IOP Concise Physics

Chapter 4

Electronic transport in semiconductors

4.1 Energy band theory

The treatment of charge transport in solids is derived from the free electron theory of metals. Because of the interaction between the electrons and the crystal lattice, the electrons are confined to states in specific bands of energy that are separated by energy gaps. Moreover, the probability that an energy state contains an electron is governed by quantum mechanics rather than classical statistics. It is found, at least near the edges of the energy bands, that the carriers behave like free electrons except that they must be assigned an effective mass m^* that is different from the free electron mass, m.

For our purposes, we may confine our attention to the two bands of highest energy, the conduction and valence bands. Electrons can take part in the conduction process only if they reside in energy states that are close to vacant states. This means that conduction in a metal is due to electrons having a narrow range of energies. There is a particular energy, the Fermi energy, at which there is a 50% probability of a state being filled. It is the states within a few kT of the Fermi level, then, that are responsible for the transport phenomena.

We are most interested in materials in which the Fermi level lies close to the edge of a band. If this is the conduction band, the carriers may be regarded as quasi-free electrons. On the other hand, if the Fermi level lies close to the upper edge of the next-lower band, the valence band, the electrons behave as if their effective mass is negative. It is convenient to regard these carriers in the valence band as if they have a positive mass and a positive charge, and they are commonly known as positive holes (or just as holes).

The density of electron states is much smaller near the band edge than it is deep within a band. Thus, when conduction is due to carriers near the band edges, the conductivity is much less than it is for a metal and the substance is known as a semiconductor. Semiconductors are called n-type or p-type according to whether the conduction is primarily due to electrons or holes. It is noted that n-type and p-type

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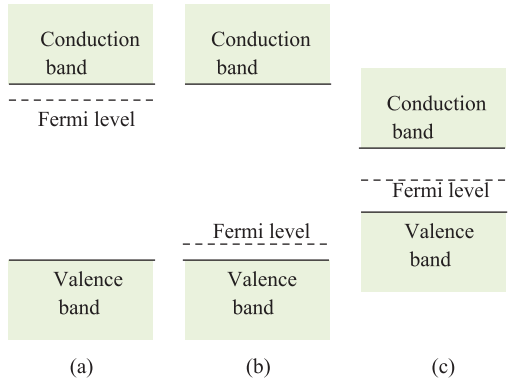

Figure 4.1. Energy band diagrams for semiconductors: (a) n-type, (b) p-type and (c) intrinsic.

semiconductors have negative and positive Seebeck coefficients respectively. Typical energy diagrams for n- and p-type semiconductors are shown in figure 4.1(a) and (b), respectively. Figure 4.1(c) shows the case of an intrinsic semiconductor with the Fermi level close to the middle of the energy gap.

For the time being we consider semiconductors in which the energy difference between the valence and conduction bands is large enough for only one type of carrier to be significant. The electrical conductivity and the Seebeck coefficient will then depend on the Fermi energy, as measured from the band edge, the effective mass, in so far as it determines the density of states in the band, and a quantity known as the carrier mobility, μ, which is defined as the drift speed of the carriers in unit electric field.

4.2 Mobility and effective mass

The energy diagrams in figure 4.1 do not show the whole picture. An electronic state is characterised not only by its energy but also by its wave vector. In the simplest case, the energy minimum occurs at zero wave vector. However, a minimum may also be found at a non-zero value for the wave vector, crystal symmetry requiring that similar minima are located at corresponding points in wave vector space. The material is then called a multi-valley conductor.

In the quasi-free electron theory, the density of electron states at an energy E is given by

$$g(E)\,\mathrm{d}E = \frac{4\pi(2m^*)^{3/2}E^{1/2}\,\mathrm{d}E}{h^3}, \tag{4.1}$$

where h is Planck's constant. This equation must be modified in an N_V-valley conductor by setting m^* equal to ${N_V}^{2/3}$ times its value for a single valley. The single-valley effective mass may exhibit directional dependence and is termed the inertial mass m_I to distinguish it from the density-of-states mass, m^*.

The mobility depends on the inertial effective mass and on the relaxation time associated with the scattering processes. It is assumed that any disturbance in the

carrier distribution will relax towards its equilibrium value with a characteristic time, τ, which it will be supposed is dependent on the energy, E, and may be written as $\tau_0 E^r$, where r depends on the scattering process. It seems that for many of the materials in which we are interested acoustic-mode lattice scattering is predominant, in which case r is equal to $-1/2$. This is in spite of the fact that the bonding may have an ionic as well as a covalent component.

4.3 Dependence of the transport properties on the Fermi energy

The density of charge carriers in any particular metal is more-or-less a fixed quantity but this is not so for a semiconductor. The carrier density and, indeed, the sign of the majority carriers can be controlled by the addition of impurities. Impurities that increase the electron concentration are called donors and those that increase the hole concentration are known as acceptors. An intrinsic semiconductor contains either no impurities or an equal number of donors and acceptors. In some materials, vacancies on lattice sites can act in the same way as foreign atoms. One of the effects of these impurities is to change the position of the Fermi level. We shall find it convenient to regard the Fermi energy, E_F, as the independent variable.

We make use of the Boltzmann equation that relates the disturbance in the electron distribution to the applied electric field and temperature gradient. It is supposed that this disturbance is small and that it relaxes towards the equilibrium distribution according to the equation

$$\frac{f(E) - f_0(E)}{\tau} = u\frac{\mathrm{d}f_0(E)}{\mathrm{d}E}\left[\frac{\mathrm{d}E_F}{\mathrm{d}x} + \frac{(E - E_F)}{T}\frac{\mathrm{d}T}{\mathrm{d}x}\right], \tag{4.2}$$

where u is the velocity of the carriers in the x direction and $f(E)$ is the Fermi distribution function that has the equilibrium value $f_0(E)$ given by

$$f_0(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}. \tag{4.3}$$

The transport properties can be found from the relations between the gradients of the electric potential and temperature, the electric current density, i, and the heat flux density, j. The expressions for the electric current and heat flux densities are

$$i = \mp\int_0^\infty euf(E)g(E)\,\mathrm{d}E, \tag{4.4}$$

and

$$j = \int_0^\infty u(E - E_F)f(E)g(E)\,\mathrm{d}E. \tag{4.5}$$

In equation (4.4) the upper sign is applicable when the carriers are electrons and the lower sign applies for hole conduction. In the latter case the energy is measured downwards from the band edge.

The electrical conductivity is found by setting the temperature gradient equal to zero, while the Seebeck coefficient and electronic thermal conductivity require the electric current to be zero. In solving these equations, it may be assumed that the disturbance in the distribution of the carriers is small enough that any alteration in u is much less than the equilibrium velocity. We also replace the disturbed distribution function $f(E)$ by $f(E) - f_0(E)$ since the electrical and thermal flows are zero in equilibrium.

It is convenient to express the transport coefficients in terms of integrals defined as

$$K_s = -\frac{2T}{3m^*}\int_0^\infty g(E)\tau_e E^{s+1}\frac{df_0(E)}{dE}\,dE. \tag{4.6}$$

This expression, in turn, may be written as

$$K_s = \frac{8\pi}{3}\left(\frac{2}{h^2}\right)^{3/2}(m^*)^{1/2}T\tau_0\left(s + r + \frac{3}{2}\right)(kT)^{s+r+3/2}F_{s+r+1/2}, \tag{4.7}$$

where

$$F_n(\xi) = \int_0^\infty \xi^n f_0(\xi)\,d\xi. \tag{4.8}$$

Here ξ is the reduced energy, E/kT. We shall also use the symbol η to represent the reduced Fermi energy, E_F/kT. The values of F are known as the Fermi–Dirac integrals.

It is found that the electronic parameters that appear in the figure of merit are

$$\sigma = \frac{e^2}{T}K_1, \tag{4.9}$$

$$\alpha = \pm\frac{1}{eT}\left(E_F - \frac{K_1}{K_0}\right), \tag{4.10}$$

and

$$\lambda_e = \frac{1}{T^2}\left(K_2 - \frac{K_1^2}{K_0}\right). \tag{4.11}$$

It must be remembered that the total thermal conductivity, λ, is the sum of the electronic component given by equation (4.11) and a lattice component, λ_L.

4.4 Degenerate and non-degenerate conductors

There are good approximations for the Fermi–Dirac integrals when the Fermi energy is either very much less than or very much greater than zero. If $E_F > 4kT$ the material is said to be degenerate and the metallic approximation is used. In this case

$$F_n(\eta) = \frac{\eta^{n+1}}{n+1} + n\eta^{n-1}\frac{\pi^2}{6} + n(n-1)(n-2)\eta^{n-3}\frac{7\pi^4}{360} + \cdots. \tag{4.12}$$

One must include as many terms as are needed for the parameter in question to have a non-zero value. Thus, the electrical conductivity requires only the first term so that

$$\sigma = \frac{8\pi}{3}\left(\frac{2}{h^2}\right)^{3/2} e^2 (m^*)^{1/2} \tau_0 E_F^{r+3/2}. \tag{4.13}$$

The electronic thermal conductivity needs the first two terms on the right-hand side of equation (4.12) to be included. Then it is found that

$$\frac{\lambda_e}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2. \tag{4.14}$$

For most metals the electronic thermal conductivity is much larger than the lattice contribution. Thus, equation (4.14) embodies the Wiedemann–Franz law which states that the ratio of the thermal conductivity to the electrical conductivity is the same for all metals, at any given temperature. The ratio $\lambda_e/\sigma T$ is known as the Lorenz number, L.

The same two terms in equation (4.12) are also needed for the Seebeck coefficient. It is found that

$$\alpha = \mp\frac{\pi^2}{3}\frac{k}{e}\frac{\left(r+\frac{3}{2}\right)}{\eta}. \tag{4.15}$$

It is clear that, as η becomes large, the Seebeck coefficient has a magnitude that is much less than k/e, which is consistent with the fact that most metals have values of α of the order of only a few $\mu V\ K^{-1}$.

We are actually much more interested in materials for which η is close to zero or negative. When η is less than -2 we may use the classical approximation in which the Femi–Dirac integrals become

$$F_n(\eta) = \exp(\eta)\Gamma(n+1). \tag{4.16}$$

The gamma function Γ is such that $\Gamma(n+1)$ is equal to $n\Gamma(n)$. When n is an integer, $\Gamma(n+1)$ is equal to $n!$ and $\Gamma(1/2)$ is equal to $\pi^{1/2}$. Thus, we can easily calculate the gamma function for both integral and half-integral values of n.

If we use the classical approximation the integrals K_s become

$$K_s = \frac{8\pi}{3}\left(\frac{2}{h^2}\right)^{3/2} (m^*)^{1/2} T\tau_0 (kT)^{s+r+3/2} \Gamma\left(s+r+\frac{5}{2}\right)\exp(\eta). \tag{4.17}$$

Then the Seebeck coefficient is

$$\alpha = \mp\frac{k}{e}\left[\eta - \left(r+\frac{5}{2}\right)\right]. \tag{4.18}$$

It will be seen that the Seebeck and Peltier coefficients are a measure of the total energy transported by the charge carriers weighted according to the scattering parameter, r. It is noted that the range for which this equation is valid covers Seebeck coefficients of greater magnitude than $4k/e$, if we suppose that r is $-1/2$.

Since k/e is 86.4 μV K^{-1}, this means that the magnitude of the Seebeck coefficient should exceed about 350 μV K^{-1} if classical statistics are to apply. For most of the thermoelectric materials that are used today, the Seebeck coefficient has a smaller value than this, so the classical condition cannot often be used, except as a gross approximation.

In the classical range the electrical conductivity is given by

$$\sigma = \frac{8\pi}{3}\left(\frac{2}{h^2}\right)^{3/2} e^2 (m^*)^{1/2} \tau_0 (kT)^{r+3/2} \Gamma\left(r + \frac{5}{2}\right) \exp(\eta). \tag{4.19}$$

It is common practice to express the electrical conductivity as

$$\sigma = ne\mu, \tag{4.20}$$

where n is the carrier concentration and μ is the mobility. The expression for the carrier concentration is

$$n = 2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} \exp(\eta), \tag{4.21}$$

where the quantity $2(2\pi m^* kT/h^2)^{3/2}$ is known as the effective density of states. If we substitute the carrier concentration in equation (4.19) we find that the mobility is given by

$$\mu = \frac{4}{3\pi^{1/2}} \Gamma\left(r + \frac{5}{2}\right) \frac{e\tau_0 (kT)^r}{m^*}. \tag{4.22}$$

It is noteworthy that the mobility does not depend directly on the Fermi energy in the classical region.

The expression for the Lorenz number in a non-degenerate conductor is

$$L = \left(\frac{k}{e}\right)^2 \left(r + \frac{5}{2}\right), \tag{4.23}$$

which is of the same order as the value given by equation (4.14) for a metal, though somewhat smaller.

Although it is better to use the classical rather than the degenerate approximation for most thermoelectric materials, neither is really applicable. Thus, one must generally use the full expressions for the Fermi–Dirac integrals, F_n. Tables of these integrals for integral and half-integral values of n may be found elsewhere [1–3].

4.5 Optimising the Seebeck coefficient

If we were restricted to metallic conductors the figure of merit would rise continuously with the Seebeck coefficient. This is because the ratio of electrical to thermal conductivity would always have the same value. However, in reality, as the carrier concentration falls, the thermal conductivity becomes greater than the value expected from the Wiedemann–Franz law. This is because of the influence of heat conduction by the lattice. We shall discuss the lattice conductivity in the next chapter

but here we take note of its existence since it affects the preferred value for the Seebeck coefficient.

If the lattice conductivity were very large compared with the electronic thermal conductivity, as it is for many semiconductors, the figure of merit would be proportional to a quantity known as the power factor, which is defined as $\alpha^2\sigma$. As shown in figure 4.2, the power factor falls off slowly as the Fermi level moves into the band and the Seebeck coefficient decreases. It also falls rapidly as the Fermi level moves into the band gap due to decrease in the carrier concentration. The maximum power factor occurs when the Fermi level is very close to the band edge.

When we take account of the lattice conductivity in calculating the figure of merit it is clear that the optimum Fermi energy will become more negative than that for the maximum power factor. This is apparent from the curves shown in figure 4.3. Here the dimensionless figure of merit is plotted against the reduced Fermi energy for different values of $(zT)_{\max}$. As $(zT)_{\max}$ becomes larger, so also does the optimum Fermi level move further into the energy gap. This means that the optimum Seebeck coefficient becomes of greater magnitude, as shown in figure 4.4.

The value of zT for any particular Fermi energy depends on the carrier mobility, the density-of-states effective mass and the lattice thermal conductivity. These three parameters can be embodied in a single quantity β which is given by [4]

$$\beta = \left(\frac{k}{e}\right)^2 \frac{\sigma_0 T}{\lambda_L}, \tag{4.24}$$

where

$$\sigma_0 = 2e\mu\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2}. \tag{4.25}$$

It may be noted that $(zT)_{\max}$ reaches a value of about 1 when β is equal to 0.4.

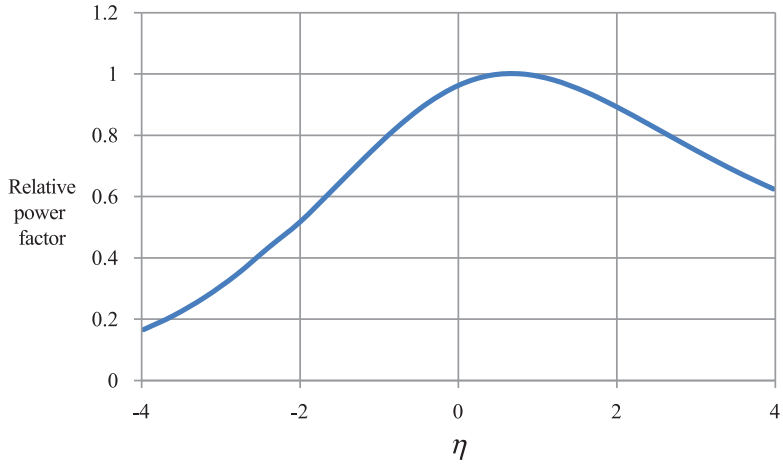

Figure 4.2. Plot of power factor against reduced Fermi energy for $r = -1/2$. The power factor is expressed as a fraction of its maximum value.

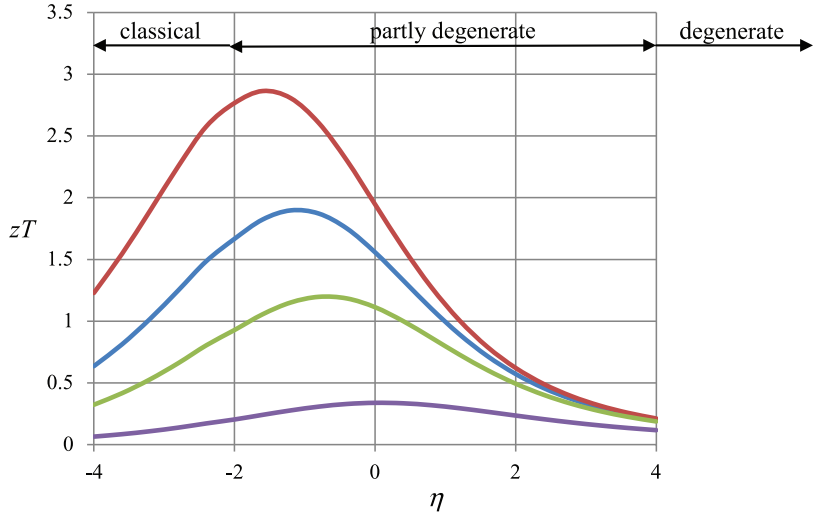

Figure 4.3. Plots of zT against reduced Fermi energy for various values of $(zT)_{max}$.

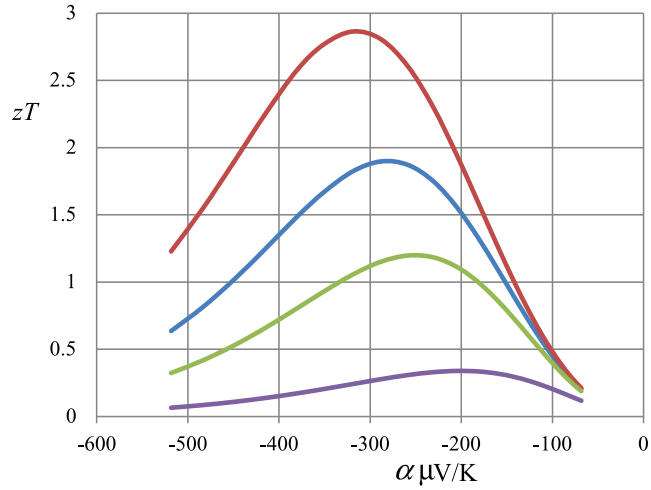

Figure 4.4. Plots of zT against Seebeck coefficient for various values of $(zT)_{max}$. The graphs are for n-type material but would be identical for p-type material apart from the sign of the Seebeck coefficient.

4.6 Bipolar conduction

As the temperature is raised it becomes possible for electrons to be thermally activated from the valence band to the conduction band. The concentration of electron–hole pairs depends on the size of the energy gap, E_g. Provided that E_g is small enough, these carriers may become more numerous than those due to donor or acceptor impurities. With increase of temperature the conductor passes from the extrinsic region into the region of mixed conduction and finally becomes intrinsic. The presence of both electrons and holes in the same conductor can have a profound effect on the thermoelectric properties.

There will be contributions i_n and i_p to the electric current density from the electrons and holes respectively. These contributions satisfy the equation

$$i_{n,p} = \sigma_{n,p}\left(\frac{dV}{dx} - \alpha_{n,p}\frac{dT}{dx}\right), \tag{4.26}$$

where $\sigma_{n,p}$ and $\alpha_{n,p}$ are the partial conductivities and Seebeck coefficients. The electrical conductivity is found by setting dT/dx equal to zero and, not surprisingly, it has the value

$$\sigma = \sigma_n + \sigma_p. \tag{4.27}$$

The Seebeck coefficient is obtained when we set $i_n + i_p$ equal to zero, whence

$$\alpha = \frac{\alpha_n\sigma_n + \alpha_p\sigma_p}{\sigma_n + \sigma_p}. \tag{4.28}$$

This equation tells us that the overall Seebeck coefficient is a weighted average of the partial Seebeck coefficients, which will be of opposite sign. This means that the Seebeck coefficient of a mixed or intrinsic semiconductor is likely to be very small.

There is a remarkable result if we determine the electronic thermal conductivity when both types of carrier are present. Then the heat flux densities for the two carriers are given by

$$j_{n,p} = \alpha_{n,p}Ti_{n,p} - \lambda_{n,p}\frac{dT}{dx}. \tag{4.29}$$

The thermal conductivity is defined for the condition of zero total electric current. Thus,

$$\lambda_e = \lambda_n + \lambda_p + \frac{\sigma_n\sigma_p}{\sigma_n + \sigma_p}(\alpha_n - \alpha_p)^2T. \tag{4.30}$$

The third term on the right-hand side of equation (4.30) is the contribution to the thermal conductivity from the bipolar effect and may be an order of magnitude greater than the partial conductivities of the single carriers [5].

It is concluded that mixed conduction should be avoided in thermoelectric materials since it not only reduces the Seebeck coefficient but also increases the thermal conductivity.

4.7 Band engineering and nanostructure effects

Here we discuss some of the ways in which the power factor for a given Fermi energy might be improved.

It is evident from equation (4.10) and, particularly, its classical form, equation (4.18), that the Seebeck coefficient has a potential energy component and a contribution from the kinetic energy. The kinetic energy component is weighted according to the form of scattering for the charge carriers. In most high mobility semiconductors the scattering parameter, r, is equal to $-1/2$ and the relaxation time is

greatest for the carriers of the lowest energy. On the other hand, if ionized-impurity scattering becomes dominant, r rises to +3/2, and the high-energy carriers are the least strongly scattered. There is then a substantial rise in the kinetic energy that is transported by the charge carriers. Of course, this is accompanied by a decrease in the mobility but, as shown by Ioffe [6], the overall effect could be advantageous. In practice it appears that this effect has never been used to advantage. It would seem to be most beneficial in semiconductors with narrow energy gaps since then the potential energy of either type of carrier cannot be equal to more than about half the gap.

Another way of improving the power factor involves the introduction of additional energy states. This may come about through the addition of specific impurities that give rise to states above the edge of the main band. There is also the possibility of selecting materials in which there are additional bands with edges not too far removed from the edge of the original band.

It was proposed by Hicks and Dresselhaus [7] that it might be advantageous to make use of nanostructured semiconductors. Nanostructures can be two-dimensional in the form of thin sheets, one-dimensional as nanowires or nanotubes, or even zero-dimensional as nanodots. In all cases, the band structure becomes modified.

Following the theory of Hicks and Dresselhaus we consider the case of a conduction band with a parabolic density of states. The simplest situation is that of a two-dimensional sheet of thickness d that is of the order of a few interatomic spacings. This means that the dispersion relation is changed from

$$E = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z}, \tag{4.31}$$

to

$$E = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 \pi^2}{2m_z d^2}. \tag{4.32}$$

We introduce a quantity η^* which is related to the reduced Fermi energy η by the relation

$$\eta^* = \eta - \frac{\hbar^2 \pi^2}{2m_x d^2 kT}. \tag{4.33}$$

In terms of this quantity the Seebeck coefficient is given by

$$\alpha = -\frac{k}{e}\left(\frac{2F_1}{F_0} - \eta^*\right), \tag{4.34}$$

where the relaxation time has been supposed to be constant. The electrical conductivity is

$$\sigma = \frac{1}{2\pi d}\left(\frac{2kT}{\hbar^2}\right)(m_x m_y)^{1/2} F_0 e\mu_x. \tag{4.35}$$

When the expression for the electronic thermal conductivity is also included, the dimensionless figure of merit becomes

$$zT = \frac{\left(2\frac{F_1}{F_0} - \eta^*\right)^2 F_0}{\frac{1}{\beta^*} + 3F_2 - 4\frac{F_1^2}{F_0}}. \tag{4.36}$$

where β^* is given by

$$\beta^* = \frac{1}{2\pi d}\left(\frac{2kT}{\hbar^2}\right)(m_x m_y)^{1/2}\frac{k^2 T\mu_x}{e\lambda_L}. \tag{4.37}$$

Equation (4.36) does not become significantly different from its three-dimensional equivalent until d is very small. Eventually, when d is small enough, the effective density of states rises and this allows zT to become greater.

Hicks and Dresselhaus applied their ideas to the most widely used thermoelectric material, bismuth telluride. They assumed a rather moderate maximum value of zT equal to 0.52 for the bulk compound and ignored any possible change in the lattice conductivity. They predicted that zT would become substantially greater than unity for specimens of less than 5 nm thickness. An even greater improvement would be expected for one-dimensional materials and quantum dots and similar behaviour has been predicted for other substances.

In the event, it seems that there are very few instances where it can be claimed that the electronic properties have been enhanced by adopting nanostructures. This is possibly due to the difficulty in dealing with materials that have a sufficiently small thickness. Nevertheless, there are numerous examples of materials that have been improved through incorporating nanostructures but this has usually been attributed to a reduction in the lattice conductivity.

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