Strong intervalley electron-phonon couplings in monolayer antimonene: revisited studies on the band-convergence strategy to enhance thermoelectricity

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Abstract

The strategy of band convergence of multi-valley conduction bands or multi-peak valence bands has been successfully used to understand or help researchers design more efficient thermoelectric materials, or guide the discovery of new thermoelectric materials. However, the phonon-assisted inter-valley scatterings due to multiple band degeneracy are generally neglected in the traditional context of band-convergence strategy, owning to computational simplifications or experimental difficulties. However, the electron-phonon coupling may play the key role in determining the electronic part of thermoelectric figure of merits. In this work, by using first-principles method, we investigated in details the (thermo)electric properties of monolayer β- and α-antimonene (Sb) considering full mode-resolved electron-phonon interactions. Our calculations reveal strong intervally-scattering between the nearly degenerate electronic valley states in both β- and α-Sb, and the deformation potential approximation based on the coupling between valley electrons and longitudinal acoustic phonons fails to describe accurately the electron-phonon scattering and thermoelectric transport properties in these multi-valley non-polar systems. As a result, by considering full electron-phonon interactions based on the rigid-band approximation, the maximum value of thermoelectric figure of merit $zT$ at room temperature reduces to 0.37 in β-Sb, by a factor of 5.7 comparing to what is predicted based on the constant relaxation-time approximation. Our work not only provides a more accurate method to theoretically investigate the thermoelectric performance of materials, but also manifests the key role of intervalley scatterings in evaluating the carrier conductivities. Our work shows that the band convergence of multi-valley is less beneficial in materials where the intervalley scattering is strong.
The thermoelectric (TE) performance of a material is quantified by a dimensionless figure of merit $zT$ ($zT = S^2\sigma T/(\kappa_e + \kappa_l)$), where $S$ represents the Seebeck coefficient, $\sigma$ is the electron conductivity, and $\kappa_e/l$ is the electronic/lattice thermal conductivity. Good TE materials generally possess good power factor $PF$ ($PF = S^2\sigma$) and poor thermal conductivity $\kappa$ ($\kappa = \kappa_e + \kappa_l$). However, the three electronic properties $S$, $\sigma$ and $\kappa_e$ are tightly coupled together, e.g., an increasing carrier concentration leads to increasing $\sigma$ and decreasing $S$ simultaneously, thus making optimization of the TE performance a daunting task. As a relatively independent quantity in $zT$, much effort has been put to reduce the $\kappa_l$ and thus to enhance $zT^{1,3}$. Past decades have witnessed the significant improvements in $zT$s, owing to the discovery of many new high-performance TE materials and several newly-emergent strategies to improve $zT$s. On the other hand, it is noted the Seebeck coefficient $S$ is proportional to the density-of-states effective mass $m^* = N_v^{2/3} m_b^*$ where $N_v$ is the band degeneracy and $m_b^*$ is the band effective mass$^{4,5}$, while $\sigma$ is inversely related with the effective mass $m^*$. Hence, high $N_v$ and low $m_b^*$ is beneficial for TE performance by achieving high $\sigma$ and $S$ simultaneously.

The $\beta$-Sb possesses complex layer-number-dependent electronic properties, which undergoes a topological transformation from a topological semimetal to a topological insulator at 22 bilayers, then to a quantum spin Hall (QSH) phase at 8 bilayers, and finally to a topologically trivial semiconductor with narrow bandgap when thinning down to 3 bilayers or thinner$^6$. Zhou et al. proposed an efficient way to realize both the large intrinsic QSH and anomalous Hall conductivity in a single honeycomb Sb monolayer grown on a ferromagnetic MnO$_2$ (H-MnO$_2$) layer$^{7,8}$. Experimentally, monolayer and few-layer $\beta$-Sb have been successfully synthesized with large scale and high quality, which can be applied in thermophotovoltaic devices, perovskite solar cell as a hole transport layer material and electrocatalysis technologies$^9$. Compared with $\beta$ structure, it is still challenging to fabricate $\alpha$-Sb although small patches of $\alpha$-Sb have been observed on islands of $\alpha$-Bi$^{10}$. Recently, Shi et al successfully synthesized $\alpha$-Sb on the substrate of bulk T$_{d}$-WTe$_2$ with tunable layers by using MBE technique$^{11}$. Monolayer $\alpha$-Sb is chemically stable when exposed to environment and possesses good electrical conductivities.

The crystal and electronic band structure of monolayer Sb are shown in Fig. S1 and Fig. S2(a, b). Both monolayer $\alpha$- and $\beta$-Sb possess convergence of multi-valley conduction bands attributed to the orbital degeneracy and crystal symmetry, which is believed to be
beneficial to the high TE performance in materials.\textsuperscript{14,12,15} As shown in Fig. 1, the conduction bands of $\beta$-Sb possess the local band-minima of $G$ and $F$ besides the global CBM of $H$, with respective minimum energies of $E_F = 250$ meV and $E_G = 290$ meV above the CBM of $V_H$ along the $\Gamma - M$ direction. For monolayer $\alpha$-Sb, more energy valleys appear with the respective energies of $E_J = 110$ meV, $E_K = 220$ meV and $E_L = 260$ meV above the global CBM of $I$. According to our previous calculations on electronic properties and thermoelectric performance of aw-Sb monolayer based on the constant relaxation-time approximation (CRTA),\textsuperscript{16,17}, which is a commonly employed approximation in the TE community, the $zT$ value of $\alpha$-Sb reaches 0.90 at room temperature (RT), which is higher than SnSe at RT and can be further optimized to 1.2 with tensile strain.\textsuperscript{17,18} For $\beta$-Sb monolayer, in spite of its large band gap (1.25 eV) compared with conventional high-$zT$ materials, the CRTA-based calculations give a $zT$ value reaching 2.15 at RT, which is far superior to conventional thermoelectric materials.\textsuperscript{19} However, special care should be taken for the system with band convergence of multi-valley conduction bands or multi-peak valence bands, when evoking the CRTA, which is generally obtained from the deformation potential approximation (DPA) theory for non-polar semiconductors, by considering only the coupling between electron and longitudinal acoustic (LA) phonons in the long-wavelength limit.\textsuperscript{20,23}

In fact, the DPA theory might fail and misestimate the electron relaxation-time $\tau$ and then the intrinsic carrier mobility $\mu$ for non-polar semiconductors with band convergence for three reasons: (1) Within the intra-valley scatterings, the contribution to $\tau$ from phonon modes other than LA phonon is neglected; (2) For band-convergence systems, the inter-valley scattering of phonons may be considerably large; (3) The widely used deformation potentials in DPA method are calculated along specific directions which is approximately correct for simple parabolic valley/peak, but fails for highly anisotropic valleys/peaks. As an example, for monolayer stanene, the intrinsic carrier mobility $\mu$ predicted by the DPA theory is equal to $\sim 10^6$ cm$^2$V$^{-1}$s$^{-1}$ at RT, but reduces to $2 \sim 3 \times 10^3$ cm$^2$V$^{-1}$s$^{-1}$ when considering full electron-phonon ($el-ph$) couplings, which is consistent with experimental results.\textsuperscript{24}

The calculated phonon dispersions for $\beta$-Sb and $\alpha$-Sb are shown in Fig. S2 (c, d), and no imaginary frequencies can be found in both phonon dispersions which indicate their good thermodynamic stabilities at low temperatures. The maximum phonon energies for $\beta$-Sb and $\alpha$-Sb are 20.90 meV and 20.92 meV respectively, and both monolayers possess phonon
bandgaps around 13.0 meV with the respective values of 7.96 meV and 3.27 meV.

To accurately calculate the electronic conductivity $\sigma$, which also determines the electronic thermal conductivity $\kappa_{el}$ according to the Wiedemann-Franz law, i.e. $\kappa_e = L \sigma T$, here $L$ is the Lorenz number, the full $el$-$ph$ interactions in semiconductors should be investigated in details. For convenience, $\beta$-antimonene is investigated firstly, with the mode-resolved $el$-$ph$ scattering rate $(1/\tau_{nk})$ near $H$ valley at 300 K within 0.40 eV above the CBM shown in Fig. 2. For conduction electrons of $(nk)$ with the eigen-energies less than $E_F$, only the intra-valley scatterings are possible due to the small energies of phonons, with the total $el$-$ph$ scattering rates denoted by blue dots in Figs. 2(a,b) approximately equal to $\sim 2 \times 10^{14} \text{s}^{-1}$, which is two orders larger than that of stanene. By comparison, we found that the acoustic phonons contribute more than optical phonons for electrons within the $H$ valley below $E_F$. Among them, the out-of-plane flexual ZA phonons around $\Gamma$ point contribute dominantly to the total $el$-$ph$ scatterings, which is different from planar graphene in which LA phonons dominate, due to the broken $\sigma_h$-symmetry in antimonene. The buckled structure in antimonene monolayers increases the overlap of the $p_z$ orbitals thus electrons are more sensitive to the ZA phonons. In addition to the dominant contribution from flexual ZA phonons, TA and TO phonons also contribute significantly to total intra-valley $el$-$ph$ scatterings within $H$ valley. The $\sigma_h$-symmetry in graphene ($D_{6h}$) and MoS$_2$ ($D_{3h}$) restricts the lattice potential associated with the flexural displacement to be odd with respect to $\sigma_h$, leading to the vanishing of odd ZA phonons in the $el$-$ph$ matrix element according to the Mermin-Wagner theorem. Hence, the coupling of electrons and ZA phonons is
suppressed in non-polar monolayer semiconductors with $\sigma_h$-symmetry, and the DPA method based on electron-LA phonon coupling works indeed.

The inter-valley scatterings of electrons from $H$ to $F$ valley via phonons with large momentums are possible when the electronic energy is higher than $E_F$, and $H - G$ inter-valley scatterings are allowed as well when the chemical potential is tuned to higher than $E_G$. As a result, the total $el$-$ph$ scattering rate $\tau$ increases abruptly near $E_F$ and increases further when $E > E_G$, as shown in Fig. 2. The total $el$-$ph$ scattering rate around 0.38 eV is three times larger than that in the region where intra-valley scatterings dominate. By comparison, we found that, in the region where $E > E_F$ and intervalley scatterings dominate, acoustic phonons also contribute more than optical phonons to the total $el$-$ph$ scatterings. For pure $H - F$ intervalley scatterings of electrons with energies in the region $E_F$ and $E_G$, flexual ZA phonons dominate the total $el$-$ph$ scatterings, and the contributions from TA, TO and LO phonons increase when $E$ increases, and become comparable near $E_G$. When the chemical potential of $E$ increases larger than $E_G$ and further, the contribution from TA phonons increases more rapidly than ZA phonons, and becomes larger than ZA phonons near 3.7 eV. However, in this region where both $H - F$ and $H - G$ intervalley scatterings are allowed, the contributions from ZA, TO and LO phonons to total $el$-$ph$ $\tau$ are not negligible compared with that from the dominant TA phonons.

To further reveal the $el$-$ph$ scatterings of the conduction electrons via different phonon modes, the mode-resolved scattering rates of conduction electrons of $\beta$-Sb as a function of wave vector $k$ located in the first Brillouin zone are shown in Fig. 3. The distribution of the $el$-$ph$ couplings of conduction electrons for $\beta$-Sb also exhibits sixfold rotation-symmetry. For $H$-valley electrons, it is obvious as shown in Fig. 3 that, flexual ZA phonons dominate the intravalley scatterings, which is in good agreement with the above discussions. Similarly, we found that, scatterings of $F$-valley electrons are dominated by LA, TO, LO and ZO phonon modes, and scatterings of $G$-valley $G$ electrons are dominated by LA and ZO phonons.

The mode-resolved scattering rates of holes for $\beta$-Sb are shown in Fig. S4. Since the maximum of valence bands is well larger than the second peak, only intra-peak scatterings of holes are allowed for shallow doping. In contrast to the general conclusion discovered in group-IV elemental materials (Silicene, Silicene, Stanene) that, the carriers (electrons and holes) in 2D semiconductors with $D_{3d}$ symmetry dominantly suffer from scatterings via ZA phonons, holes in $\beta$-Sb suffer dominantly from scattering via LA phonons. For group-
FIG. 2: The scattering rate of electrons in the $H$ valley with energies within $\sim 0.4$ eV of the CBM. (a) The contributions of acoustic branch phonons to the total scattering rate. (b) The contributions of optical branch phonons to the total scattering rate. Atomic displacements of phonon modes are also shown in the figure. The sequences are according to the phonon energies seen in Fig. S2(c, d).

IV elemental materials with $D_{3d}$ symmetry, the band structure near CBM and VBM are dominantly attributed to the $p_z$ orbitals, thus the electrons and holes are dominantly scattered by ZA phonons, due to the fact that the phonon-induced variation of the self-consistent potential relates to the overlap of atomic orbitals. For $\beta$-Sb, the VBM is mainly attributed to $p_x$ and $p_y$ orbitals of Sb atoms, and the absence of $p_z$ orbitals to VBM compared with CBM, makes holes less sensitive to out-of-plane vibrations compared with conduction electrons.

Secondly, the mode-resolved $el-ph$ scattering rates ($1/\tau_{nk}$) near $I$ valley at 300 K within 0.40 eV above the global CBM for $\alpha$-Sb are shown in Figure. Composed with $\beta$-Sb, which exhibits rapid growth of electron-phonon interaction near the CBM band edge, the carrier scattering rate in $\alpha$-Sb is close to zero within the energy range of $\sim 0.1$ eV, which means that, the intravalley scatterings of $I$-valley electrons are weak. When the chemical potential exceeds $E_J$, $I - J$ intervalley scatterings are allowed, and the total $el-ph$ scattering rates increase due to the enhanced scatterings by the combination of LA, LO$_1$, TO$_1$ and TO$_2$.
FIG. 3: The scattering rate of electrons in the conduction band for $\beta$-Sb as a function of wave vector $k$ at first Brillouin zone. The labels $\Gamma$, $M$ and $K$ represent the high symmetry point of wave vector $k$.

phonons. When the electronic energies are higher than $E_K$, $I-K$ intervalley scatterings are allowed leading to the rapid increase of the total $el-ph$ scattering rate, mainly attributed to LA, LO$_1$, TO$_1$, TO$_2$ and LO$_3$ phonons. When the chemical potential increases further and larger than $E_L$, an enhancement of the total $el-ph$ scattering rates with five times larger than those where only $I-J$ intervalley scatterings are allowed, can be identified. The considerable enhancement is mainly due to the additive scatterings via TA and ZA phonons, as shown in Figure 4(a).

The mode-resolved $el-ph$ scattering rates of holes along $\Gamma-Y$ direction within $\sim 0.4$ eV below the VBM for $\alpha$-Sb are shown in Figure S7. Similarly with $\beta$-Sb, the energy level of VBM for $\alpha$-Sb is well above the second peak, only the intravalley scatterings of holes are considered. It is clear that, The total $el-ph$ intravalley scattering rates of holes are mainly attributed to the combination of ZA, LA, LO$_1$ and TO$_2$ phonons.

Based on the calculated mode-resolved $el-ph$ scattering rates of electrons and holes, the carrier mobility can be calculated by solving the Boltzmann transport theory and written as,
FIG. 4: The scattering rate of electrons in the $I$ valley for $\alpha$-Sb with energies within $\sim 0.4$ eV of the CBM. (a) The contributions of acoustic branch phonons to the total scattering rate. (b-d) The contributions of optical branch phonons to the total scattering rate.

$$
\mu_{\alpha\beta} = \frac{-e}{n_e \Omega} \sum_{n\in CB} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \frac{\partial f^0_{nk}}{\partial \epsilon_{nk}} v_{nk,\alpha} v_{nk,\beta} \tau_{nk}
$$  \hspace{1cm} (1)

where $n_e$ is the electron density, $\Omega$ and $\Omega_{BZ}$ denote the volume of the unit cell and the first Brillouin zone, respectively, $v_{nk,\alpha} = h^{-1} \partial \epsilon_{nk}/\partial k_\alpha$ is the velocity of the single-particle $nk$ electron along $\alpha$ direction. Fine $k$ and $q$ meshes are needed to obtain the convergence of carrier mobility. In order to investigate the temperature-dependent mobilities, we first carried out the \textit{ab initio} molecular dynamics (AIMD) calculations to simulate the behavior of monolayer $\beta$-Sb and $\alpha$-Sb at 300 K, 500 K and 600 K respectively, and the results are shown in Fig. S4, which confirm the thermal stabilities of both $\alpha$- and $\beta$-Sb at these temperatures.

The calculated intrinsic temperature-dependent carrier mobilities for $\beta$-Sb and $\alpha$-Sb ranging from 100 K to 500 K are shown in Figure 5 as solid lines. The carrier mobilities decrease gradually as the increase of the temperature, which is due to more phonons excited at higher temperature. At 300 K, the calculated electron and hole mobilities for $\beta$-Sb are $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $61 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively, when considering full $el$-$ph$ interactions for
FIG. 5: The calculated carrier mobility for electrons (solid line) and holes (dashed line) for (a) $\beta$-Sb and (b) $\alpha$-Sb.

electrons and holes. As a comparison, the calculated electron and hole mobilities at 300 K given by the DPA method which only considering the coupling between electrons/holes and LA phonons, are 785 cm$^2$V$^{-1}$s$^{-1}$ and 205 cm$^2$V$^{-1}$s$^{-1}$, respectively, which are 19.6 and 3.4 times larger than those calculated based on full $el$-$ph$ interactions. The relatively smaller ratio of hole mobilities compared with electron mobilities is due to the fact that, the intravalley scatterings of holes via LA as well as TO phonons play the key role in determining hole mobilities for $\beta$-Sb, which is partly similar to the underlying mechanism of the DPA method. When only considering the interactions between long-wavelength acoustic branches of phonons and the electrons/holes near the CBM and VBM, and excluding the intervalley-scattering events using the Atomistix ToolKit (ATK) package, the calculated electron and hole mobilities at 300 K are 150 cm$^2$V$^{-1}$s$^{-1}$ and 510 cm$^2$V$^{-1}$s$^{-1}$, respectively, which are 4 and 8 times larger than this work. The deviation reveals the importance of intervalley scattering to the carrier mobilities in $\beta$-Sb.

The calculated electron and hole carrier mobilities for $\alpha$-Sb at 300 K along $a$ and $b$ directions considering full $el$-$ph$ interactions are 5370 cm$^2$V$^{-1}$s$^{-1}$ and 8635 cm$^2$V$^{-1}$s$^{-1}$, and 4961 cm$^2$V$^{-1}$s$^{-1}$ and 9818 cm$^2$V$^{-1}$s$^{-1}$, respectively. As a comparison, the modified DPA method gives electron and hole mobilities at 300 K along $a$ and $b$ directions of 2125.62 cm$^2$V$^{-1}$s$^{-1}$ and 6818.51 cm$^2$V$^{-1}$s$^{-1}$, and 2593.66 cm$^2$V$^{-1}$s$^{-1}$ and 17313.09 cm$^2$V$^{-1}$s$^{-1}$.

The Seebeck coefficients $S$, electronic conductances $\sigma$ and electronic thermal conductivities $\kappa_e$ based on the rigid-band approximations for $\beta$- and $\alpha$-Sb are calculated and shown...
FIG. 6: The (a) seebeck coefficients (b) electrical conductivity (c) electronic thermal conductivity and (d) $zT$ value as a function of chemical potential at 300 K for $\beta$-Sb.

in Figs. 6(a-c) and Figs. 7(a-c), respectively. For comparison, the electronic parts in the $zT$ parameter of $S$, $\sigma$ and $\kappa_e$ are calculated based on the constant relaxation time approximation (CRTA) and full el-ph interactions respectively, and both CRTA and full el-ph calculations are performed using the BoltzTrap2 package$^{30}$. For CRTA calculations, the constant electronic relaxation time (new-$\tau$) is obtained according to the DPA method as listed in Table S1. The Seebeck coefficient $S$ is insensitive to electron-phonon couplings and reaches nearly 1500 $\mu$V/K when the chemical potential is $\pm 0.13$ eV. As we know, $S$ can be determined by the well-known Mott relation,

$$S = \frac{2k_B T}{3e\hbar^2} m_{DOS} \left( \frac{\pi}{3n} \right)^{2/3},$$  \hspace{1cm} (2)

where $n$ is the carrier concentration, and $m_{DOS} = n_d m^*$, in which $n_d$ is the number of degenerate valleys or peaks. The band convergence of multi-valley conduction bands or multi-peak valence bands enlarges $m_{DOS}$, thus the Seebeck coefficient $S$ is enhanced by $n_d$ times, compared with single parabolic conduction valley or valence peak.

However, as mentioned above, the introduction of multi-valley conduction bands or multi-
peak valence bands may introduce strong intervalley scatterings, which results in the enhancement of full \(el-ph\) scatterings. The electronic conductance of \(\sigma\) is related to the electron-phonon couplings via the formulae of \(\sigma = n e \mu\), where \(n\) is the concentration of carriers determined by the bandstructure and the Dirac-Fermi statistics.

The total thermal conductivities are the sum of the electronic thermal conductivities \(\kappa_e\) and the lattice thermal conductivities \(\kappa_l\), i.e. \(\kappa = \kappa_e + \kappa_l\). At low temperature, phonons are dominantly scattered by impurities and boundaries and \(\kappa_l\) is proportional to the square of the temperature, \(\kappa_l \propto T^2\) in two dimensions according to Debye model. When the temperature is well larger than Debye temperature \(\Theta_D\), Umklapp processes of phonon-phonon scattering dominates and \(\kappa_l \propto 1/T\). The calculated \(\Theta_D\) for \(\beta\)-Sb and \(\alpha\)-Sb are 98.4 K and 230 K (272 K) respectively. Thus at RT, the lattice thermal conductance \(\kappa_l\) inversely depends on temperatures. In addition, although the electron-phonon couplings may provide the lifetime to the total phonon lifetime according to the Mattiessen’s Rule, the lifetimes by electron scatterings to phonons, as shown in Fig. S8, are considerably small and can be neglected. Hence, we calculated \(\kappa_l\) by only considering three-phonon scatterings.

The dimensionless figure of merit \(zT\) for \(\beta\)- and \(\alpha\)-Sb are subsequently calculated and shown in Fig. 6(d) Fig. 7(d), respectively. At 300 K, a maximum value of \(zT \sim 1.88\) at \(E_f = 0.62\) eV for \(\beta\)-Sb under CRTA is realized, compared with conventional thermoelectric materials like \(\text{Bi}_2\text{Te}_3\) (1.2), \(\text{PbTe}\) (0.30), \(\text{SnSe}\) (0.70). However, for more accurate calculations and comparison with experiments, when we considered full \(el-ph\) interactions, the maximum \(zT\) value decreases by 5.1 times due to the sharp decrease of electronic conductance of \(\sigma\).

For \(\alpha\)-Sb along a direction (Fig. 7), the Seebeck coefficient \(S\) is also not sensitive to the consideration of the relaxation time as \(\beta\)-Sb and the peak position and value are all consistent with our previous results. The curves of \(\sigma\) and \(\kappa_e\) in CRTA near \(E_f = 0\) are in good agreement with the full electron-phonon coupling results. This is due to the fact that the constant relaxation time obtained using modified DPA method is consistent with the full electron-phonon coupling theory at CBM(VBM)(\(\sim 10^{-13}\) s). However, with the increase of \(E_f\), \(\sigma\) and \(\kappa_e\) in CRTA deviate far from the actual value due to the underestimation of scattering rate which is further amplified by the increase of injected carrier concentration. Fig. 7(d) shows the calculated \(zT\) for \(\alpha\)-Sb within two methods. We can find that in CRTA the maximum occurs at \(E_f = -0.08\) eV with \(zT=1.78\) which is very close to the full electron-
FIG. 7: The (a) seebeck coefficients (b) electrical conductivity (c) electronic thermal conductivity and (d) $zT$ value as a function of chemical potential at 300 K for $\alpha$-Sb along $a$ direction.

phonon coupling result but nearly twice of our previous result (0.90). It is attributed to that the widely used DPA method is a rough approximation to evaluate the mobility of anisotropic materials which assumes that moving carriers would be scattered by phonons from the same direction. Hence, the calculated relaxation time is smaller by an order for holes along a direction (Table S1) which leads the undervaluation of $\sigma$ near $E_f = 0$. For electron injection situation ($E_f > 0$), the maximum $zT$ is 1.62 under the CRTA theory larger than the result of 1.13 under the full electron-phonon coupling theory which is mainly due to the neglect of the intervalley scattering effect. The case for $b$ direction is shown in Fig.S9. We can get a conclusion that the CRTA theory is a good approximation to describe the carrier transport properties for light doped $\alpha$-Sb and also a good approach to evaluate the TE performance of p-type $\alpha$-Sb.

In summary, we systematically analyze the electron-phonon interactions in $\beta$- and $\alpha$-Sb. For $\beta$-Sb, the ZA phonon scattering is dominant similar to the 2D stanene and the intervalley channels play an important role to the scattering of electrons. The calculated
electron mobilities are $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature, which are reasonably smaller than the DPA results. For holes in $\beta$-Sb, DPA method gives a good approximation due to the fact that the LA phonons dominate the scattering process. As a result, the maximum $zT$ value at room temperature experiences almost 5.1 times reduction to 0.37 when injecting electrons. For $\alpha$-Sb, the carriers at band edge experience little scattering by phonons and LA branch contributes most. Thus, $\alpha$-Sb maintains ultrahigh carrier mobilities in a wide temperature range and the DPA methods can work to some extent. However, due to neglect of intervalley scattering effect, the maximum $zT$ value decrease to 1.13 for n-type $\alpha$-Sb along $a$ direction. Therefore, to the multi-band system, the $zT$ value can be underestimated for TE application using the constant relaxation time from DPA and the intervalley scattering can not be simply ignored.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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