

## Optimum band gap of a thermoelectric material

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Transport properties of direct-gap semiconductors are calculated in order to find the best thermoelectrics. Previous calculations on semiconductors with indirect band gaps found that the best thermoelectrics had gaps equal to  $nk_B T$ , where  $n = 6 - 10$  and  $T$  is the operating temperature of the thermoelectric device. Here we report similar calculations on direct-gap materials. We find that the optimum gap is always greater than  $6k_B T$ , but can be much larger depending on the specific mechanism of electron scattering.

### I. INTRODUCTION

Thermoelectric devices are usually made from semiconductors.<sup>1</sup> The best performance is found with materials whose energy gap, between electron and holes, is about  $10k_B T$ , where  $T$  is the operating temperature of the device and  $k_B$  is the Boltzmann constant. This empirical rule suggests that low temperature thermoelectric refrigerators should be made from semiconductors of small energy gap. Here we model the efficiency of narrow-gap semiconductors which have direct gap.

Chasmar and Stratton<sup>2</sup> (CS) first investigated the optimum gap of a thermoelectric semiconductor. Their model was valid for indirect gaps. They found that the best gap was about  $6k_B T$ . Later Mahan<sup>3</sup> did a similar analysis and found  $10k_B T$  for indirect-gap materials. Most narrow-gap semiconductors have direct gaps, and the present analysis is intended to investigate this case. For indirect gaps, neither the effective masses nor the dielectric functions are strong functions of the gap. By contrast, in direct-gap materials all of the transport parameters, such as effective masses, dielectric screening, and band nonparabolicity, depend strongly upon energy gap.<sup>4,5</sup> The present analysis is very different in detail from the previous calculations.

To quantify the quality of different materials for thermoelectric applications, we need to assign a number to each material. This number is the thermoelectric figure of merit  $Z$  defined as<sup>1</sup>

$$Z = \frac{S^2 \sigma}{\kappa} . \quad (1)$$

Here  $\sigma$  is the electrical conductivity,  $S$  the Seebeck coefficient, and  $\kappa$  the thermal conductivity. If we are trying to pump heat from a cooler region to a hotter one, we need high pumping efficiency (high  $S$ ), low production of heat through Joule heating (high  $\sigma$ ), and low backwards conduction of heat (low  $\kappa$ ).  $Z$  has units of inverse temperature, so it is generally quoted as  $ZT$ , with  $T$  the absolute temperature. At present, bismuth telluride alloys have the highest value, with  $ZT \approx 1$  at room temperature.

To obtain the figure of merit of a given material, we need to calculate the transport coefficients that appear in Eq. (1). In semiconductors, this has often been studied during the past 50 years, resulting in a good understanding of their properties.<sup>4,6-8</sup> We want to use this knowledge to search materials for improved thermoelectrics.

A calculation of transport coefficients in semiconductors can be characterized by specifying the band structure, the scattering mechanisms, and the density of conduction electrons or holes. After the pioneering work by Ioffe,<sup>9</sup> there have been many attempts to model  $ZT$  on different levels of approximation. CS (Ref. 2) did a careful analysis considering parabolic bands and included the scattering in the relaxation time approximation; they found that  $6k_B T$  is the optimum gap. They assumed Maxwell-Boltzmann statistics for the electron gas. A similar calculation by Mahan<sup>3</sup> also considered a semiconductor with parabolic valence and conduction bands in the relaxation time approximation. He found that a value of the gap of  $10k_B T$  is more realistic in both the degenerate and the classical regimes. Both values  $6k_B T$  and  $10k_B T$  are pointing to the family of narrow-gap semiconductors, a family where most of its components are direct gap materials and therefore their bands are strongly nonparabolic.

In this work, we include the nonparabolicity of the bands using  $\mathbf{k} \cdot \mathbf{p}$  theory, in a two band Kane model.<sup>10</sup> Section II A is a brief description of this model. We use the classical Boltzmann equation to describe the effect of external fields on the electron system. Narrow band gap semiconductors are made of elements with a large electronegativity difference. Therefore the polar optical mode scattering is one of the most important scattering mechanisms to be considered in our calculation. In semiconductors, the energy of the optical phonons is comparable to the electronic energy scale, and scattering of an electron with polar optical modes will take the electron out of its energy shell. This makes the relaxation time approximation inappropriate for our purpose. We use the iteration method first reported by Rode<sup>11</sup> to solve the Boltzmann equation. The most important effect as-

sociated with the nonparabolicity of the bands is the dependence of the effective mass on the value of the energy gap. As a result, the dependence of the scattering mechanism on the effective mass plays an important role in our analysis. We use two of the most important scattering mechanisms in these materials that show different dependence on the effective mass. These mechanisms are polar optical modes and ionized impurity scattering, and their respective scattering rates are discussed in Sec. II C. We calculate the integrals involved in the calculation of the transport coefficients (see Sec. II D) numerically, to avoid assumptions on the degeneracy of the electron system. In this work we will not model the lattice thermal conductivity and it will be included as a parameter in our calculations.

We found that  $ZT$  is maximum when the chemical potential is around the bottom of the conduction band. The behavior of  $ZT$  as a function of the band gap  $E_G$  has two regimes. For  $E_G \ll k_B T$ ,  $ZT$  decreases as  $E_G$  decreases. The system cannot satisfy both requirements: to have the chemical potential near the bottom of the band and at the same time to avoid the existence of holes as minority carriers—a well known undesired effect. For  $E_G \gg k_B T$ ,  $ZT$  is flat without dependence on the value of the gap. The figure of merit depends only on the parameters of one band through the  $B$  parameter of CS.<sup>2</sup> We will give a definition of  $B$  in Sec. II D. However, if the band structure of the system is nonparabolic, the effective mass is changed as we are changing the band gap, and therefore the  $B$  parameter is changed. In this regime, the behavior of  $ZT$  depends on the behavior of  $B$  with the effective mass, as we will describe when presenting our results.

## II. MODEL FOR A NARROW-GAP SEMICONDUCTOR

The low field transport coefficients that enter the definition of  $Z$  are the response function of the system to a small electric field or temperature gradient. These excitations produce a particle current, defined as

$$j_z^{(i)} = \frac{1}{4\pi^3} \int d\mathbf{k} v_{\mathbf{k}z}^{(i)} f_{\mathbf{k}}^{(i)}, \quad (2)$$

and heat current given by

$$j_{Qz}^{(i)} = \frac{1}{4\pi^3} \int d\mathbf{k} v_{\mathbf{k}z}^{(i)} (\varepsilon_{\mathbf{k}}^{(i)} - \mu) f_{\mathbf{k}}^{(i)}, \quad (3)$$

where  $i = e, h$  for electrons and holes respectively,  $\varepsilon_{\mathbf{k}}^{(i)}$  is the band dispersion relation of electrons or holes, and  $v_{\mathbf{k}z}^{(i)} = 1/\hbar \partial \varepsilon_{\mathbf{k}}^{(i)} / \partial k_z$  is the pertinent group velocity. The distribution of electrons or holes  $f_{\mathbf{k}}^{(i)}$  in an electric field or temperature gradient is the quantity calculated as the solution of the Boltzmann equation. The total electric and heat currents are then given by

$$J_z = e(j_z^{(e)} - j_z^{(h)}), \quad (4)$$

$$J_{Qz} = j_{Qz}^{(e)} + j_{Qz}^{(h)}, \quad (5)$$

where  $e$  is the electron charge. In the following subsections we will describe in detail each ingredient for the calculation of these quantities and derive thereafter the transport coefficients of the model material.

### A. Band structure

As we mentioned in the Introduction we will use the two band Kane model<sup>10</sup> to describe the bands near the  $\Gamma$  point of the Brillouin zone of our model semiconductor. This description has been used successfully to describe real materials such as InSb, HgTe, CdSe, and many others.<sup>5</sup> The dispersion relation of the bands is given by the equation

$$\frac{\hbar^2 k^2}{2m^*} = \varepsilon_k \left( 1 + \frac{\varepsilon_k}{E_G} \right) \equiv \gamma(\varepsilon_k), \quad (6)$$

where  $m^*$  is the effective mass at the band edge and  $E_G$  the band gap. This dispersion relation is a good approximation when the spin-orbit splitting is either much greater or much less than the band gap  $E_G$ .<sup>12</sup> From this equation we can calculate the density of states

$$\rho(\varepsilon) = \frac{2^{1/2} m^{*3/2}}{\pi^2 \hbar^3} \gamma'(\varepsilon) \gamma^{1/2}(\varepsilon), \quad (7)$$

where  $\gamma'(\varepsilon) = d\gamma(\varepsilon)/d\varepsilon$ , and the group velocity of the electrons or holes

$$v(\varepsilon) = \left( \frac{2}{m^*} \right)^{1/2} \frac{\gamma^{1/2}(\varepsilon)}{\gamma'(\varepsilon)}. \quad (8)$$

The  $\mathbf{k} \cdot \mathbf{p}$  theory just described allows us to know the dispersion relation of the material given the experimental values of the effective mass  $m^*$  and the band gap  $E_G$ . As we will show in our results, regarding the thermoelectric properties of the material the most important effect of the nonparabolicity is not the change in shape of the energy bands, which is only important far from the band edge, but the variation of the effective mass with the band gap. This dependence can be parametrized as<sup>13</sup>

$$m^* = \frac{3\hbar^2}{4P^2} E_G \quad (9)$$

within very good approximation. Here  $P$  represents the Kane matrix element.

### B. Boltzmann equation

During the past 50 years the classical Boltzmann equation has been used to describe the effect of external fields in solids. Although a more formally justified description should be given using the quantum Boltzmann equation,<sup>14</sup> for the calculation of low field dc transport coefficients the classical equation gives results in very good agreement with the experiments.<sup>4,5</sup>

We will only show here the form of the Boltzmann equation that we used in our calculation. The derivation of this form is too long to be presented here, and can

be found in detail in Ref. 4. The classical Boltzmann equation reduces to the following two equations:

$$\gamma'(\varepsilon) L_c[\phi_1] = 1 \quad (10)$$

and

$$\gamma'(\varepsilon) L_c[\phi_2] = \varepsilon - \mu, \quad (11)$$

where we have used

$$f_{\mathbf{k}} = f_0(\varepsilon_{\mathbf{k}}) + x \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{\hbar k}{m^*} \left[ eE\phi_1(\varepsilon_{\mathbf{k}}) - \frac{\nabla T}{T}\phi_2(\varepsilon_{\mathbf{k}}) \right], \quad (12)$$

$f_0$  is the Fermi function,  $x$  is the cosine of the angle between the electric field  $E$  or the thermal gradient (we assume both are parallel) and the wave vector  $\mathbf{k}$ , and  $L_c$  is the collision operator given by

$$L_c[\phi] = \frac{V_c}{(2\pi)^3} \int d\mathbf{k} S(\mathbf{k}, \mathbf{k}') \frac{1 - f_0(\varepsilon_{\mathbf{k}'})}{1 - f_0(\varepsilon_{\mathbf{k}})} \times \left[ \phi(\varepsilon_{\mathbf{k}}) - X \frac{k'}{k} \phi(\varepsilon_{\mathbf{k}'}) \right]. \quad (13)$$

In this definition of the collision operator,  $X$  is the cosine of the angle between  $\mathbf{k}$  and  $\mathbf{k}'$  and  $S(\mathbf{k}, \mathbf{k}')$  is the differential scattering rate for an electron in the state characterized by  $\mathbf{k}$  to make a transition into the state characterized by  $\mathbf{k}'$ . These scattering rates will be discussed in the next section. We will solve Eqs. (10) and (11) by the iteration method first described by Rode.<sup>11</sup> In the case of elastic scattering, it gives the same result as the relaxation time approximation, but it also works very well in the case of inelastic scattering, where the relaxation time approximation fails.

### C. Scattering mechanisms

As mentioned in the preceding section, the scattering mechanisms are included in this formalism through the differential scattering rate  $S(\mathbf{k}, \mathbf{k}')$ . We consider here the scattering of electrons with ionized impurities (II) and polar optical modes (POP). These are good representatives of the two different classes of scattering, i.e., elastic and inelastic, and they have different dependence on the effective mass. We need the last property to show different behavior of  $ZT$  for large band gap later in this work.

Let us present first the ionized impurities scattering. It comes from the screened Coulomb interaction of an impurity of electric charge  $Z_{II}e$  with the carriers. We consider the simplest possible screening, represented by the Thomas-Fermi approximation with characteristic wave vector given by

$$q_{if}^2 = \frac{e^2}{\epsilon_s} \int \frac{k^2 dk}{\pi^2} \left( -\frac{\partial f_0}{\partial \varepsilon} \right), \quad (14)$$

where  $\epsilon_s$  is the static permittivity of the material. The differential scattering rate due to ionized impurities is

$$S_{II}(\mathbf{k}, \mathbf{k}') = \frac{2\pi N_i Z_{II}^2 e^4}{V_c \hbar \epsilon_s^2} \frac{O(k, k', X)}{[k^2 + k'^2 - 2kk'X + q_{if}^2]^2} \times \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}). \quad (15)$$

In this equation, the function  $O$  is the overlap integral between the wave functions describing the state with impulse  $\mathbf{k}$  and the one corresponding to  $\mathbf{k}'$ . We have  $O = 1$  for parabolic bands. This equation assumes random distribution of impurities with concentration  $N_i$ . After replacing this differential scattering rate in the collision operator given in Eq. (13), the latter has the simple form

$$L_c[\phi] = S_{II}(\varepsilon) \phi(\varepsilon), \quad (16)$$

where the function  $S_{II}(\varepsilon)$  is given by

$$S_{II}(\varepsilon) = \frac{m^* N_i Z_{II}^2 e^4}{8\pi \hbar^3 \epsilon_s^2} \frac{\gamma'(\varepsilon)}{k^3} \int_{-1}^1 dX \frac{(1-X)O(k, k', X)}{\left[1 - X + \frac{q_{if}^2}{2k^2}\right]^2}. \quad (17)$$

In this case, the solution of the Boltzmann equation given in Eqs. (10) and (11) is very simple, with the relaxation time given by

$$\tau_{II}(\varepsilon) = S_{II}(\varepsilon)^{-1} = \gamma'(\varepsilon)\phi_1(\varepsilon). \quad (18)$$

The reason for this is that ionized impurity scattering is elastic, that is, the energy of the electron is the same before and after the collision. The situation is different in scattering with polar optical modes that we are going to discuss next.

For polar optical modes we will assume that the optical phonon branch has an energy  $\hbar\omega_0$  independent of the momentum of the phonon and, as with ionized impurities, the screening is well described by a Thomas-Fermi approximation. Under these assumptions the differential scattering rate is

$$S_{POP}^{(\pm)}(\mathbf{k}, \mathbf{k}') = \frac{\pi e^2 \omega_0}{V_c \epsilon_0} \left( \frac{1}{K_\infty} - \frac{1}{K_s} \right) \times \frac{(k^2 + k'^2 - 2kk'X)O(k, k', X)}{(k^2 + k'^2 - 2kk'X + q_{if}^2)^2} \times \left( n + \frac{1}{2} \mp \frac{1}{2} \right) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'} \pm \hbar\omega_0). \quad (19)$$

In this equation  $\epsilon_0$  is the permittivity of vacuum and  $K_\infty$  and  $K_s$  are the high frequency and static dielectric constant, respectively. The upper sign corresponds to the process of absorption of a phonon and the lower sign to the emission. Using this to calculate the collision operator of Eq. (13) yields

$$L_c[\phi] = S_{POP}^{(0)}(\varepsilon) \phi(\varepsilon) - S_{POP}^{(+)}(\varepsilon) \phi(\varepsilon + \hbar\omega_0) - S_{POP}^{(-)}(\varepsilon) \times \phi(\varepsilon - \hbar\omega_0). \quad (20)$$

The explicit form of  $S_{POP}^{(i)}(\varepsilon)$  ( $i = 0, +, -$ ) is obtained directly from the definition of  $L_c$ . The solution of the Boltzmann equation in the case of inelastic scattering is not so straightforward as in the elastic case. The collision

operator mixes different energy shells because the energy of the optical phonons cannot be neglected. There are two methods that are generally used in this situation: the variational method<sup>15</sup> and the iteration method.<sup>5</sup> We used the iteration method in the Gauss-Seidel formulation.<sup>16</sup>

We have described the way to obtain the distribution of electrons as a response to the applied fields. The information is in the functions  $\phi_1(\varepsilon)$  and  $\phi_2(\varepsilon)$ . We are now ready to define the transport coefficients and lastly to obtain  $Z$ , the thermoelectric figure of merit.

#### D. Transport coefficients

The transport coefficients are usually defined as the factors relating the applied field with the response function, i.e., here the electrical and heat current,

$$\begin{aligned} \mathbf{J} &= \sigma \mathbf{E} - \sigma S \nabla T \\ \mathbf{J}_Q &= T \sigma S \mathbf{E} - \kappa_0 \nabla T, \end{aligned} \quad (21)$$

where  $\kappa_0$  is the electronic contribution to the thermal conductivity at zero electric field. The thermal conductivity  $\kappa$  is usually defined and measured at zero electric current and is the sum of the lattice contribution  $\kappa_L$  and the electronic part at zero current  $\kappa_e$ , then

$$\kappa = \kappa_L + \kappa_0 - T \sigma S^2. \quad (22)$$

This is the magnitude in the definition of the thermoelectric figure of merit in Eq. (1). In this work we will model the electronic part of the thermal conductivity while the lattice contribution will be taken as a given constant. About 10 mW/cmK is a reasonable value for most of the semiconductors under consideration.<sup>17</sup>

After solving the Boltzmann equation we obtain the  $\phi$ 's, and with them we can calculate the electron distribution function under the influence of the applied fields using Eq. (12). Replacing this form of the distribution function  $f_{\mathbf{k}}$  in the definition of the currents, Eqs. (2) and (3), we can identify the transport coefficients as

$$\begin{aligned} \sigma &= \frac{e^2}{3\pi^2} \frac{2^{3/2} m^{*1/2}}{\hbar^3} G_1, \\ \sigma S &= \frac{e}{3\pi^2} \frac{2^{3/2} m^{*1/2}}{\hbar^3} G_2, \\ \kappa_0 &= \frac{1}{3\pi^2} \frac{2^{3/2} m^{*1/2}}{\hbar^3} G_3, \end{aligned} \quad (23)$$

where the  $G_i$ 's are defined by

$$\begin{aligned} G_1^{(e)} &= \int_0^\infty d\varepsilon \gamma^{3/2}(\varepsilon) \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \phi_1^{(e)}(\varepsilon), \\ G_2^{(e)} &= \int_0^\infty d\varepsilon \gamma^{3/2}(\varepsilon) \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \left( \frac{\varepsilon - \mu}{T} \right) \phi_1^{(e)}(\varepsilon), \\ G_3^{(e)} &= \int_0^\infty d\varepsilon \gamma^{3/2}(\varepsilon) \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \left( \frac{\varepsilon - \mu}{T} \right)^2 \phi_2^{(e)}(\varepsilon). \end{aligned} \quad (24)$$

These quantities are proportional to the electric-electric, heat-electric, and heat-heat current correlation function respectively. The superscript index  $e$  is showing that

these definitions are for electrons; the analog definitions for holes are obtained substituting  $-E_G - \mu$  for  $\mu$  everywhere. Total quantities in Eq. (23) are obtained by adding these, i.e.,

$$\begin{aligned} G_1 &= G_1^{(e)} + G_1^{(h)}, \\ G_2 &= G_2^{(e)} - G_2^{(h)}, \\ G_3 &= G_3^{(e)} + G_3^{(h)}. \end{aligned} \quad (25)$$

Finally we are able now to express  $ZT$  as a function of the calculated quantities  $G_i$ . Using the definition of  $Z$  given in Eq. (1) we obtain

$$ZT = \frac{T G_2^2}{G_1/B_0 + G_1 G_3 - T G_2^2}, \quad (26)$$

where we have defined

$$B_0 = \frac{2^{3/2} m^{*1/2}}{\kappa_L 3\pi^2 \hbar^3}. \quad (27)$$

The parameter  $B_0$  is related with the parameter  $B$  defined by CS.<sup>2</sup> This relation will be explained in the next section where we present our results.

### III. RESULTS AND DISCUSSION

Our model semiconductor is defined after specifying the charge of the impurities ( $Z_{II}$ ), its density ( $N_i$ ), the frequency of the polar optical modes ( $\omega_0$ ), the high frequency dielectric constant ( $K_\infty$ ), the static dielectric constant ( $K_s$ ), the lattice contribution to the thermal conductivity ( $\kappa_L$ ), the energy band gap ( $E_G$ ), and the effective mass at the band edge ( $m^*$ ). These two last parameters are linearly related through Eq. (9) in the case of direct-gap semiconductors. We have chosen typical values for these parameters. Our results have been obtained using single ionized impurities with a density of  $5 \times 10^{15} \text{ cm}^{-3}$ , an optical phonon energy  $\hbar\omega_0 = 19.5 \text{ meV}$ , dielectric constants  $K_\infty = 10.29$  and  $K_s = 14.15$ , and  $\kappa_L = 10 \text{ mW K}^{-1} \text{ cm}^{-1}$  for the lattice thermal conductivity. The Kane matrix element  $P$  [Eq. (9)] that gives the relation between the effective mass and the band gap was chosen as  $3.5 \times 10^{-8} \text{ eV cm}$ .

We have calculated the thermoelectric figure of merit for parabolic bands, and for non-parabolic bands in two cases, viz., when the only scattering mechanism is by polar optical modes and when the only scattering mechanism is due to ionized impurities. We show these results in Fig. 1 as a function of the band gap  $E_G$  in units of temperature, which is 150 K. In all these calculations we have adjusted the chemical potential to maximize the figure of merit. In Fig 1 two regions can be clearly distinguished: for  $E_G < 10k_B T$ ,  $ZT$  decreases always; for  $E_G > 10k_B T$  the behavior of  $ZT$  depends on the scattering mechanisms and the band structure.

For large band gap, the problem is reduced to a one band problem. The chemical potential lies near the bottom of the conduction band. In this way, a compromise is reached between the thermoelectric power and conductivity. Increasing the value of the chemical potential

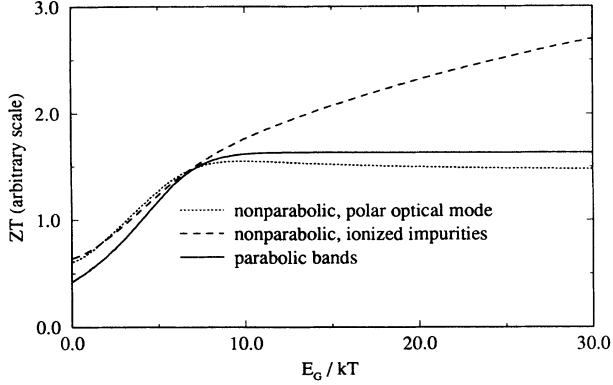


FIG. 1. Maximum value of  $ZT$  as a function of the energy band gap  $E_G$  in units of thermal energy  $k_B T$ , for parabolic bands and for nonparabolic bands with two different scattering mechanisms.

from the conduction band edge improves the conductivity but decreases the thermoelectric power. Decreasing the value of the chemical potential produces the opposite effect. The better situation is obtained when the chemical potential is around the band edge. This is clear in Fig. 2 where we show the chemical potential that maximizes  $ZT$  as a function of the energy band gap (given in terms of the thermal energy). When we reduce the band gap, this picture is changed by the appearance of holes—or minority carriers to cover the case of  $p$ -type materials—that reduce the thermopower of the system. Therefore, as the band gap is reduced, the chemical potential that maximizes the figure of merit increases while avoiding as much as possible the existence of holes. But in this case, the magnitude of the figure of merit is reduced. To stress this assertion we show in Fig. 3 the density of holes in the system, as a function of the energy band gap. As a general picture, the thermoelectric figure of merit decreases when the chemical potential of the system is closer than  $5k_B T - 6k_B T$  to the top of the valence band, and this situation is reached when the energy band gap is less than  $5k_B T - 10k_B T$ .

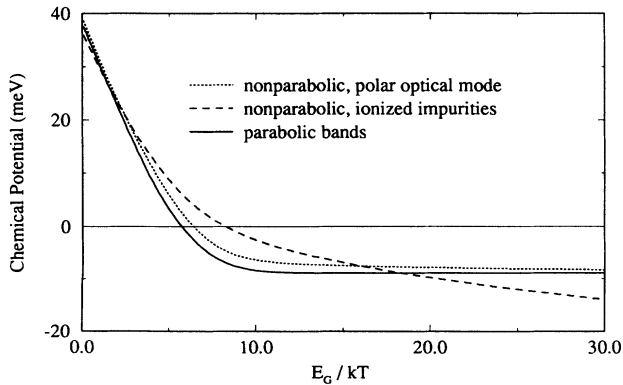


FIG. 2. Chemical potential that maximizes  $ZT$  as a function of the energy band gap  $E_G$  in units of thermal energy  $k_B T$ .

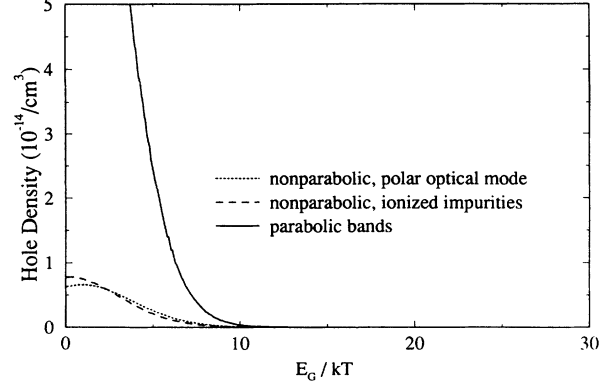


FIG. 3. Density of holes as a function of the energy band gap  $E_G$  in units of thermal energy  $k_B T$ .

While for small band gap  $ZT$  always decreases, for large values of  $E_G/k_B T$  the figure of merit may decrease or increase depending on the dominant scattering mechanism. The key point to understanding this behavior is that it does not occur for parabolic bands. In nonparabolic band systems, when the effective mass changes the band gap is changed. The behavior of  $ZT$  shows the dependence of the  $B$  parameter<sup>18</sup> of CS (Ref. 2) on the effective mass. First, let us define this parameter in terms of our present calculation and then we will be able to use it for analyzing this situation.

CS used the relaxation time approximation to describe the scattering mechanisms by factorizing the relaxation time as

$$\tau(\varepsilon) = \tau'_v(\varepsilon/k_B T)^\nu, \quad (28)$$

where  $\tau'$  contains the dependence on temperature, effective mass, and other material parameters. In the case of elastic scattering (like the ionized impurity scattering) our approximation is equivalent to theirs when using

$$\phi_1(\varepsilon) = \tau(\varepsilon)/\gamma'(\varepsilon) \quad (29)$$

and

$$\phi_2(\varepsilon) = \phi_1(\varepsilon) (\varepsilon - \mu). \quad (30)$$

Then, we have that  $B = B_0 \cdot \tau'$ . For inelastic scattering (like the polar optical modes) it is not possible to do this separation but we may still extract the dependence of the  $\phi$ 's on the effective mass and assimilate it into a parameter equivalent to  $B$ . Therefore we see that for ionized impurities  $S_{II} \sim 1/m^{*1/2}$  and hence  $B \sim m^*$ , thus explaining why  $ZT$  increases as the energy band gap increases. For polar optical modes  $S_{POP} \sim m^{*1/2}$  and  $B$  does not depend on the effective mass. As can be seen in Fig. 1 the figure of merit here is nearly flat. As another example, for acoustic phonon scattering through the deformation potential interaction,  $ZT$  will decrease with increasing energy band gap, because here  $S_{ac} \sim m^{*3/2}$ . In a mixed situation—which is the case for real materials— $B = B_0/S_{tot}$  where  $S_{tot}$  is the sum of the scattering rates for the different scattering modes in the material. Then

the behavior of  $ZT$  as a function of  $E_G$  will depend on the relative weight of each scattering mechanism. For a given material, we should in fact go beyond a general analysis, and this will be done in a future publication.

In summary, we have presented a calculation of the thermoelectric figure of merit in narrow band gap semiconductors. Our model incorporates the nonparabolicity of the conduction and valence bands, and the elastic and inelastic scattering mechanisms. We found that the behavior of  $ZT$  as a function of the energy band gap can be divided into two well defined regions. For  $E_G < 6k_B T$ ,  $ZT$  decreases for decreasing  $E_G$  because of the appearance of minority carriers. For  $E_G > 10k_B T$ ,  $ZT$  may decrease or increase as the energy band gap increases, depending on the dominant scattering mechanism in the material. In narrow band gap semiconductors for ther-

moelectric applications the optimum band gap will not be lower than  $6k_B T$  and may be higher than this value if a material is found in which the  $B$  parameter of Chasmar and Stratton increases with increasing energy band gap.

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<sup>11</sup> D. L. Rode, *Phys. Rev. B* **2**, 1012 (1970).

<sup>12</sup> B. R. Nag and A. N. Chakravarti, *Phys. Status Solidi B* **71**, K45 (1975).

<sup>13</sup> J. L. Schmit, *J. Appl. Phys.* **41**, 2876 (1970).

<sup>14</sup> G. D. Mahan, *Phys. Rep.* **145**, 251 (1987).

<sup>15</sup> A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, England, 1936), p. 300.

<sup>16</sup> B. R. Nag, Ref. 4, *Electron Transport in Compound Semiconductors*, p. 153.

<sup>17</sup> For example, the total thermal conductivity of mercury cadmium telluride is 20–80 mW/cmK depending on composition. J. C. Brice, in *Properties of Mercury Cadmium Telluride*, edited by John Brice and Peter Capper (INSPEC, Surrey, England, 1987), p. 16.

<sup>18</sup> Chasmar and Stratton called it  $\beta$  but in recent years its name has been changed to  $B$  to avoid confusion with  $1/k_B T$ .