# Bipolar effects and bandgap
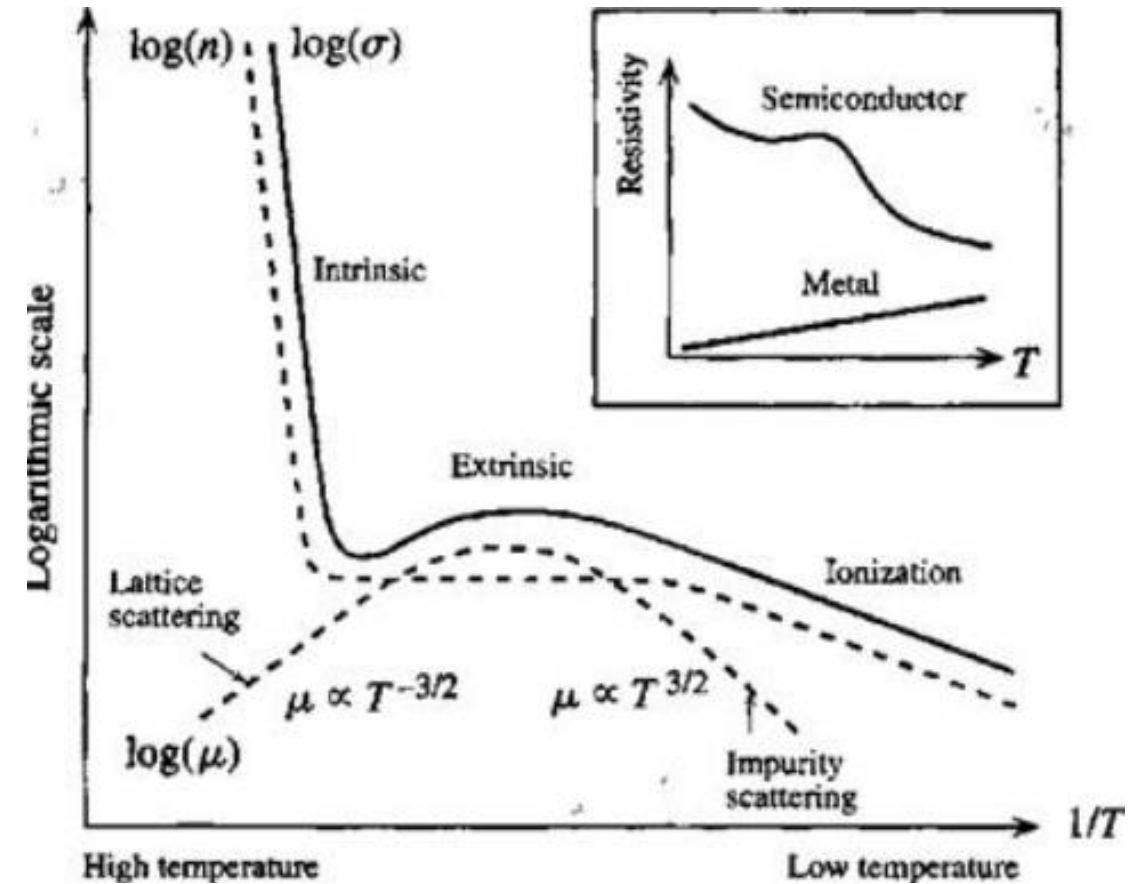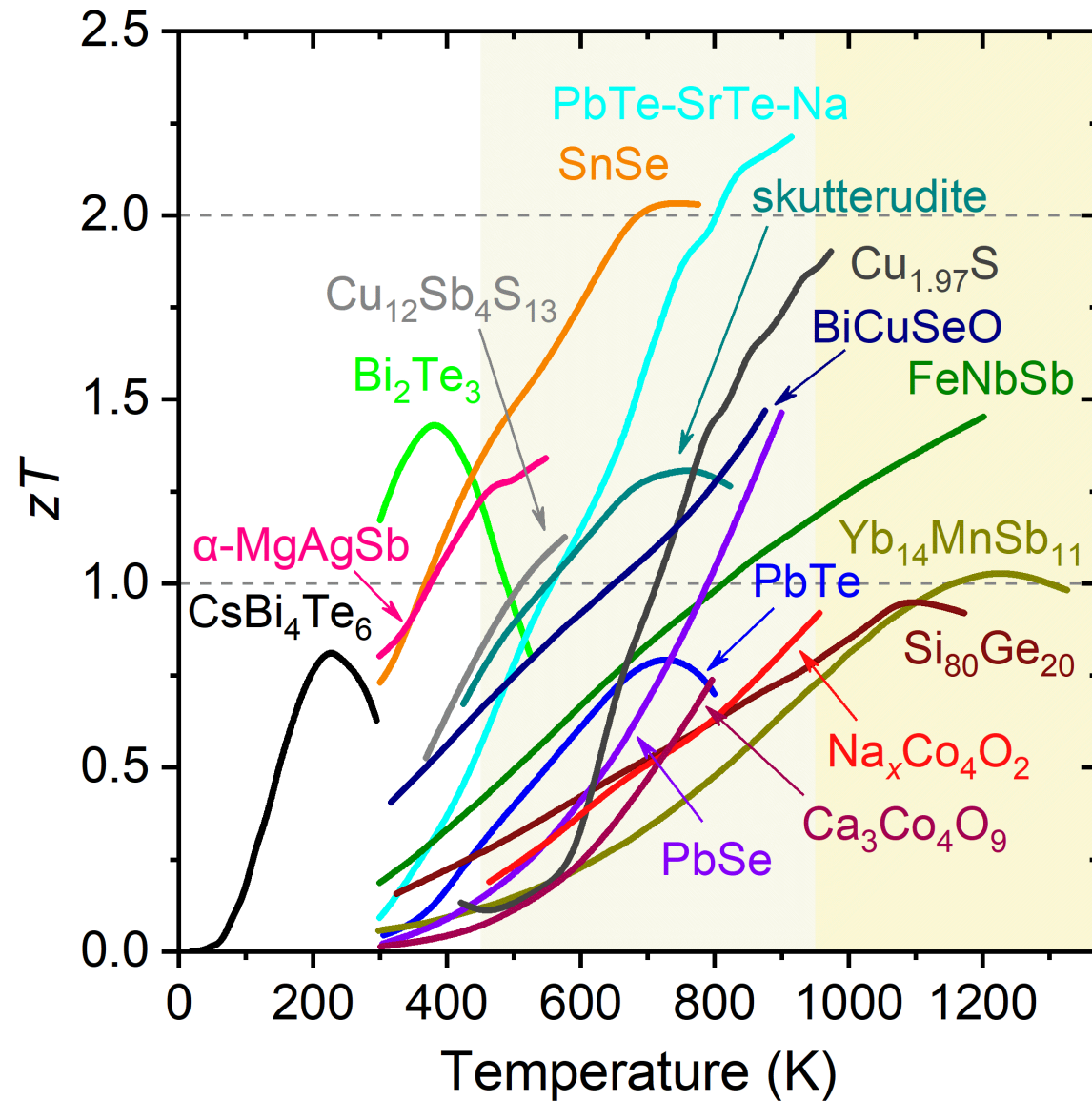
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# Bipolar Seebeck and conductivity

The Seebeck coefficient is dramatically affected because the minority charge carriers add a Seebeck voltage of opposite sign as the majority carriers greatly reducing the thermopower $|\alpha|$. The contribution of each charge carrier to the total Seebeck coefficient is weighted by the electrical conductivity:[1]

$$\alpha_{total} = \frac{\sigma_{major}\alpha_{major} - \sigma_{minor}\alpha_{minor}}{\sigma_{major} + \sigma_{minor}}$$

The electrical conductivity is least affected because both electrons can holes contribute to the electrical transport with the same sign:

$$\sigma_{total} = \sigma_{major} + \sigma_{minor} = en_{major}\mu_{major} + en_{minor}\mu_{minor}$$

Reminder: for *p*-type holes are the major charge carriers

for *n*-type electrons are the major charge carriers

# Bipolar Hall constant

The Hall voltage, which is also opposite for electrons and holes, is also compensated when both electrons and holes are present making the apparent Hall carrier concentration $n_H = \dfrac{1}{eR_H}$ increase much faster than the real majority carrier concentration. The individual contributions are even more strongly weighted by the electrical conductivity (mobility) than is the Seebeck coefficient (note that in this notation $\mu > 0$ for holes and $\mu < 0$ for electrons):

$$R_H = \frac{1}{en_H} = \frac{\sigma_{major}\mu_{major} - \sigma_{minor}\mu_{minor}}{\left(\sigma_{major} + \sigma_{minor}\right)^2}$$

Reminder: for *p*-type holes are the major charge carriers

for *n*-type electrons are the major charge carriers

The thermal conductivity is also affected by the bipolar effect, but it is often not noticed because of the lattice contribution. Because there are more electron-hole pairs at high temperature then low temperature, in a temperature gradient there will be an effect of absorbing heat at the hot end by creating electron-hole pairs and releasing heat at the cold end when they recombine:

$$\kappa_{el} = \sigma_{major}L_{major}T - \sigma_{minor}L_{minor}T + \left(\alpha_{major} + \alpha_{minor}\right)^2 \frac{\sigma_{major}\sigma_{minor}T}{\sigma_{major} + \sigma_{minor}}$$

where the last term can be considered the bipolar thermal conductivity that increases exponentially with temperature as $e^{E_g/k_B T}$.

Reminder: for $p$-type holes are the major charge carriers
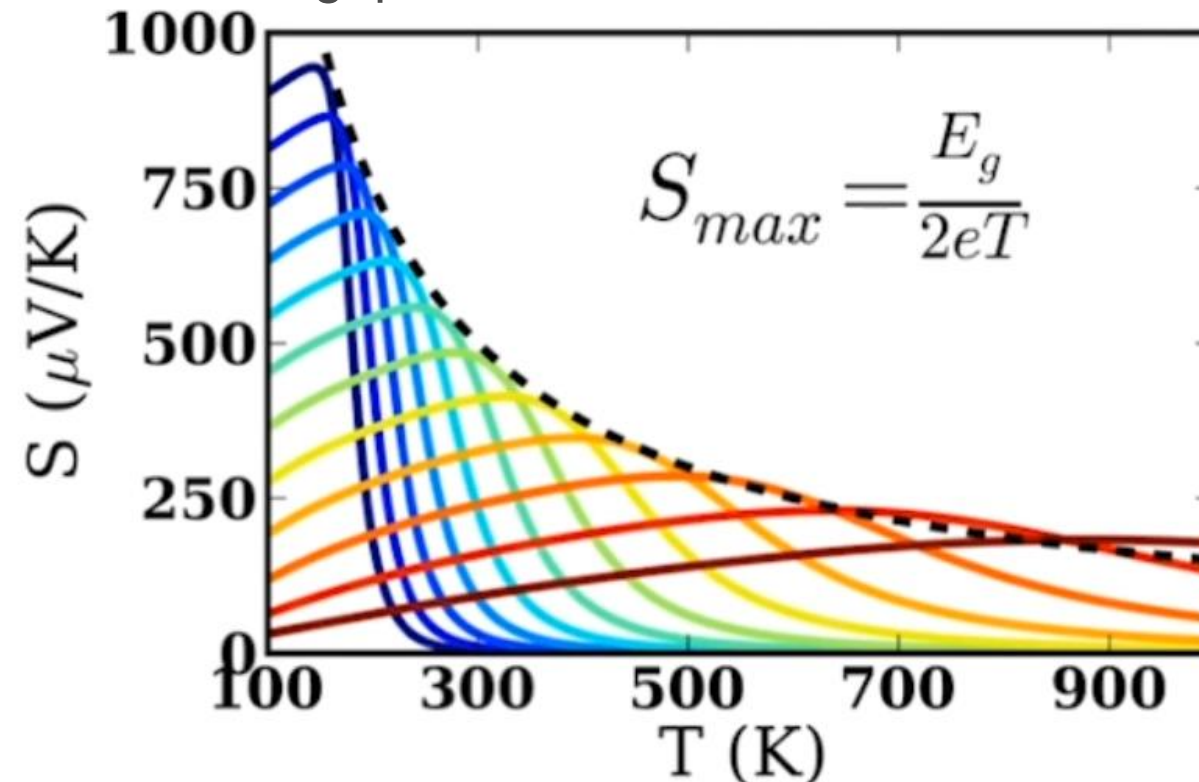for $n$-type electrons are the major charge carriers

Doping changes temperature dependence of $\alpha$ (from lightly doped in blue to heavily doped in red), but the maximum of $\alpha$ value is limited by $E_g$:[2]

$$E_g = 2e|\alpha_{\max}|T_{\max}$$

This equation can be reasonably accurate when both electrons and holes have similar weighted mobility. If one type of carriers exhibits higher weighted mobility, it will have a stronger influence and affect the estimation of band gap.
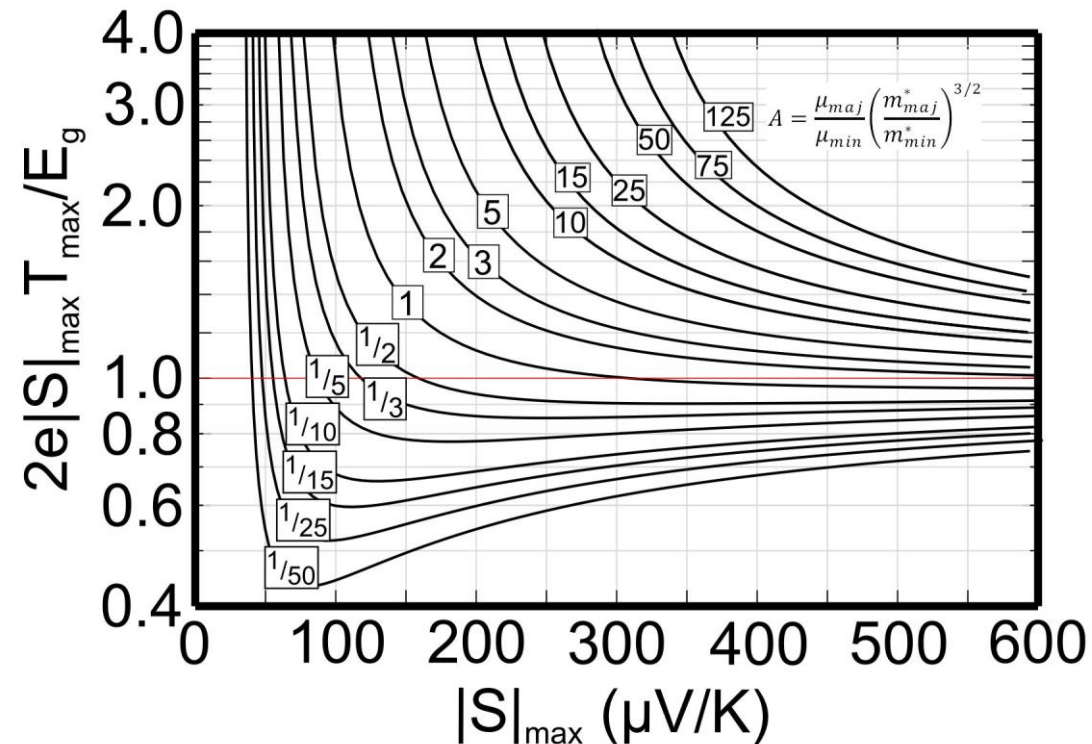
This can be corrected by using ratio of the weighted mobilities:[3]

$$A = \frac{\mu_{w,major}}{\mu_{w,minor}} = \frac{\mu_{major}}{\mu_{minor}} \left(\frac{m^*_{major}}{m^*_{minor}}\right)^{3/2}$$

The following figure can be used to estimate the error from the bandgap equation. When the Seebeck peak is greater than 150 µV/K this method for estimation of the bandgap at high temperature is likely to be accurate. For details see Refs. [2,3].

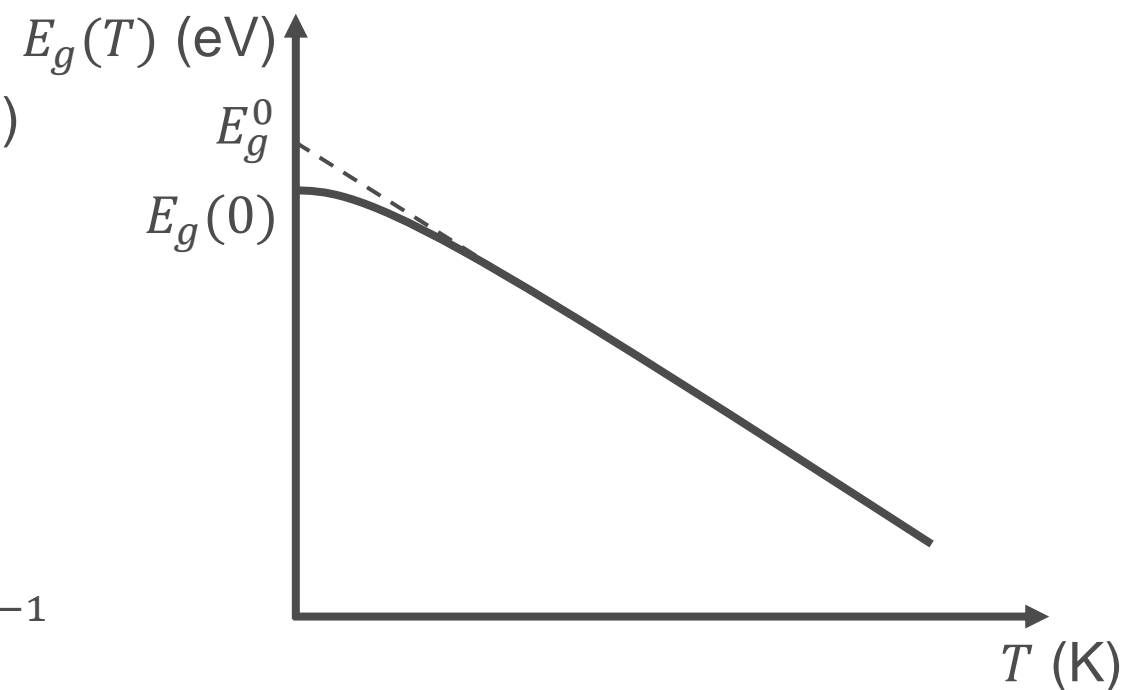# Intrinsic region in $\sigma$ and bandgap

$$\sigma = en\mu$$
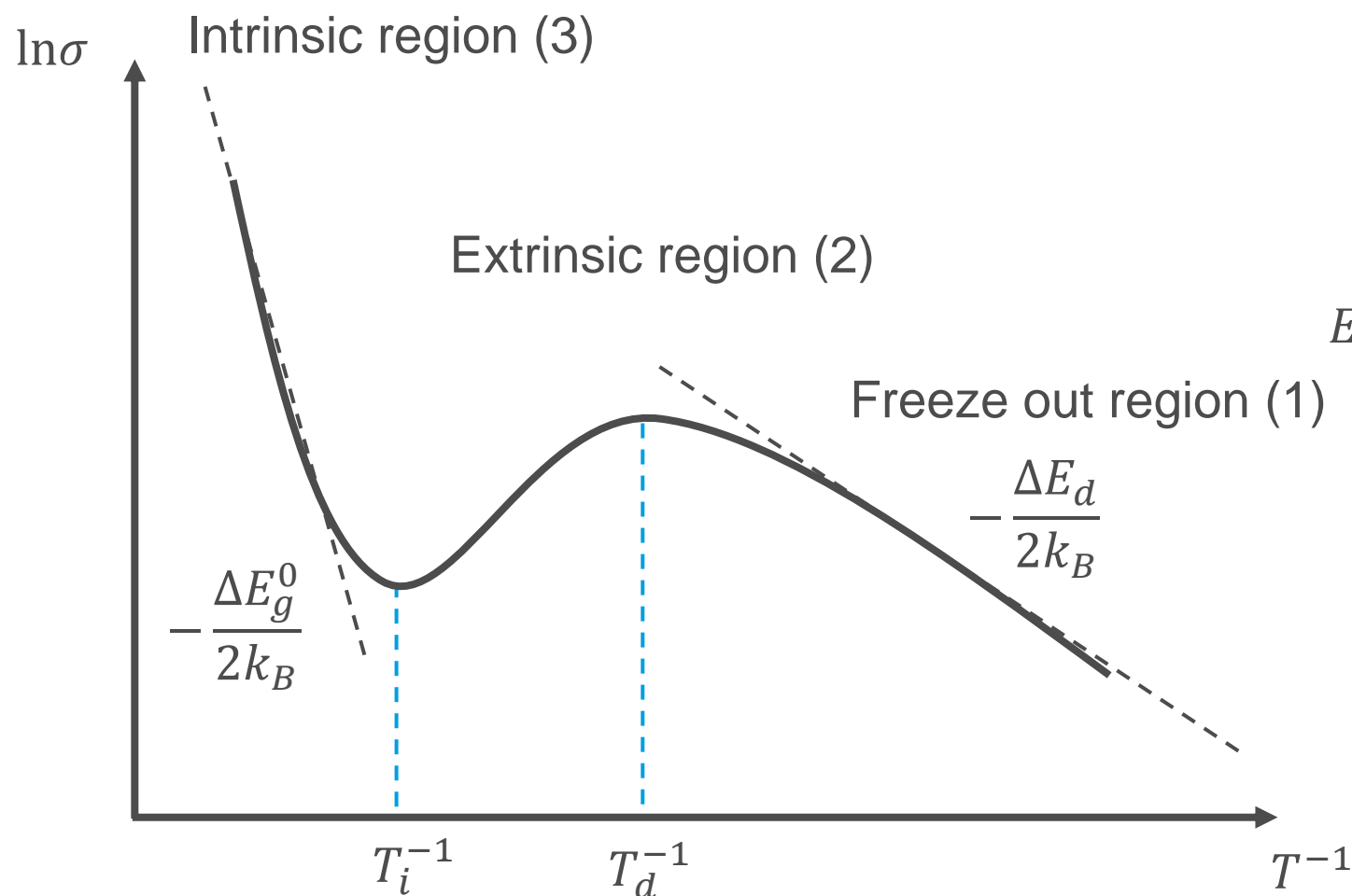
(1) $\sigma \propto T^{3/2+m} e^{-\Delta E_d/2k_B}$

(2) $\sigma \propto T^m$

(3) $\sigma \propto T^{3/2+m} e^{-\alpha_t/2k_B} e^{-\Delta E_g^0/2k_B}$

assuming $E_g(T) = E_g^0 + \alpha_t T$,

where $\alpha_t$ is thermal coefficient.

Intrinsic region (3)

Extrinsic region (2)

Freeze out region (1)

$-\dfrac{\Delta E_d}{2k_B}$

$-\dfrac{\Delta E_g^0}{2k_B}$

$\ln\sigma$

$T_i^{-1}$   $T_d^{-1}$   $T^{-1}$

$E_g(T)$ (eV)

$E_g^0$

$E_g(0)$

$T$ (K)

The absorption coefficient $\alpha$ is derived from the probability of transition from $E$ to $E'$, the occupied density of states at $E$ in the VB from which electrons are excited, and the unoccupied density of states in the CB at $E + h\upsilon$.

Near the band edges, the density of states can be approximated by a parabolic band, and $\alpha$ rises with the photon energy following $\alpha h\upsilon = A\sqrt{h\upsilon - E_g}$, where $A$ is the constant related to the electron and hole effective mass and refractive index.[4]
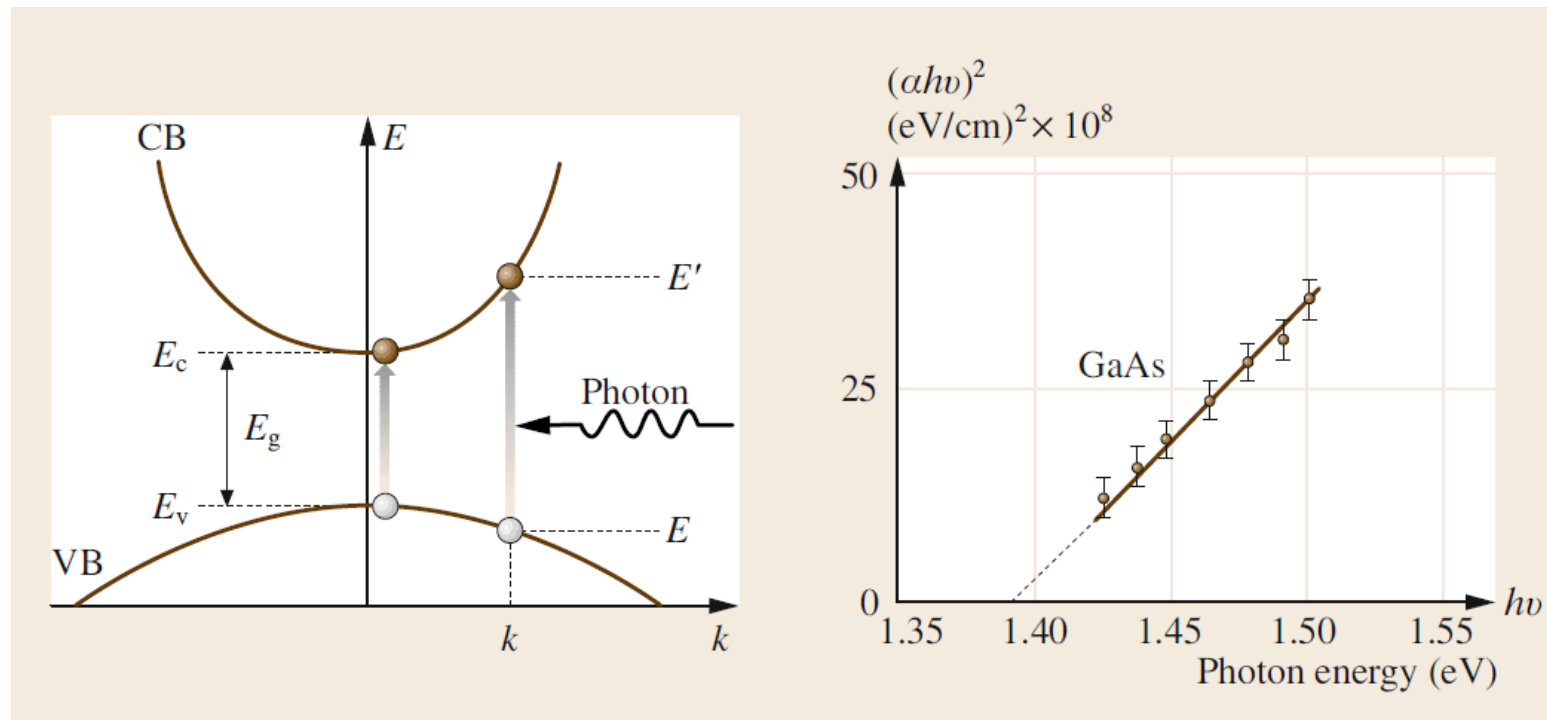
In indirect bandgap semiconductors, the photon absorption for photon energies near $E_g$ requires the absorption and emission of phonons during the absorption process (see Fig.). Thus, the absorption corresponds to a photon energy of $E + h\vartheta$, which represents the absorption of a phonon with energy $h\vartheta$. For the latter, $\alpha$ is proportional to $[h\upsilon - (E_g - h\vartheta)]^2$. Once the photon energy reaches $E + h\vartheta$, then the photon absorption process can also occur by phonon emission, for which the absorption coefficient is larger than that for phonon absorption.[4]
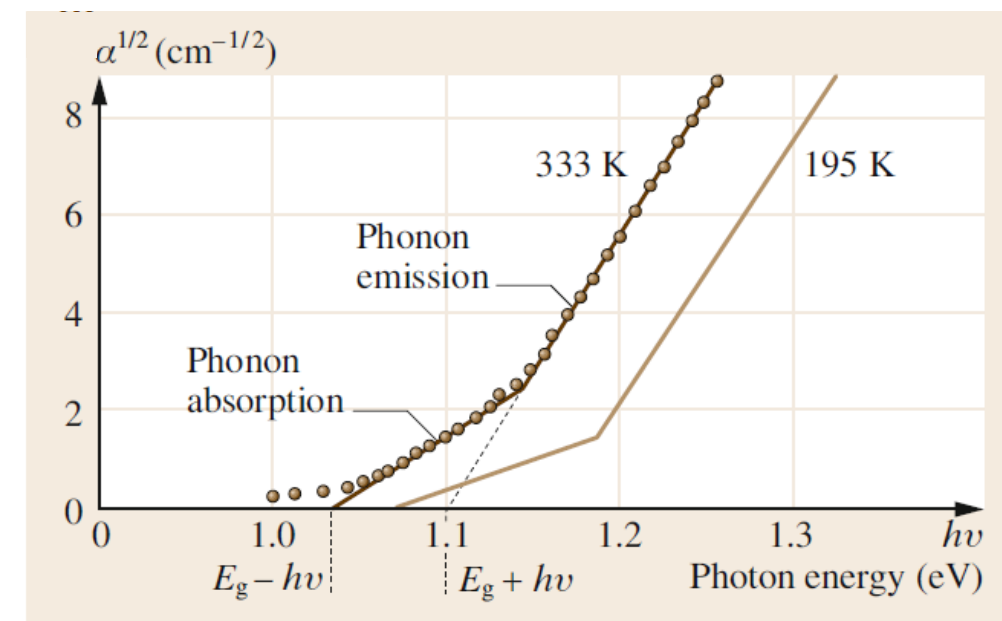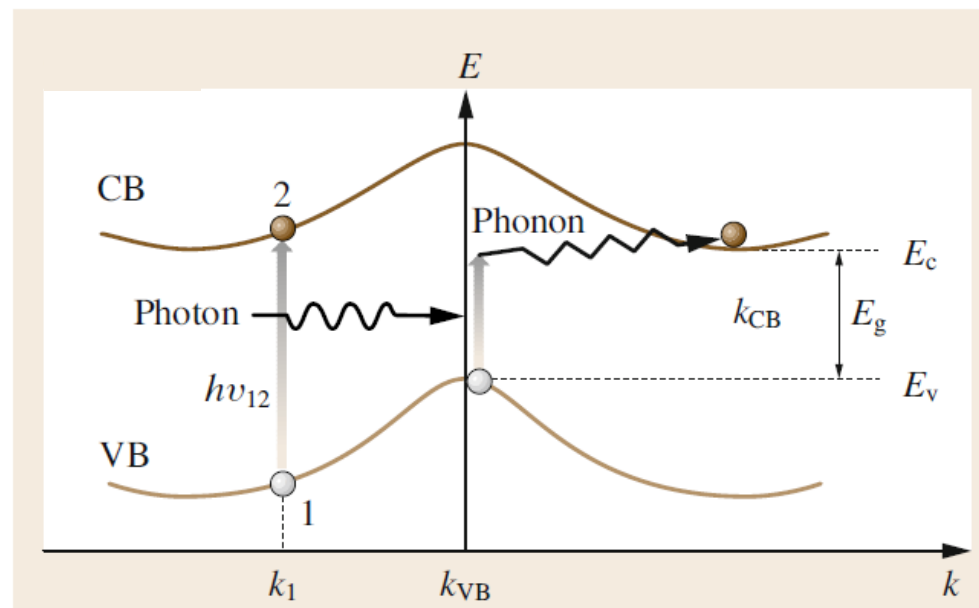
In degenerate semiconductors, the Fermi level $E_F$ is in a band, for example, in the CB for a degenerate *n*-type semiconductor. Electrons in the VB can only be excited to states above $E_F$ in the CB rather than to the bottom of the CB. The absorption coefficient then depends on the free-carrier concentration since the latter determines $E_F$. Fundamental absorption is then said to depend on band filling, and there is an apparent shift in the absorption edge, called the Burstein–Moss shift. Furthermore, in degenerate indirect semiconductors, the indirect transition may involve a non-phonon scattering process, such as impurity or electron-electron scattering, which can change the electron's wavevector $\vec{k}$. Thus, in degenerate indirect bandgap semiconductors, absorption can occur without phonon assistance and the absorption coefficient becomes $\alpha \propto \left[ h\upsilon - \left( E_g + \Delta E_F \right) \right]^2$, where $\Delta E_F$ is the energy depth of $E_F$ into the band measured from the band edge.[4]

Heavy doping of degenerate semiconductors normally leads to a phenomenon called bandgap narrowing and bandtailing. Bandtailing means that the band edges at $E_v$ and $E_c$ are no longer well-defined cut-off energies, and there are electronic states above $E_v$ and below $E_c$ where the density of states falls sharply away with energy from the band edges. Consider a degenerate direct bandgap *p*-type semiconductor. One can excite electrons from states below $E_F$ in the VB, where the band is nearly parabolic, to tail states below $E_c$, where the density of states decreases exponentially with energy into the bandgap, away from $E_c$. Such excitations lead to $\alpha$ depending exponentially on $h\upsilon$, a dependence that is called the Urbach rule, given by

$$\alpha = \alpha_0 e^{\frac{h\upsilon - E_0}{\Delta E}}$$

where $\alpha_0$ and $E_0$ are material-dependent constants, and $\Delta E$, called the Urbach width, is also a material dependent constant.[4]

Kubelka Munk theory derives a simple relation between the fraction of reflected light ($R$) and the absorption coefficient ($\alpha$):

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{\widetilde{K}}$$

where $R$ is the diffuse reflectance of the sample as referred to a non-absorbing standard, $\alpha$ is the molar absorption coefficient, $\widetilde{K}$ is the diffuse reflection coefficient (unknown parameter).[5] For particle sizes greater than the light wavelengths measured, the scattering coefficient is understood to be approximately independent of frequency.
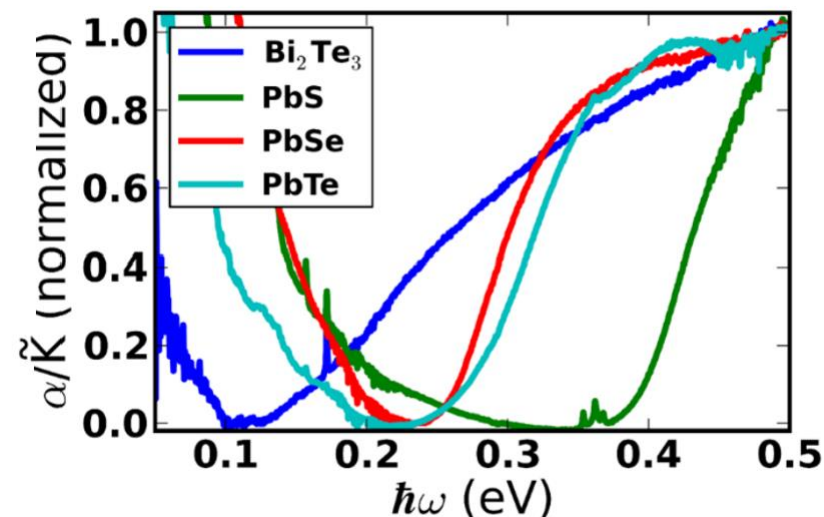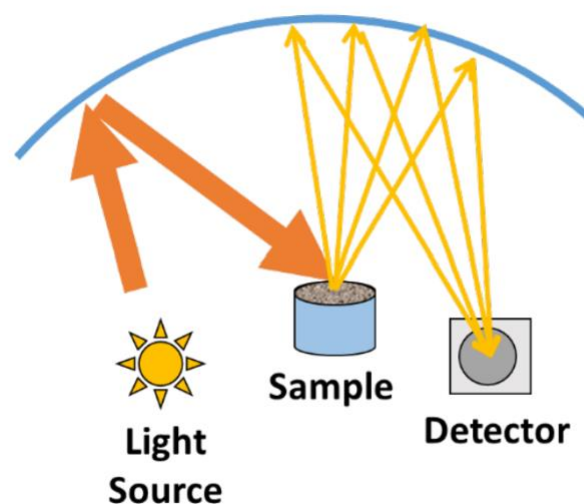
In summary. For direct transitions:

$$\alpha h\upsilon \propto \left(h\upsilon - E_g\right)^{1/2}$$

for $h\upsilon > E_g$ according to the Tauc method.[6,7] In some studies authors used the $\alpha^2$ vs. $h\upsilon$ plot for estimation of the direct bandgap. But both methods give similar results within the measurement uncertainty.

In the case of indirect transition:

$$\alpha h\upsilon \propto \left(h\upsilon - E_g\right)^{2}$$

Some works suggest $\alpha \propto \left(h\upsilon - E_g\right)^{2}$, but as was the case in direct gaps, the results do not change significantly.

Thus, optical bandgap, can be estimated using the Tauc method where $(\alpha h\upsilon)^n$ ($n = 2$ for direct transitions and $n = 1/2$ for indirect) plotted versus photon energy $h\upsilon$ and is extrapolated to zero (normalized) absorption. The zero is determined by either normalizing the sample to the minimum absorption coefficient value or by fitting and subtracting the free carrier absorption contribution: $\alpha_{FC} = \alpha(h\upsilon)^b + c$.

An example of Tauc plot is shown in the Figure below, where optical diffuse reflectance data plotted as the indirect bandgap transformation of the Kubelka Munk function for pure ZrNiSn. A linear fit (red dotted line) was used to estimate the band gap by extrapolating to zero absorption, indicating that the band gap is ~0.13 eV.
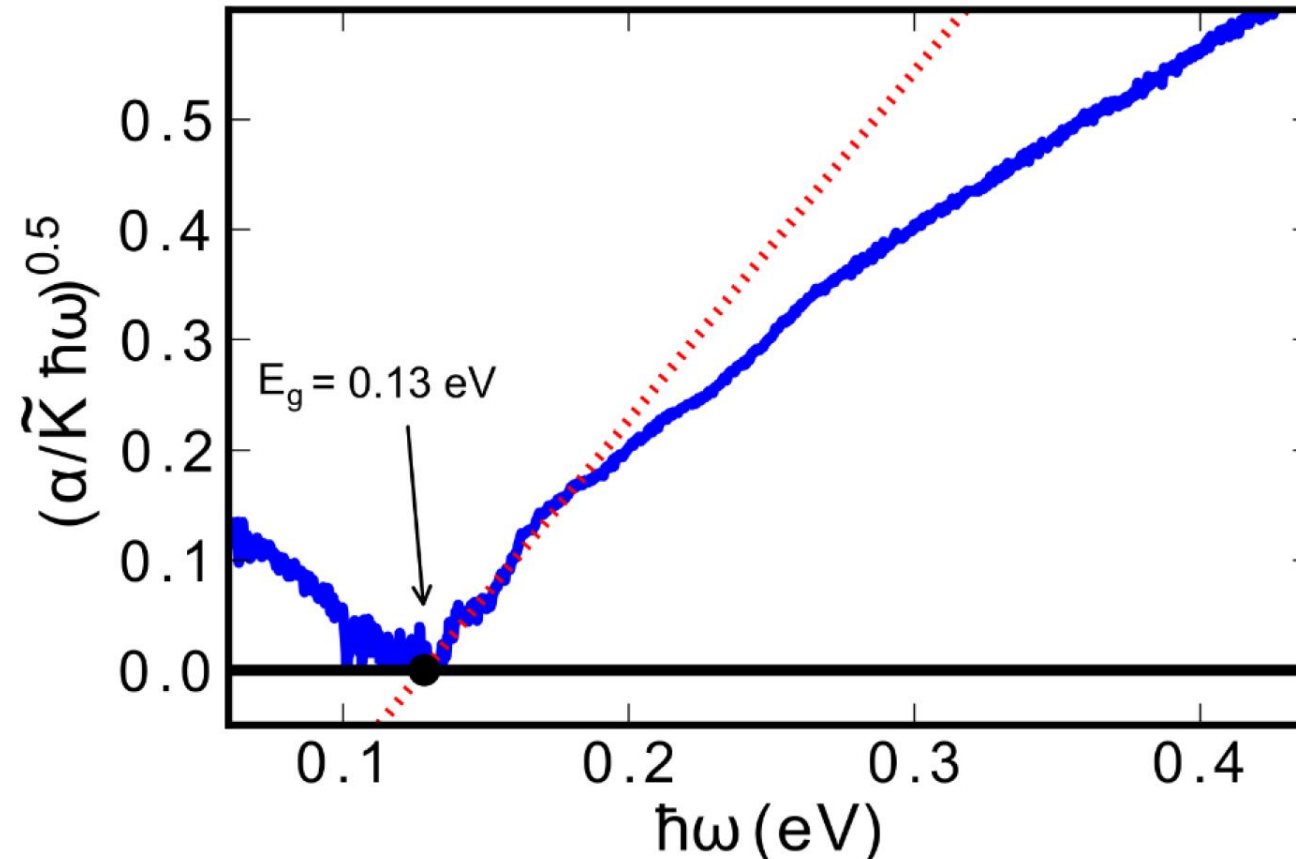


For more details and discussion on bandgap determination see Ref. [8].

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