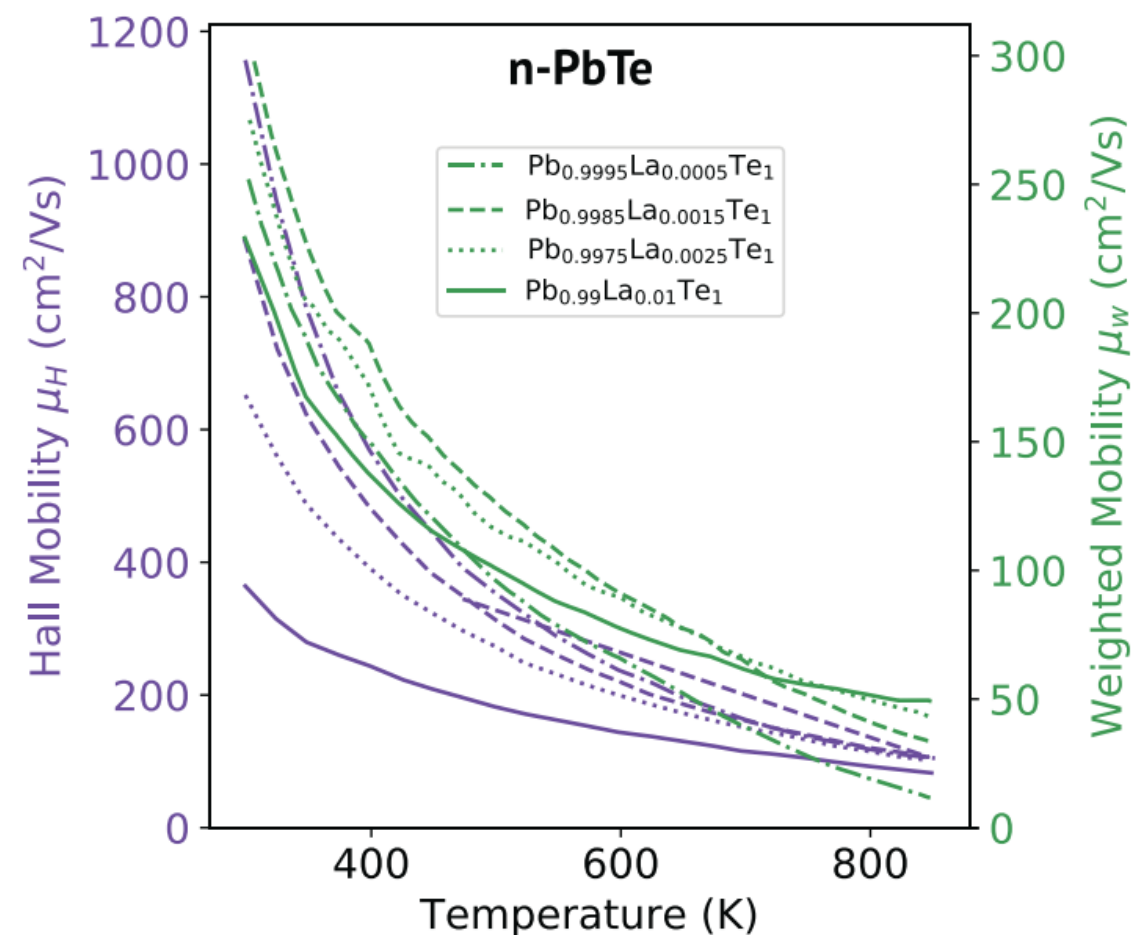
Hall and weighted mobilities

μ_H and μ_w are highly correlated except in samples with very high carrier concentration. This is because the Hall mobility depends on Fermi level through the Fermi integrals. This reduces the μ_H at high carrier concentrations. The weighted mobility should only depend on the intrinsic mobility parameter and the density of states m^* , which shouldn't change much in a parabolic band.^[8]



$$\mu_H = \sigma R_H = \mu_0 \frac{F_{-1/2}}{2F_0}$$

$$\mu_w = f(\alpha, \sigma) = \mu_0 \left(\frac{m_d^*}{m_e} \right)^{\frac{3}{2}}$$



Often the Hall mobility measurements are not accurate enough to notice the trend. The weighted mobility, in contrast, only depends on the mobility parameter and not Fermi level, so it is reasonable to expect it to be a constant with carrier concentration.^[8]

$$\left. \begin{aligned} \mu_H &= \mu_0 \frac{F_{-1/2}}{2F_0} \\ \mu_w &= \mu_0 \left(\frac{m_d^*}{m_e} \right)^{\frac{3}{2}} \end{aligned} \right\} \frac{m_d^*}{m_e} = \left(\frac{\mu_w}{\mu_0} \right)^{\frac{2}{3}} = \left(\frac{\mu_w}{\mu_H} \frac{F_{-1/2}}{2F_0} \right)^{\frac{2}{3}}$$

Thus:

$$\frac{\mu_w}{\mu_H} = \left(\frac{m_d^*}{m_e} \right)^{\frac{3}{2}} \frac{2F_0}{F_{-1/2}}$$



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