Impact of Fermi Surface Shape Engineering on Calculated Electronic Transport Properties of Bi-Sb-Te

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Abstract: Using thermoelectric refrigerators can address climate change because they do not utilize harmful greenhouse gases as refrigerants. To compete with current vapor compression cycle refrigerators, the thermoelectric performance of materials needs to be improved. However, improving thermoelectric performance is challenging because of the trade-off relationship between the Seebeck coefficient and electrical conductivity. Here, we demonstrate that decreasing conductivity effective mass by engineering the shape of the Fermi surface pocket (non-parabolicity factor) can decouple electrical conductivity from the Seebeck coefficient. The effect of engineering the non-parabolicity factor was shown by calculating the electronic transport properties of a state-of-the-art Bi-Sb-Te ingot via two-band model with varying non-parabolicity. The power factor (the product of the Seebeck coefficient squared and electrical conductivity) was calculated to be improved because of enhanced electrical conductivity, with an approximately constant Seebeck coefficient, using a non-parabolicity factor other than unity. Engineering the non-parabolicity factor to achieve lighter conductivity effective mass can improve the electronic transport properties of thermoelectric materials because it only improves electrical conductivity without decreasing the Seebeck coefficient (which is directly proportional to the band mass of a single Fermi surface pocket and not to the conductivity effective mass). Theoretically, it is demonstrated that a thermoelectric figure-of-merit \( zT \) higher than 1.3 can be achieved with a Bi-Sb-Te ingot if the non-parabolicity factor is engineered to be 0.2. Engineering the non-parabolicity factor is another effective band engineering approach, similar to band convergence, to achieve an effective improvement in power factor.

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Keywords: thermoelectric, non-parabolicity factor, power factor, conductivity effective mass, band mass of a single Fermi pocket

1. Introduction

Replacing current vapor-compression refrigerators with thermoelectric refrigerators can reduce the rate of climate change. Unlike vapor-compression refrigerators, which utilize harmful greenhouse gases as refrigerants, thermoelectric refrigerators do not require any greenhouse gases to operate. Thermoelectric refrigerators can produce cooling using a two-dimensional array of alternating \( p \)- and \( n \)-type thermoelectric materials connected in series via the Peltier effect [1]. The efficiency of thermoelectric refrigerators depends on the performance of the thermoelectric materials, which is characterized by a dimensionless figure-of-merit, \( zT = S^2\sigma T/\kappa \).
Band engineering is frequently adopted to maximize $\kappa$, where $S$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity and the absolute temperature, respectively. However, currently the $\kappa T$ of known thermoelectric materials is not high enough to compete with vapor-compression refrigerators.

Considerable efforts have been devoted to improving $\kappa T$. Band engineering is frequently adopted to maximize $S^2 \sigma$ (power factor). Enhancing the power factor is challenging because of the trade-off between $S$ and $\sigma$. If $S$ is increased by making the band mass of a single Fermi surface pocket ($m^*$) heavier, the relevant $\sigma$ will be decreased (band flattening). However, band convergence is an effective approach to enhance the power factor, as it enhances $S$ (via increasing valley degeneracy ($N_v$) with a constant $m^*$) without deteriorating $\sigma$ [2-4]. Identifying a band parameter that is not coupled to both $S$ and $\sigma$ is key to successful power factor improvement.

Although it has often been neglected to avoid complication, the types of band masses that determine $S$ and $\sigma$ are different. While $S$ is directly proportional to the product of $N_v^{2/3}$ and $m^*$, which is equivalent to density-of-states effective mass ($m^*_j = N_v^{2/3} m^*_j$), $\sigma$ is inversely proportional to conductivity effective mass ($m^*_c$) [5-7]. For a spherical Fermi surface pocket, its $m^*_c$ is identical to $m^*_c$. However, for an ellipsoidal pocket, the $m^*_c$ becomes smaller than the $m^*_b$ [8]. Therefore, controlling Fermi surface nonparabolicity ($K$) can decouple $\sigma$ from the $S$.

Here, we theoretically demonstrate that control of $K$ is another effective band engineering approach to improve $\kappa T$. The effects of engineering $K$ on each of the electronic transport properties are calculated using a two-band model, where fitted band parameters of Bi-Sb-Te (the best candidate for thermoelectric refrigerators) are used. We find that $K$ engineering enhances the power factor by increasing $\sigma$ while keeping $S$ constant.

2. Experimental Procedure

The two-band model (solutions of the Boltzmann transport equations) was fitted to the experimental $S$, and $\sigma$ of a state-of-the-art $p$-type Bi-Sb-Te ingot measured as a function of $T$ to obtain the band parameters ($m^*_b$ and deformation potential, $\Xi$) of the valence and conduction bands in the Bi-Sb-Te (spherical Fermi surface pockets assumed) [9]. For 300 K, 0.3, and 0.6 $m_e$ (electron rest mass) were adopted for $m^*_b$, corresponding to the valence and conduction bands, respectively. The $N_v$ of both bands were set to be six, and an energy gap ($E_g$) of 0.19 eV was adopted in the two-band model [10-12]. It was assumed that acoustic phonon scattering limited the carrier mobility of both bands in the Bi-Sb-Te. Details on the two-band model fitting can be found in our previous works [4, 13, 14, 15]. While keeping the aforementioned parameters ($m^*_b$, $\Xi$, $N_v$, and $E_g$) constant, electronic transport properties were calculated for different valence band $K (= 0.2, 0.5, 1, 2.5,$ and $4)$ via the two-band model ($K = 1$ was assumed for the conduction band). Here, each electronic transport property was calculated as a function of the chemical carrier concentration ($n$) for $T = 300$ K. The effect of $K$ engineering was evaluated by comparing the electronic transport properties calculated for $K \neq 1$ to those obtained for $K = 1$ (where Fermi surface pockets are spherical).

3. Results and Discussion

3.1. Decoupling $m^*_c$ from $m^*_b$ with $K \neq 1$

To theoretically demonstrate how changing the shape of Fermi surface pockets affects the thermoelectric performance of $p$-type Bi-Sb-Te, its electronic transport properties were calculated using varying valence band $K$ with constant band parameters ($m^*_b$, $\Xi$, $N_v$, and $E_g$) under the acoustic phonon scattering assumption. The band parameters of Bi-Sb-Te were first obtained via the two-band model while assuming its Fermi surface pockets were spherical ($K = 1$ for both bands). The $K$ is defined as a ratio of $m^*_c$ along the longitudinal ellipsoid direction ($m^*_b \parallel$) to that along the transverse ellipsoid direction ($m^*_b \perp$).

$$K = \frac{m^*_b \parallel}{m^*_b \perp}$$

(1)

In terms of $K$, the degree of decoupling $m^*_c$ from $m^*_b$ is determined as below.

$$\frac{m^*_c}{m^*_b} = \frac{3K^{2/3}}{2K + 1}$$

(2)

When $K$ in Eq. (2) equals to unity, the $m^*_c$ and $m^*_b$ are identical, but for $K \neq 1$, the $m^*_c$ becomes lighter than $m^*_b$ as
presented in Fig. 1(a) [8]. The solid black line in Fig. 1(a) represents \(m^*_c/m^*_b\) as a function of \(K\). The symbols indicate \(m^*_c/m^*_b\) for each \(K\) in the range from 0.2 to 4. The specific \(K\)s were chosen so that their corresponding \(m^*_c/m^*_b\) ratios in the valence band were all different. Engineering \(K\) to be less than 1 (\(m^*_b, \parallel^{\ast}\) being heavier than \(m^*_b, \perp\)) is more effective for decoupling \(m^*_c\) from \(m^*_b\) than changing \(K\) to be larger than 1, according to Fig. 1(a). In other words, decoupling \(\sigma\) from \(S\) becomes possible for a \(K\) other than 1.

The \(\mu_d\) of Bi-Sb-Te was calculated as a function of \(n\) for varying valence band \(K\) (0.2, 0.5, 1, 2.5, and 4) to evaluate the effect of engineering \(K\) in drift mobility (\(\mu_d\)) as shown in Fig. 1(b). Commonly, the \(\mu_d\) was described to be inversely proportional to \(m^*_b^{5/2}\) assuming \(K = 1\). However, the \(\mu_d\) is more accurately described by a product of \(m^{-1}_c\) and \(m^{-3/2}_b\) for \(K \neq 1\), as given in Eq. (3).

\[
\mu_d \propto \frac{1}{m^*_c \times m^*_b^{1+3K/2}} = \left(\frac{2K+1}{3K^2}\right) \mu_d^1 \mu_d^2
\]  

(3)

If the \(m^*_c\) in Eq. (3) is expressed in terms of \(m^*_b\) and \(K\) (as in Eq. (2)), Eq. (3) becomes

\[
\mu_d \propto \frac{1}{m^*_c \times m^*_b^{1+3K/2}} = \frac{1}{m^*_b^{5/2}} \left(\frac{2K+1}{3K^2}\right) \mu_d^1 \mu_d^2
\]  

(4)

According to Eq. (4), the \(\mu_d\) is inversely proportional to the \(m^*_c/m^*_b^*\) ratios, which depend on \(K\) (Fig. 1(a)). In Fig. 1(b), the \(\mu_d\) calculated with \(K = 1\) is the lowest for all ranges of \(n\) (green triangle and line). In contrast, the \(\mu_d\) calculated with \(K = 0.2\) is the highest (orange square and line). Because the \(m^*_c/m^*_b^*\) ratio for \(K = 0.2\) (\(m^*_c/m^*_b^* = 0.73\)) is smaller than that for \(K = 1\) (\(m^*_c/m^*_b^* = 1\)), the \(\mu_d\) for \(K = 0.2\) is calculated to be higher than that for \(K = 1\). For other \(K\), the corresponding \(\mu_d\) also depends on the reciprocal of the \(m^*_c/m^*_b^*\) ratio (Eq. (4)). Therefore, a higher \(\mu_d\) is expected with a \(K\) that gives a smaller \(m^*_c/m^*_b^*\) ratio.
3.2. Effect of varying \( m_i^* / m_b^* \) on \( \sigma \) via \( K \) engineering

To examine the effect of engineering \( K \) on \( \sigma \), the \( \sigma \) of Bi-Sb-Te was calculated for varying valence band \( K (0.2 - 4) \), as shown in Fig. 2(a). Because the \( \sigma \) is directly proportional to \( \mu_d \) as given below (\( e \) is the electric charge),

\[
\sigma = ne\mu_d
\]

(5)
a similar trend was observed in \( \mu_d \) for different \( K \) (Fig. 1(b)), and this is also expected for \( \sigma \). According to Fig. 2(a), \( \sigma \) for \( K \) other than unity were calculated to be higher than that for \( K = 1 \). Again, it is the value of \( m_i^* / m_b^* \) determined from a given \( K \), and not the \( K \) itself that is correlated to \( \sigma \). The \( m_i^* / m_b^* \) ratios which correspond to \( K (0.2 - 4) \) are provided in Table 1 (Eq. (2)).

From Table 1, the \( K \) arranged in order of decreasing \( m_i^* / m_b^* \) are: 1, 0.5, 2.5, 4, and 0.2. The calculated \( \sigma \) is also increased with decreasing \( m_i^* / m_b^* \) (\( K: 1 \to 0.5 \to 2.5 \to 4 \to 0.2 \)) as shown in Fig. 2(a). Engineering \( K \) to reduce \( m_i^* / m_b^* \) was found to be beneficial to increase \( \sigma \).

A minor difference between \( \sigma \) and \( \mu_d \) is that \( \sigma \) only depends on \( m_b^* \). Because \( n \) is directly proportional to \( m_b^* \), \( m_b^* \) is inversely proportional to \( \sigma \) only as below:

\[
\sigma \propto n\mu_d \times \left(m_b^* \right)^{3/2} \left(\frac{1}{m_i^* \times m_b^*} \right) \left(\frac{1}{m_c^*} \right)
\]

(6)

In other words, \( \sigma \) is the electronic transport parameter, which can be separated from \( S \) most effectively with relevant \( K \) engineering.

The effect of varying \( m_i^* / m_b^* \) (via \( K \) engineering) on electronic thermal conductivity (\( \kappa_e \)) was also studied. The heat-carrying carrier conduction (\( \kappa_e \)) contribute to the total \( \kappa \) along with heat conduction via lattice vibrations (lattice thermal conductivity, \( \kappa_l \)) and bipolar conduction (bipolar thermal conductivity, \( \kappa_{bp} \)) as in Eq. (7).

\[
\kappa = \kappa_i + \kappa_e + \kappa_{bp}
\]

(7)

Among \( \kappa_i, \kappa_e \), and \( \kappa_{bp} \), the \( \kappa_e \) is the most directly related to \( \sigma \) via the Wiedemann-Franz law, as below, where \( L \) is the Lorenz number [16].

\[
\kappa_e = L\sigma T
\]

(8)

This is because the \( L \) is independent of both \( m_b^* \) and \( m_i^* \), the \( \kappa_e \) in Eq. (8) is directly proportional to \( \sigma \) at constant \( T \). Therefore, a higher \( \kappa_e \) is expected with a \( K \) that corresponds to a lower \( m_i^* / m_b^* \) like \( \sigma \), but the higher \( \kappa_e \) decreases \( zT \). Fig. 2(b) shows the \( \kappa_e \) for varying \( K \) as a function of \( n \). The \( \kappa_e \) with \( K = 0.2 \) (the lowest \( m_i^* / m_b^* \), orange square and line) was calculated to be the largest, and that with \( K = 1 \) (the maximum \( m_i^* / m_b^* \), green triangle, and line) was calculated to be the smallest. The inset in Fig. 2(b) shows the \( L \) calculated for varying \( K \) as a function of \( n \). Because the \( L \) is not a function of \( m_i^* \), the calculated \( L \) are all identical for different \( K \). The discrepancy among \( \kappa_e \) for different \( K \) is calculated to increase at higher \( n \). For the range of \( n \) where the thermoelectric performance of most materials is optimized \((-10^9 \text{ cm}^{-3})\), the increase in \( \kappa_e \) due to \( K \) engineering is negligible. Although decreasing \( m_i^* / m_b^* \) increases both \( \kappa_e \) and \( \sigma \), the improvement in \( \sigma \) outweighs the increase in \( \kappa_e \).

3.3. Effect of varying \( m_i^* / m_b^* \) on \( S \) via \( K \) engineering

To examine how varying \( m_i^* / m_b^* \) (via \( K \) engineering) affects \( S \), the \( S \) of Bi-Sb-Te was calculated for varying valence band \( K (0.2 - 4) \) at 300 K, as shown in Fig. 3(a). The \( S \) for different \( K \) are almost identical for \( n \geq -5 \times 10^{18} \text{ cm}^{-3} \), but they are different for \( n < -5 \times 10^{18} \text{ cm}^{-3} \). Although \( S \) calculated from a single band is independent of \( m_i^* \) (but dependent on \( m_b^* \) instead), the overall \( S \) calculated from two bands does depend on \( m_b^* \) via \( \sigma \) contributions from each band. The overall \( S \) is calculated by Eq. (9) below, where \( S_l \) and \( S_t \) are the partial contributions from each band (\( i = \text{VB} \) (valence band), \( \text{CB} \) (conduction band)).

\[
S = \sigma \text{vb} S_{\text{vb}} + \sigma \text{vb} S_{\text{cb}} \sigma \text{vb} + \sigma \text{cb}
\]

(9)

When \( \sigma \text{vb} \) and \( \sigma \text{cb} \) in Eq. (9) are comparable at low \( n \), the
difference in $\sigma_{VB}$ due to varying valence band $K$ is well captured in the overall $S$. For example, the $\sigma_{VB}$ for $K = 0.2$ is the highest among $K$ in the range from 0.2 to 4 (Fig. 2(a)). Hence, the $S$ for $K = 0.2$ is calculated to be the highest for $n < \sim 5 \times 10^{18}$ cm$^{-3}$, as in Fig. 3(a) ($S_{VB}$, $S_{CB}$, and $\sigma_{CB}$ being constant with respect to $K$). In Fig. 2(a), we simply stated that the overall $\sigma$ increased because of the decrease in the $m^*_c/m^*_b$ ratio. To be more specific, the increase in the overall $\sigma$ was due to the increase in $\sigma_{VB}$ originating from a decrease in the valence band $m^*_c/m^*_b$ ratio ($K$ of the conduction band was fixed). However, once the $\sigma_{VB}$ becomes much greater than $\sigma_{CB}$ at high $n$, the $S$ in Eq. (9) converges to $S_{VB}$, as shown below.

$$S \approx \frac{\sigma_{VB} S_{VB}}{\sigma_{VB}} = S_{VB}$$

(10)

Because $S_{VB}$ is independent of $m^*_c$, the $S$ is calculated to be approximately invariant with respect to $K$ at $n \geq \sim 5 \times 10^{18}$ cm$^{-3}$, as in Fig. 3(a). Given that the optimum properties of thermoelectric materials are frequently realized at $n \sim 1 \times 10^{19}$ cm$^{-3}$, it can be concluded that the $S$ is not affected by varying $K$.

The effect of varying $m^*_c/m^*_b$ (via $K$ engineering) on $\kappa_{np}$ was also examined. Unlike $\kappa_c$, both $S_i$ and $\sigma_i$ ($i = VB, CB$) are required to calculate $\kappa_{np}$, as shown below.

$$\kappa_{np} = \frac{\sigma_{VB} \sigma_{CB}}{\sigma_{VB} + \sigma_{CB}} (S_{VB} - S_{CB})^2 T$$

(11)

In Eq. (11), the $S_{VB}$ and $S_{CB}$ are independent of varying $K$, as they do not depend on $m^*_c$. And because we assume that the $K$ of the conduction band is unity for simplicity, only the $\sigma_{VB}$ is changed with varying $K$. Therefore, it is expected that the $\kappa_{np}$ with a low $m^*_c/m^*_b$ will be high because of high $\sigma_{VB}$, as in the case of $S$. However as calculated in Fig. 3(b), the discrepancy in $\kappa_{np}$ due to different $K$ is negligible for all $n$. Hence, varying $K$ does not affect $\kappa_{np}$.

### 3.4. Effect of varying $m^*_c/m^*_b$ on power factor via $K$ engineering

To demonstrate the effect of varying $m^*_c/m^*_b$ (via $K$ engineering) on the power factor, the power factor of Bi-Sb-Te was calculated for varying valence band $K (0.2 – 4)$ at 300 K as shown in Fig. 4. Since suppressing $m^*_c/m^*_b$ is beneficial to $\sigma$ (Fig. 2(a)), while causing a negligible change in $S$ (Fig. 3(a)), an improvement in the power factor is expected. According to Fig. 4(a), the highest power factor was calculated for the $K = 0.2$ (orange square and line), which corresponds to the lowest $m^*_c/m^*_b$ (Table 1), and the lowest power factor was calculated for $K = 1$ (green triangle and line) which corresponds to the maximum $m^*_c/m^*_b$. The calculated power factor increased with decreasing $m^*_c/m^*_b$ ($K: 1 \rightarrow 0.5 \rightarrow 2.5 \rightarrow 4 \rightarrow 0.2$), as observed in $\sigma$ in Fig. 2(a). Therefore, engineering $K$ to be other than unity will always improve the power factor.

Lastly, to investigate the effect of varying $m^*_c/m^*_b$ (via $K$ engineering) on $zT$, the $zT$ of Bi-Sb-Te was calculated for varying valence band $K (0.2 – 4)$ at 300 K as shown in Fig. 4(b). For the $zT$ calculation, $\kappa_i$ is required in addition to the $\kappa_c$ and $\kappa_{np}$ calculated in Fig. 2(b) and 3(b), respectively. Because the $\kappa_i$ cannot be calculated using the two-band model, the experimental $\kappa_i$ of a state-of-the-art Bi-Sb-Te

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**Fig. 3.** (a) $S$, and (b) bipolar thermal conductivity ($\kappa_{np}$) calculated for different $K$ as a function of $n$ at 300 K.
Although calculation. that engineering 10 increase is negligible compared to the Fig. 4. $zT$ set of band parameters. the fitted what they should be (with materials. Making approach to improve the power factor of thermoelectric 19 approach to improve $zT$ as shown in Fig. 4(b). Its optimum $zT$ was achieved near $n \sim 10^{19} \text{cm}^{-3}$. The sharp decrease in $zT$ for $n > 10^{19} \text{cm}^{-3}$ is attributed to the increasing $\kappa_c$ and $\kappa_{\mu}$ at high $n$. This confirms that engineering $K$ to decrease $m^*_c/m^*_b$ is another effective approach to improve $zT$.

Engineering $K$ is another effective band engineering approach to improve the power factor of thermoelectric materials. Making $K$ other than unity decouples $m^*_c$ from $m^*_b$, which enables us to break the trade-off between $S$ and $\sigma$. As $m^*_c/m^*_b$ decreases, $\sigma$ is improved without deteriorating $S$. Although $\kappa_c$ is also increased with decreasing $m^*_c/m^*_b$, the $\kappa_c$ increase is negligible compared to the $\sigma$ increase. Therefore, $zT$ improvement is guaranteed if the $m^*_c/m^*_b$ is reduced by engineering $K$.

We assumed that the $K$ of both the valence and conduction bands were unity when obtaining the band parameters of the state-of-the-art Bi-Sb-Te ingot from the two-band model fitting. However, it has been reported that the valence band $K$ of Bi-Sb-Te was optically determined to be approximately 2 [17]. Consequently, the determined band parameters of Bi-Sb-Te ($m^*_b$, $\Xi$) with $K = 1$ can be marginally different from what they should be (with $K = 2$). The discrepancy between the fitted $\Xi$ and the actual $\Xi$ will be higher than that expected between the fitted and actual $m^*_b$ because $K$ only affects $m^*_b$-related parameters. Nonetheless, the fact that engineering $K$ improves power factor remains intact because the beneficial effect of decreasing $m^*_c/m^*_b$ on power factor applies to any set of band parameters.

Both decreasing $m^*_c/m^*_b$ by engineering $K$ and decreasing $\Xi$ have similar impacts on $\mu_d$ as the $\mu_d$ is inversely proportional to the product of $\Xi^2$, $m^*_c$ and $m^*_b$. In addition, because $S$ is independent of $\Xi$, the effect of suppressing $\Xi$ on electronic transport properties is almost identical to the effect of engineering $K$ on electronic transport properties. Therefore, an additional optical study that measures $m^*_c$ at different principal axes is required to confirm that an improvement in power factor originates from $K$ engineering.

No experimental approach to engineer only $K$ has been suggested yet. Although alloying is known to alter $K$, it also changes other band parameters at the same time, making the evaluation of the effect of $K$ change difficult [17]. As an alternative, materials with innately low $m^*_c/m^*_b$ have been theoretically sought as potential candidates for new high-performance thermoelectric materials [18].

Although the effect of engineering $K$ was investigated using narrow band gap Bi-Sb-Te, its effect will be even greater for large band gap materials since the potential increase in $\kappa_{\mu}$ due to $K$ engineering will be minimized because of their substantially low $\kappa_{\mu}$ [19]. Moreover, since we know that $K$ other than unity can significantly alter the electronic transport properties of thermoelectric materials, accurate $K$ input (obtained via measurements or simulations) is important to accurately determine materials’ band parameters via band modeling.

### 4. Conclusions

A new band engineering approach that by-passes the trade-
off between $S$ and $\sigma$ has been suggested. Engineering the shape of Fermi surface pockets ($K$, non-parabolicity factor) to be ellipsoidal was found to decouple conductivity effective mass ($m_c^*$) from the band mass of a single Fermi pocket ($m_b^*$). When $K$ is engineered to lower the $m_c^* / m_b^*$ ratio, the $\sigma$ is calculated to increase while $S$ remains constant. It was calculated that the thermoelectric figure-of-merit ($zT$) of a Bi-Sb-Te ingot can be improved to higher than 1.3 if the non-parabolicity factor is engineered to be 0.2. Although alloying is known to change $K$, it also simultaneously alters other band parameters. However, it is suspected that alloying, combined with carefully designed doping, might only change $K$ so that it improves the power factor of materials effectively.

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