Thermally induced band gap increase and high thermoelectric figure of merit of n-type PbTe

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Abstract

Unlike in many other semiconductors, the band gap of PbTe increases considerably with temperature. We compute the thermoelectric transport properties of n-type PbTe from first principles including the temperature variation of the electronic band structure. The calculated temperature dependence of the thermoelectric quantities of PbTe is in good agreement with previous experiments when the temperature changes of the band structure are accounted for. We also calculate the optimum band gap values which would maximize the thermoelectric figure of merit of n-type PbTe at various temperatures. We show that the actual gap values in PbTe closely follow the optimum ones between 300 K and 900 K, resulting in the high figure of merit. Our results indicate that an appreciable increase of the band gap with temperature in direct narrow-gap semiconductors is very beneficial for achieving high thermoelectric performance.

Keywords: Thermoelectric transport properties, Boltzmann transport equation, first-principles, temperature-dependent band structure

1. Introduction

Thermoelectric (TE) materials convert reversibly thermal energy to electrical energy. The TE figure of merit is defined as $zT = \sigma S^2 T/\kappa$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the temperature, and $\kappa$ is the thermal conductivity \cite{1}. The efficiency of TE refrigerators and power generators increases with larger values of $zT$. At higher temperatures, minority carriers caused by thermal activation contribute negatively to Seebeck coefficient and decrease $zT$ \cite{2}. An increasing band gap with temperature can suppress these bipolar effects and increase $zT$. Such band gaps would also lead to larger effective masses and Seebeck coefficient at higher $T$ in direct gap semiconductors \cite{3}.

Previous model calculations have determined the ideal values of band gaps that would result in maximal $zT$ values for semiconductors with indirect and direct gaps and relatively parabolic bands \cite{4, 5, 6}. For direct gap semiconductors, if the band gap $E_G$ is smaller than $6k_B T$, where $k_B$ is the Boltzmann constant, it was found that $zT$ decreases when $E_G$ decreases due to the presence of minority carriers. If $E_G > 10k_B T$, $zT$ may decrease or increase with increasing $E_G$ depending on the dominant electron scattering mechanism in the material. However, for real TE materials, where different scattering mechanisms compete, no previous work has calculated the optimum band gap values at different temperatures from first principles.

In most semiconductors, the band gap decreases with increasing temperature. A particularly interesting exception is the group of lead chalcogenides (PbS, PbSe, PbTe), whose direct narrow gap increases with increasing temperature \cite{7, 8, 9}. A positive temperature coefficient of the band gap, $\partial E_G/\partial T$, could lead to the optimum gap values in a wider temperature range than if this coefficient is negative. The band gap of PbTe increases from 0.19 eV at 30 K to 0.38 eV at 500 K \cite{8, 9} \cite{\partial E_G/\partial T \approx 4.7k_B T}. Recent calculations suggested that this peculiar increase of $E_G$ with $T$ may be correlated with large anharmonicity \cite{10}. Our recent first-principles work revealed that this effect stems from the Debye-Waller and thermal expansion contributions to the temperature renormalization of PbTe’s gap \cite{11}.

First-principles calculations of thermoelectric transport quantities are typically carried out using the electronic band structure obtained from density functional or higher level theories, where the band shifts due to temperature are not accounted for \cite{12, 13, 14, 15, 16, 17, 18, 19, 20}. For example, recent \textit{ab-initio} calculations of TE transport in PbTe used a fixed band gap value at all temperatures \cite{17}. In contrast, an earlier study indicated the importance of accounting for the temperature variations of the band structure when modelling TE transport in PbTe \cite{21, 22}. Our previous work on this subject \cite{23} focused on the electronic mobility of n-type PbTe up to room temperature, where this effect is not so prominent.

In this work, we calculate all thermoelectric transport properties of PbTe from first principles, explicitly accounting for the temperature renormalization of the electronic band structure. We find much better agreement between our results and...
experiments when we include the temperature induced changes of the band structure. The ideal band gap values that would maximize $zT$ at different temperatures have also been obtained. The optimum gap values vary from $10k_BT$ at 300 K to $6.5k_BT$ at 900 K, due to the competition between longitudinal optical and acoustic phonon scattering at high doping concentrations and temperatures. The actual band gap values of PbTe are very similar to the optimum ones in the whole temperature range. Therefore, the sizeable positive temperature coefficient of the narrow band gap in PbTe enables its high efficiency at 900 K, due to the competition between longitudinal optical and electron-phonon coupling.

2. Method

2.1. Temperature-dependent band structure

PbTe is a direct narrow gap semiconductor with the gap located at four equivalent L points. The L valleys give the largest contribution to the electronic conduction and TE transport in n-type PbTe [33]. At higher temperatures, the energies of the valence band maxima at $\Sigma$ become similar to those of the valence band maxima at L. We neglect this effect in the present calculations. The electronic band structure near the L point in PbTe is well described using the two-band Kane model derived from $k \cdot p$ theory [3]. The electronic band structure near L at a finite temperature are then computed using the two-band Kane model as [39]

$$m^*_0(T)/m^*_0(0 \text{ K}) = E_G(T)/E_G(0 \text{ K}),$$

where $d$ denotes the parallel or perpendicular direction. We note that due to the small calculated value of the zero-point renormalization of the gap ($\sim 20 \text{ meV}$ [11]), we approximate the values of the effective masses at 0 K with their values obtained using the HSE03 functional.

2.2. Thermoelectric properties

To study thermoelectric transport in n-type PbTe, we use the Boltzmann transport theory within the relaxation time approximation. Thermoelectric transport properties can be calculated as

$$\sigma^{ij} = L^{ij}_0,$$

$$S^{ij} = -L^{ij}_0/\epsilon T L^{ij}_0,$$

$$k^{ij}_0 = L^{ij}_0/\epsilon T,$$

where $\sigma$ is the dc electrical conductivity tensor, $S$ is the Seebeck coefficient tensor, $k_0$ is the thermal conductivity tensor defined when the electric field across the material is zero, $i$ and $j$ are the Cartesian directions, and $\epsilon$ is the electron charge. The transport kernel functions for the CB are defined by

$$L^{ij}_0 = \int_{BZ} \frac{e^2}{4\pi^2} \left( \frac{\partial f}{\partial E} \right) \tau_{k,\text{tot}} v_i^j (E_k - E_F)^\alpha,$$

where $E_k$ and $v_i^j$ are the energy and the group velocity of an electronic state with the crystal momentum $k$, $f$ is the equilibrium Fermi-Dirac occupation function, $E_F$ is the Fermi level, and $\tau_{k,\text{tot}}$ is the relaxation time. Unlike $k_0$, the total thermal conductivity $k$ is defined at zero electric current across the material, and is the sum of the lattice contribution $k_L$ and the electronic contribution $k_e$, which can be given as

$$k = k_L + k_e = k_L + k_0 - T\sigma S^2.$$

We calculate the gap variation due to thermal expansion using the lattice constant values that account for thermal expansion, and computing the corresponding band gap change using DFT [11]. We compute the temperature dependence of the lattice constant using lattice dynamics from first principles, as explained in Ref. [11]. The electron-phonon renormalization of the band gap is calculated using the Allen-Heine-Carhonan theory [31, 32, 33] and its density functional perturbation theory (DFPT) implementation in the ABINIT code [34, 35]. We use the local density approximation (LDA) [36, 37] and Hartwigsen-Goedecker-Hutter norm-conserving pseudopotentials [38] with the 6$s^2$6$p^2$ states of Pb and 5$s^2$5$p^2$ states of Te explicitly included in the valence states. Spin-orbit interactions are included. We use the cutoff energy of 45 Ha, and a $12 \times 12 \times 12$ Monkhorst-Pack $k$-point grid.

We calculate the temperature dependence of the band gap of PbTe with respect to its LDA value, $\Delta E_G(T) = E_G(T) - E_G(\text{LDA})$, and its temperature derivative $\partial E_G/\partial T$. These temperature changes are added to the band gap values obtained using the HSE03 functional to obtain $E_G(T)$ used in the two-band Kane model. The effective masses of the renormalized bands near L at a finite temperature are then computed using the two-band Kane model as [39]
Since PbTe is cubic, $\sigma^{ij}$, $S^{ij}$, and $\kappa_{ij}^{l}$ can be expressed as

$$\sigma^{ij} = \delta_{ij}\sigma; \quad S^{ij} = \delta_{ij}S; \quad \kappa_{ij}^{l} = \delta_{ij}\kappa_{0};$$  \hspace{1cm} (6)

where $\delta_{ij}$ is the Kronecker delta, and $\sigma$, $S$, and $\kappa_{0}$ are given as:

$$\sigma = \sum_{l} \sigma^{ij}/3, \quad S = \sum_{l} S^{ij}/3, \quad \text{and} \quad \kappa_{0} = \sum_{l} \kappa_{ij}^{l}/3.$$

We note that the superscript index $(\epsilon)$ in Eq. 4 refers to electrons. We also include the contribution from holes by treating the VB as a mirror-image of the CB in the two-band Kane model. The analogue definitions of the transport kernel functions for holes are obtained by simply substituting $E_F$ by $-E_G-E_F$ in Eq. 4. By combining the contributions from electrons and holes, we obtain the total transport kernel functions $L_{\omega} = L_{\omega}^{(e)} + L_{\omega}^{(h)}$. Our calculations show that the effect of holes on the electronic transport properties is negligible at the optimum doping concentrations for TE applications (~$10^{19}$ cm$^{-3}$).

The total relaxation time $\tau_{\text{tot}}$ is determined by the contributions of different scattering mechanisms: acoustic (ac) phonons, transverse optical (TO) phonons, longitudinal optical (LO) phonons, and ionized impurities (imp) [17, 23, 40, 41], and can be calculated via Matthiessen’s rule:

$$\tau_{k,\text{tot}}^{-1} = \tau_{1}^{-1} + \tau_{2}^{-1} + \tau_{3,\text{TO}}^{-1} + \tau_{4,\text{imp}}^{-1}.$$  \hspace{1cm} (7)

The relaxation time of a single scattering channel is given by [14, 15]

$$\tau_{k}^{-1} = \frac{2\pi}{\hbar} \sum_{q} \frac{1}{1-f_k} \left(1-\hat{v}_k \cdot \hat{v}_k\right) S_{k^{'}}.$$  \hspace{1cm} (8)

where $S_{k^{''}}$ denotes the transition rate from initial $k$ to final state $k^{''}$ due to scattering, and $\hat{v}_k$ is the unit vector in the direction of the group velocity at $k$. The velocity factor $(1-\hat{v}_k \cdot \hat{v}_k)$ accounts for the change of direction of scattered carriers. For electron-phonon scattering, we can write

$$S_{k}^{k+q} = \left|g_{k}^{k+q}\right|^2 \left\langle N^0(\omega_q)\delta(E_k + \hbar\omega_q - E_{k+q}) + \left[N^0(\omega_q) + 1\right]\delta(E_k - \hbar\omega_q - E_{k+q})\right\rangle,$$  \hspace{1cm} (9)

where $N^0$ and $\omega_q$ are the equilibrium distribution and the frequency of a phonon with the crystal momentum $q$, and $g_{k}^{k+q}$ is the electron-phonon matrix element. The two terms in the curly brackets correspond to phonon absorption and emission, respectively.

We parametrize the electron-phonon matrix elements $g_{k}^{k+q}$ due to acoustic, TO and LO phonons as described in detail in our previous work [23]. This requires calculations of acoustic and optical deformation potentials, phonon frequencies, elastic and dielectric constants [23]. Some of these parameters, such as phonon frequencies, elastic and dielectric constants, can be computed straightforwardly from first principles, using DFPT. Our earlier work [27] describes several methods to calculate acoustic deformation potentials of PbTe from first principles, one of which uses DFPT. We use the same DFPT method to obtain optical deformation potentials of PbTe. The values of all these parameters are listed in Table I of Ref. [23]. Since the VB is described as a mirror image of the CB, the absolute values of deformation potentials for the VB of PbTe are taken to be the same as those for the CB. All these parameters are calculated using the LDA excluding SOC that gives a positive band gap and the correct character of the conduction and valence band states near the L point in PbTe, in contrast to the LDA including SOC [27]. We note that we do not include the temperature changes of the parameters characterizing the strength of electron-phonon coupling in this work. We also account for ionized impurity scattering using the Brooks-Herring model with the Thomas-Fermi model for carrier screening, which was also used for screening of LO phonon scattering [23].

3. Results and Discussion

![Figure 1](attachment:image.png)

**Figure 1**: (a) The lowest conduction band and the highest valence band of PbTe near the L point and the Fermi level for the doping concentration of $10^{19}$ cm$^{-3}$. The conduction band minima from different temperature calculations are shown in different colors. The Fermi levels at different temperatures are calculated using $dE_F/dT = 4.4 \times 10^{-4}$ eV/K. The conduction band minima from the different temperature calculations are aligned. (b) Temperature dependence of the density-of-states (DOS) effective mass calculated with the two-band Kane model (lines) and measured experimentally (dots) [42].

Using the HSE03 hybrid functional, we obtain the band gap value of $E_G = 0.237$ eV for PbTe, [27], which compares well to the experimental value of 0.19 eV at 4 K [43]. We calculate the temperature dependence of the band gap using DFPT and the LDA excluding and including SOC. The top valence

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1. We note that we obtain similar values of acoustic deformation potentials using the LDA excluding SOC and the HSE03 functional including SOC [23].
and bottom conduction bands at L of PbTe correspond to the representations $L^6\sigma$ and $L^6\pi$, respectively [44], but that order is inverted in the LDA including SOC [27]. To account for the correct ordering of these states, we define the direct gap at L as $E_G = E_{L^6\pi} - E_{L^6\sigma}$ [11]. Using a linear fit for $E_G$ with respect to $T$ in the range of 200 – 800 K, we compute $\partial E_G/\partial T \approx 3.0 \times 10^{-3}$ eV/K and $\partial E_G/\partial T \approx 4.4 \times 10^{-4}$ eV/K excluding and including SOC, respectively [11]. Both values compare very well to the available optical absorption measurements of $\partial E_G/\partial T \sim 3.0 - 5.1 \times 10^{-4}$ eV/K [8, 9, 45, 46, 27]. These results suggest that accounting for SOC or the correct order of the states near the gap does not affect the computed $\partial E_G/\partial T$ values very much.

The temperature dependence of the CB and VB near the L point is shown in Fig. 1(a), where the CB minima from different temperature calculations are aligned. The increasing effective mass with temperature obtained in our calculations has also been observed experimentally. As shown in Fig. 1(b), the computed conduction band density-of-states (DOS) effective mass is in fairly good agreement with the measurements of Ref. [42], particularly when we use the value of $\partial E_G/\partial T \approx 4.4 \times 10^{-4}$ eV/K which includes the effects of SOC. Therefore, $\partial E_G/\partial T \approx 4.4 \times 10^{-4}$ eV/K is used in the rest of the paper. We have verified that the conclusions of this work do not change if we use the value of $\partial E_G/\partial T \approx 3.0 \times 10^{-3}$ eV/K in our simulations.

We next show the calculated energy dependence of the inverse relaxation time associated with the four scattering mechanisms ($\tau_{\text{el}}^{-1}$, $\tau_{\text{LO}}^{-1}$, $\tau_{\text{TO}}^{-1}$, $\tau_{\text{imp}}^{-1}$) and $\tau_{\text{el}}^{-1}$ for $T = 100$ K and $T = 600$ K at the doping concentrations of $n = 1 \times 10^{19}$ cm$^{-3}$, see Fig. 2. We also plotted $(-\partial f/\partial E)$ to indicate the energy range that contributes to electronic transport and understand the relative importance of different scattering mechanisms in this range. We find that LO phonon scattering is the strongest scattering mechanism, while acoustic and, to a lesser extent, TO scattering become comparable only when $T$ and doping are very high. LO scattering includes long-range polar and short-range non-polar interactions, whose relaxation times are also plotted in Fig. 2. Since the matrix elements $8_k^{k'q}$ of these two contributions are added up, the non-polar contribution considerably modifies the energy dependence of $\tau_{\text{LO}}^{-1}$ despite its relatively small magnitude. In general, ionized impurity scattering is negligible compared to electron-phonon scattering, except at low $T$ and low doping concentrations. At low temperatures ($T = 100$ K), there is a dip in $\tau_{\text{LO}}^{-1}$ around the Fermi level, which is a consequence of the Pauli exclusion principle for this inelastic process (see Appendix A).

The importance of accounting for the temperature dependence of the band structure (T-depBS) to compute the electronic transport properties of PbTe is illustrated in Fig. 3. The electronic mobility for $n = 2.3 \times 10^{19}$ cm$^{-3}$ as a function of temperature excluding and including the T-depBS is given by the black solid and dashed lines, respectively. Squares and circles show the mobility measurements from Refs. [40, 48]. Including the T-depBS decreases the mobility about 25% at 300 K and 50% at 900 K, and gives a much better agreement with the experimental values and their temperature dependence. The difference between our results including and excluding the T-depBS becomes larger as $T$ increases. This is because $m_t^* \propto T$ and $m_t^* \propto T$ increase with $T$ due to the increased band gap, leading to a decrease of the band curvature near the band edge and an increase of the radius of constant energy surface. These effects result in smaller group velocities and a larger phase space for scattering, thus reducing the mobility.

We also calculated the individual contributions of various scattering channels to the electronic mobility of PbTe, shown by the colored lines in Fig. 3. LO phonon scattering is the dominant scattering channel limiting the mobility between 300 K and 900 K, even at high doping concentrations, since screening is relatively weak due to a large dielectric constant of PbTe [23]. In contrast, TO phonon scattering is the weakest electron-phonon scattering mechanism even for high temperatures, since this type of scattering between the CB minima at L and the zone center TO mode is forbidden by symmetry [23]. Acoustic phonon scattering is the second strongest scattering channel, whose importance increases at high temperatures and doping concentrations.

We note that the T-depBS makes the mobility limited by individual electron-phonon scattering channels exhibit very simi-
Figure 3: Electronic drift mobility versus temperature for the doping concentration of $n = 2.3 \times 10^{19}$ cm$^{-3}$. Solid black line is calculated including all scattering channels, while colored lines correspond to the contributions to the mobility from individual scattering channels. Dashed black line represents the total mobility calculated without accounting for the temperature dependence of the electronic band structure (T-depBS). Experimental data are shown in full squares (Ref. [18]) and circles (Ref. [14]).

lar T dependence, as shown by the colored lines in Fig. 3. One would expect that LO phonon scattering has a characteristic T dependence that is different from that of acoustic phonons due to the different energy dependence of their relaxation times $\tau$. However, the T dependence of the mobility is not very sensitive to the energy dependence of $\tau$ over a large range of T when the temperature dependence of the band structure is accounted for in our calculations. Instead, the T dependence of the mobility comes from three sources: (1) the T dependence of phonon occupations ($N^0 \approx k_B T/\hbar \omega$ for $k_B T \gg \hbar \omega$), (2) the T dependence of the electronic band structure, and (3) the T dependence of the Fermi level $E_F$. Our results suggest that it is not reliable to deduce the relative weight of different electron-phonon scattering processes only by considering the T dependence of the mobility in the case of direct narrow-gap semiconductors with band gaps strongly renormalized by temperature.

The calculated temperature dependence of the electrical conductivity and the Seebeck coefficient for $n = 4.8 \times 10^{18}$ cm$^{-3}$ including and excluding the T-depBS is illustrated in Fig. 4. At high T, the discrepancy between the results excluding and including the T-depBS comes from two factors: (1) increasing $E_G$ with T which reduces the hole contribution to electronic transport, and (2) increasing effective masses with T. To identify the role of each of these factors, we calculate the conductivity and Seebeck coefficient using the temperature-dependent gap values but keeping the effective masses constant at their 0 K values, shown by the red lines with empty circles in Fig. 4. The difference between the red empty and full circles shows the effect of increased hole concentration due to the increased $E_G$: (1) the electrical conductivity increases, and (2) the Seebeck coefficient decreases because the energy term $(E_k - E_F)$ in Eq. 4 is negative for $S^{(h)}$. These effects become strong only at low doping concentrations and high T. On the other hand, as shown by the difference between the green full squares and the red empty circles, the temperature induced band flattening increases the Seebeck coefficient and decreases the conductivity over the entire temperature range. We note that these effects become weaker as the doping concentration increases because the Fermi level increases and the electronic states relevant for transport are less influenced by the temperature variations of effective masses.

The comparison between the computed and measured electrical conductivity as a function of temperature for $n = 4.8 \times 10^{18}$ cm$^{-3}$ clearly shows that it is important to include the T-depBS to obtain good agreement with experiments [48, 49] (see Fig. 4(a)). On the other hand, the Seebeck coefficient is somewhat underestimated compared to experiment when the T-depBS is accounted for (Fig. 4(b)), likely due to the fact that our first principles calculations somewhat overestimate the effective masses of PbTe (Fig. 1(b)). We also note that the calculated Seebeck coefficient for $n = 4.8 \times 10^{18}$ cm$^{-3}$ keeps increasing with temperature, and is overestimated at $T > 700$ K (see Fig. 5). In PbTe, the valence bands at $\Sigma$ become aligned with the valence bands at L for $T \sim 620$ K [8, 11]. This effect will also increase the hole concentration and decrease the Seebeck coefficient with respect to our present results.

The temperature dependence of the electrical conductivity, Seebeck coefficient, total and electronic contribution to the ther-
Figure 5: Calculated and experimental temperature dependence of (a) the electrical conductivity, (b) the absolute Seebeck coefficient, (c) the total thermal conductivity and (d) the electrical thermal conductivity of n-type PbTe for several doping concentrations. Experimental data are shown in full symbols (Ref. [48]).
doping concentration (cm$^{-3}$).

Figure 6: Color maps of the calculated figure of merit $zT$ versus temperature and doping concentration (a) including and (b) excluding the temperature dependence of the electronic band structure (T-depBS). (c) Calculated $zT$ versus doping concentration for different temperatures including and excluding T-depBS.

Figure 7: (a) Maximum value of $zT$ ($zT_{\text{max}}$) and (b) chemical potential corresponding to $zT_{\text{max}}$ as a function of the band gap $E_G$ in units of thermal energy $k_B T$ for different temperatures between 300 and 900 K. $zT_{\text{max}}$ values are obtained by adjusting the doping concentration for each $E_G$ and $T$. The band gap values giving maximum $zT_{\text{max}}$ values are indicated by circles. The calculated band gap values of PbTe where their temperature variation is accounted for are indicated by squares, while the ground state band gap value of $E_G = 0.237$ eV is given by crosses.

Figure 8: Maximum value of $zT$ ($zT_{\text{max}}$) as function of the band gap $E_G$ in units of thermal energy $k_B T$ due to: (a) acoustic phonon scattering, and (b) polar longitudinal phonon scattering. In these plots, only the $zT_{\text{max}}$ dependence on $E_G$ is relevant, while the $zT$ values on the vertical axis are given on an arbitrary scale.

are related to the dependence of the quality factor $B$, which was first introduced by Chasmar and Straton [4], on the effective masses, which change with temperature in direct gap semiconductors [5]. In the case of PbTe, polar LO phonon scattering has a major effect at low temperatures and low doping concentrations, which is why the $zT_{\text{max}}$ curves in Fig. 8(a) are nearly flat around room temperature. When $T$ increases and screening becomes larger at high doping concentrations, acoustic and non-polar optical phonon scattering contributions exceed that of polar LO phonons, leading to the $zT_{\text{max}}$ peaks in the range of
6 · 10$^3 T$.

Finally, we analyze where the actual values of the band gap of PbTe lie on the $zT_{\text{max}}$ curves given in Fig. 3(a). The squares on the $zT_{\text{max}}$ curves correspond to our calculated band gaps renormalized by temperature, while the crosses correspond to the DFT-HSE03 gap value of $E_G = 0.237$ eV that does not change with $T$. The $zT_{\text{max}}$ values obtained using the gap values that account for the T-depBS are very close to the $zT_{\text{max}}$ maxima, especially at high temperatures, as a result of the considerable thermally induced increase of the band gap.

In contrast, if the band gap is constant (or decreasing with $T$), it becomes much smaller than the optimum band gap at high temperatures, leading to a substantial decrease of $zT_{\text{max}}$. We thus conclude that the unusual increase of the band gap with temperature is an important factor for the high $zT$ of n-type PbTe. Our results also indicate that other direct narrow-gap semiconductors with positive temperature coefficients resulting in the band gaps of $\sim$6–10 $k_BT$ may be potentially good TE materials for a relatively wide range of temperatures, similarly to PbTe.

4. Conclusion

We developed the first-principles thermoelectric transport model that includes the temperature variations of the electronic band structure, and accurately describes the temperature dependence of all thermoelectric transport properties for n-type PbTe between 300 K and 900 K. We also computed the optimum band gap values for which the $zT$ values of n-type PbTe would be maximized, that vary between 10$k_BT$ at 300 K and 6.5$k_BT$ at 900 K. We showed that the actual band gap values in PbTe are very close to the predicted optimum values in a broad range of temperatures, which contributes largely to the good thermoelectric figure of merit of n-type PbTe in addition to its low thermal conductivity. We propose that materials with positive temperature coefficients producing the band gaps of $\sim$6–10 $k_BT$ in a range of temperatures could be promising candidates in the search for efficient thermoelectric materials.

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Appendix A. Inelastic scattering at low temperatures

Fig. 2 shows a dip in $\tau_{\text{L0}}^{-1}$ around the Fermi level $E_F$ at $T=100$ K. This is a direct consequence of the Pauli exclusion principle for this inelastic process. At low temperatures, most electrons occupy the states below $E_F$, which are nearly completely occupied. Due to the Pauli exclusion principle, they preferentially scatter to the states above $E_F$, thus absorbing phonons. Since there are few thermally excited phonons at low temperatures, this scattering rate is very low. As $T$ increases, this dip disappears as electronic and phonon occupations broaden, as shown in Fig. 2(b) for $T=600$ K.

Appendix B. Transport Properties at Room Temperature

The calculated thermoelectric transport properties as a function of the doping concentration for n-type PbTe at 300 K including and excluding the temperature dependence of the electronic band structure (T-depBS) are illustrated in Fig. 5. The colored lines represent our calculations while the symbols show the measurements from various experiments [40, 51, 48, 49]. The calculated transport properties that account for the T-depBS are all in very good agreement with the measurements. Including the T-depBS yields lower mobility and conductivity, and higher absolute Seebeck coefficient.

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Figure B.9: Calculated and experimental dependence of (a) the mobility, (b) the conductivity, (c) the absolute Seebeck coefficient and (d) the power factor on the doping concentration at $T = 300$ K. Experimental data are shown in squares (Ref. [51]), circles (Ref. [48]), triangles up and down (Ref. [40]), and crosses (Ref. [49]).

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