Valleytronics in thermoelectric materials

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The central theme of valleytronics lies in the manipulation of valley degree of freedom for certain materials to fulfill specific application needs. While thermoelectric (TE) materials rely on carriers as working medium to absorb heat and generate power, their performance is intrinsically constrained by the energy valleys to which the carriers reside. Therefore, valleytronics can be extended to the TE field to include strategies for enhancing TE performance by engineering band structures. This review focuses on the recent progress in TE materials from the perspective of valleytronics, which includes three valley parameters (valley degeneracy, valley distortion, and valley anisotropy) and their influencing factors. The underlying physical mechanisms are discussed and related strategies that enable effective tuning of valley structures for better TE performance are presented and highlighted. It is shown that valleytronics could be a powerful tool in searching for promising TE materials, understanding complex mechanisms of carrier transport, and optimizing TE performance.

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INTRODUCTION

The demand for renewable energy harvesting has been growing because of the limited fossil fuels and increasing worldwide energy consumption. Thermoelectric (TE) materials, which have the capability of converting heat directly into electricity under a temperature gradient, have been regarded as an alternative option to alleviate energy shortage.1 Though TE devices have already been applied in deep space exploration and solid state cooling, the relatively low energy conversion efficiency limits their widespread commercialization, which is mainly constrained by the performance of TE materials as characterized by the dimensionless figure of merit, $zT = \frac{\alpha^2 \sigma T}{\kappa_L}$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa_L$ and $\kappa_e$ are, respectively, the electronic and lattice contributions to the total thermal conductivity, $\kappa_e$ and $T$ is the absolute temperature.5 Since all three physical properties ($\alpha$, $\sigma$, and $\kappa$) are carrier concentration dependent, $zT$ could reach its maximum value at an optimized carrier concentration. $zT_{\text{max}}$ is determined by a combination of intrinsic physical parameters as well as the temperature, all of which integrated into a term called the TE quality factor, $B$. Higher quality factor $B$ leads to higher $zT_{\text{max}}$ at a fixed temperature. With a single parabolic band model in the nondegenerate limit, $B$ could be expressed as:

$$B = \frac{2k_B^2}{e^2h^2} \left( \frac{\kappa_L^0 m_0^* \mu_0}{2\pi} \right)^{3/2} \frac{\mu_0 \gamma^{3/2}}{k_L}$$

where $k_B$ is the Boltzmann constant, $h$ is the reduced Plank constant, $e$ is the electron charge, $\mu_0$ is the carrier mobility in the nondegenerate limit, $m_0^*$ is the effective mass for a single valley.

Recent TE research demonstrates outstanding progress with $zT$ values exceeding the barrier of unity easily and sometimes even above 2, due to inspirations by the low-dimensional design for TE materials and the Phonon-Glass-Electron-Crystal concept proposed in 1990s.11 The rational design strategies for $zT$ enhancement, together with the underlying mechanisms toward high TE performance, can be classified into two categories. One is the reduction of $\kappa_L$ and the other is the increase of TE power factor (PF, $\sigma^2 \alpha$).12,13 The current realization of large $zT$ enhancement ($zT > 2$) is mainly due to the significantly reduced $\kappa_L$, e.g., with all-scale hierarchical phonon scattering,14 using materials with strong anharmonicity,15 and discovering liquid-like phonon behavior.16 Some excellent reviews focusing on the thermal transport aspects of TE study as well as several good comprehensive TE reviews introducing the synergistic design strategies of TE materials have been published in recent years.17,18

Nevertheless, there exists a threshold for $zT$ improvement from reducing the thermal conductivity, which is limited to a theoretical minimum (amorphous limit).20 In contrast there is no theoretical bound to the PF, which leads to the boundless nature of $zT$.22 TE materials are mostly heavily doped semiconductors. It is only the bottom part of conduction band or the top part of valence band that determines the electrical transport properties. This specific dispersive region in the electronic band structure is named as energy valley or carrier pocket due to the morphology of fermi surface. As the $\alpha$ and $\sigma$ are highly coupled physical parameters, adjusting the electron chemical potential with changing the doping level would only get a limited maximum PF. Therefore, it is necessary to alter the valley structure in order to improve the TE performance.

The term “Valleytronics” relates to the approaches that adjust the parameters describing the conduction valleys.24,25 This idea, similar to spintronics, was initially applied to construct new quantum computation devices, which tune the valley polarization to store and carry information.26,27 Subsequent applications of this concept include designing new optoelectronic devices and ferrovalley materials (Fig. 1).26,27 Here, this concept is extended to the TE field to include strategies for $zT$ enhancement concerning the modification of valley structures, which is the
main aim of this review. There are three valley parameters that allow for modification (seen in Fig. 2): the number of valleys contributing to the electronic transport (valley degeneracy), the distortion of density of states (DOS) by resonant dopants (valley distortion), and the exact shape of valleys which can be expressed as the effective mass of carriers (valley anisotropy). The approaches that enable effective tuning of valley structures for better TE performance are presented and discussed below.

VALLEY DEGENERACY

Valley degeneracy \( N_v \) is a quantitative description for the number of valleys that contribute to the carrier transport.\(^{28}\) Compared to the single valley case, TE materials with multiple valleys possess more states for carriers to occupy and contribute to transport. Thus, the valley degeneracy \( N_v \) should be taken into account such that the DOS effective mass \( m_d^* = N_v^{2/3} m_b^* \) assuming each valley has the same \( m_b^* \) to the single valley case is used in Eq. (1), instead of \( m_b^* \). To better elucidate the role of \( N_v \) on the TE performance, it is necessary to unfold the mobility term and rewrite Eq. (1) under the deformation potential theory when acoustic phonon scattering dominates in the scattering process,\(^{29}\)

\[
B = T \frac{2k_B^2 \hbar}{3\pi} \frac{C_i N_v}{m_I^* \Xi \kappa_L}.
\]

where \( C_i \) is a combination of elastic constants, \( m_I^* \) is the inertial effective mass, and \( \Xi \) is the deformation potential. For an isotropic band structure, \( m_I^* = m_b^* \).

Larger \( N_v \) increases DOS effective mass \( m_d^* \), leading to higher \( \alpha \) at the same carrier concentration, meanwhile it has no influence on the \( m_b^* \) that relates to carrier mobility (\( \mu \)). Therefore, large \( N_v \) generally leads to a high PF and hence good TE performance.\(^{30}\) However, it has to be pointed out that in the multi-valley case the scattering of carriers between different valleys (inter-valley phonon scattering) could bring detrimental effect on \( \mu \) and leads to a deviation from the estimated \( zT \) value based on the model mentioned above.\(^{31}\) As studies on the influence of the inter-valley scattering on TE performance are scarce, no practical criterion has been proposed so far to determine if a certain TE material with multi-valley band structure would suffer from inter-valley scattering. To our knowledge, optimistic view could be normally held that such influence, detrimental though it is, is not significantly influential for multi-valley TE materials, as seen from the study on
Indeed, the reason for high PF, as confirmed by theoretical calculations and experimental measurements, the actual convergence temperature is above 700 K, much higher than the previous results. Moreover, as the Fermi energy in heavily doped TE semiconductors usually lies deep in the valence band, the secondary valence band should have considerable contribution to the carrier transport and lead to enhanced PF, even before the valley convergence actually happens.

Besides valley convergence due to different temperature dependence of multi-valleys, valley convergence could also result from optimized valley positions through alloying. Many experimental works were performed with alloying to adjust the convergence temperature to desired range. The band structure modifications of PbTe-based materials through isovalent alloying with certain kinds of point defects lead to valley convergence, thus resulting in increased $N_v$ and enhanced PF. PbSe and SnTe are among the limited class of TE materials that possess such band features. The valence band structure of PbTe consists of two distinct valleys with different temperature dependence. The higher one which determines the energy gap at room temperature is located at L point ($N_v = 4$) in the Brillouin zone, while the lower and heavier one is along the Γ–K line, labeled as Σ ($N_v = 12$) as shown in Fig. 3a. The energy position of L valley lowers down with increasing temperature, while the energy position of Σ valley changes little, as seen in Fig. 3b. These two valleys become converged at high temperature, leading to enhanced PF as well as higher optimized carrier concentration. Though such temperature-dependent energy valley convergence was first proposed in early 1960s, huge success on experiments for TE investigations was reported 40 years later by Pei et al., which inspires a new wave of research on both the optimizations of TE performance and the investigation of intrinsic mechanisms related to this valley convergence behavior.

To date, the study of the mechanisms on temperature-induced valley convergence is still at the stage of rationalization and requires further efforts. Lattice thermal expansion is always regarded as the first reason leading to the increase of electronic band gap with increasing temperature (the lowering L valleys in energy position, seen in Fig. 3b). Moreover, a thermal-disordered lead chalcogenide structure (Pb atoms are moved further off-centered compared to the chalcogenide atoms with increasing $T$) was proposed and adopted to fully explain the temperature-dependent band convergence of lead chalcogenides. Theoretical calculation of this thermal-disordered structure based on ab initio molecular dynamics has been performed and finds that the convergence temperature for PbTe is about 450 K, which is consistent with the former experimental results from electrical and optical measurement with photon energies less than the fundamental gap. However, recent free carrier absorption measurements, temperature-dependent angle-resolved photoemission spectroscopy study, and theoretical calculations reveal that the actual convergence temperature is above 700 K, much higher than the previous results. Moreover, as the Fermi energy in heavily doped TE semiconductors usually lies deep in the valence band, the secondary valence band should have considerable contribution to the carrier transport and lead to enhanced PF, even before the valley convergence actually happens.

Effect of temperature and alloying

Different temperature dependence of multi-valleys (with the valley edges located at different points in the Brillouin zone) might lead to valley convergence, thus resulting in increased $N_v$ and enhanced PF. PbTe and similar IV–VI rock-salt semiconductors like Mg$_2$(Si, Sn)$_3$, SiGe alloys, and other good TE materials are among the limited class of TE materials that possess such band features. The valence band structure of PbTe consists of two distinct valleys with different temperature dependence. The higher one which determines the energy gap at room temperature is located at L point ($N_v = 4$) in the Brillouin zone, while the lower and heavier one is along the Γ–K line, labeled as Σ ($N_v = 12$) as shown in Fig. 3a. The energy position of L valley lowers down with increasing temperature, while the energy position of Σ valley changes little, as seen in Fig. 3b. These two valleys become converged at high temperature, leading to enhanced PF as well as higher optimized carrier concentration. Though such temperature-dependent energy valley convergence was first proposed in early 1960s, huge success on experiments for TE investigations was reported 40 years later by Pei et al., which inspires a new wave of research on both the optimizations of TE performance and the investigation of intrinsic mechanisms related to this valley convergence behavior.

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substitutions by Mn, IIB, and IIA elements were originally studied before 1980s, and have been revisited with intensive investigation for TE applications. Compared to lead chalcogenides, the strategy of valley convergence through alloying plays a more important role in the $zT$ enhancement for SnTe, since the room temperature energy offset between L and $\Sigma$ valleys for SnTe is much higher (~0.3 eV for SnTe, ~0.1 eV for PbTe). Hence, more amounts of dopants or more effective dopants are needed to lower down the valley convergence temperature. It is reported that Mn has relatively high solubility in SnTe (>9 mol%), and that the valley convergence temperature could be adjusted to below 450 K for SnTe when doped with 9 mol% Mn, leading to 40% increase for PF compared with pristine SnTe.

Forming solid solutions between the sister compounds with inverse valley configurations in energy is an effective approach to realize valley convergence. As composition varies, the energies of converging valleys change in opposite direction such that valley convergence could be achieved at a specific composition, given that the required composition is within the solubility limit.

N-type Mg$_x$X-Mg$_2$Sn ($X = $ Si, Ge) solid solutions are typical examples illustrating how valley degeneracy can be increased through alloying. In Mg$_x$X above the conduction band minimum, there exists another sub-band which usually does not contribute to the transport due to large splitting energy from the band minimum (~0.4 eV for Mg$_2$Si and 0.16 eV for Mg$_2$Sn). As the two conduction band edges (one heavier and another lighter) are reversely positioned in Mg$_x$Sn, compared with that in Mg$_2$Si and Mg$_2$Ge, it is possible to converge these two band edges (with splitting energy = 0) through alloying, as revealed in Fig. 4a. A PF as high as ~50 $\mu$W cm$^{-1}$ K$^{-2}$ is reached in both quasi-binary and quasi-ternary solid solutions of Mg$_x$X-Mg$_2$Sn when the alloy compositions are tuned within the convergence range.

Some solid solutions of II-V materials also exhibit similar band crossing features, though this class of materials is less favorable in the TE research field due to their high thermal conductivity. For example, InP and GaP have similar band features with three band edges at $L$, $\Gamma$, and $X$ points, valley degeneracy for each band being 4, 1, and 3; however, the conduction band minimum of InP and GaP is located at $\Gamma$ point and $X$ point, respectively. In the n-type Ga$_{1-x}$In$_x$P solid solutions, as the Ga concentration increases from 0 to 1 the conduction band minimum changes from $\Gamma$ to L point at $x = 0.67$ and then from L to X point at $x = 0.77$, leading to $N_v = 8$, higher than the valley degeneracy of each parent material. At $zT$ value close to 1 at 873 K is predicted for heavily doped n-type Ga$_{0.74}$In$_{0.26}$P.

### Symmetry change

While the electronic band structures are closely related to the symmetry of the crystal structures as mentioned above, it is very difficult to tune the system symmetry for a given TE material. Common methods involve phase transitions by tuning either directed substitutions by Mn, IIB, and IIA elements, via changing the system symmetry from non-cubic to pseudo-cubic structure. The crystal structure of tetragonal chalcopryites can be regarded as variants from the cubic zinblend structure with $N_v = 3$

![Fig. 4](image)

**Fig. 4** a Composition dependence of energy gaps for both the light and heavy one from the valence band maximum in Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions (inset is the schematic diagram for the band structure of Mg$_2$Si$_{1-x}$Sn$_x$ with regard to valence band maximum) (inset is the schematic diagram for the band structure of SnP).

(b) Composition dependence of $E_g$ for specific valleys in Ga$_{1-x}$In$_x$P. (Contributed by $\Gamma_{SV}$ ($N_v = 2$) and $\Gamma_{AV}$ ($N_v = 1$)). Ordered cation substitution with two kinds of metal atoms further lowers the symmetry leading to the chalcopyrite structure type $A^B^C^B$ as well as the observed crystal-field splitting, $\Delta CF = \Gamma_{SV} - \Gamma_{AV}$ which lowers $N_v$. Theoretical calculation reveals that $\Delta CF$ could be tuned to 0 when the crystal structure parameter $\eta$ is equal to 1 ($\eta = c/2a$, where $c$ and $a$ are lattice parameters for tetragonal chalcopyrites). This conclusion can be easily understood if putting two unit cells together as seen in Fig. 5b: the sub-lattice shows nearly cubic framework once $\eta = 1$. And this long-range cubic-like structure regains the three-fold valley degeneracy and keeps the localized non-cubic lattice distortion simultaneously, leading to an enhanced TE performance. Through rational alloying, the lattice parameters could be tuned into a desired range and this unity-$\eta$ design strategy (for tetragonal chalcopyrites with $\eta = 1$) could be realized experimentally, like the case in Cu$_{0.875}$Ag$_{0.125}$InTe$_{2.75}$.

**Size effect**

First introduced in the 1990s, the idea of using low-dimensional nanostructured TE materials to realize extraordinary enhancement of $zT$ has attracted numerous attention, due to both promising theoretical predictions and subsequent proof-of-principle experiments. When the size of TE materials is reduced to a critical
length scale, e.g., in an ultra-thin film of only a few nanometers thickness, the carrier transport in the direction perpendicular to the film is restricted and a quantum well in that direction is thus built. Due to the effect of quantum confinement, the original continuous energy dependence of DOS (DOS~\(E^{1/2}\)) near the band edge is altered to a step-like relationship,\(^7^9\) which helps gain a large \(\alpha\) and improve the PF.\(^9\) These effects would surely influence conduction valleys for TE materials. While the influence of low-dimensional nanostructures on the reduction of \(\kappa\) is relatively intuitive, the exact inner mechanisms for PF enhancement introduced by the low-dimensional structures are still controversial (e.g., a non-monotonous relationship between PF and system size was also proposed and qualitatively supported by some experiments).\(^8^0\) There have been some comprehensive reviews summarizing the current works on this aspect.\(^9,^8^1\)

For better focus, we only mention here the effects of low-dimensional nanostructures on the valley specificities. In the two-dimensional superlattice, this approach is also called the carrier pocket engineering as proposed in the theoretical study of \(n\)-type GaAs/AlAs 2D superlattices by Koga et al.\(^8^2\) The early work on 2D superlattices only consider the valley for bulk GaAs and AlAs can be seen in Fig. 6b. Such an reversed configuration makes it possible to reach valley convergence through forming solid solutions.\(^8^3\) However, the PF of Ga\(_{1-x}\)Al\(_x\)As solid solutions with composition in the valley convergence condition suffer greatly from the mobility reduction caused by inter-valley scattering.\(^3^8\) On the contrary, in the GaAs/AlAs 2D superlattice, due to the quantum confinement, the electrons in the \(\Gamma\) and \(L\) valleys are confined in the GaAs layers, whereas the electrons in the \(X\) valleys are confined in the AlAs layers. Since the electron wave functions for the \(\Gamma\) and \(L\) valleys are spatially separated from those for the \(X\) valleys, the inter-valley scattering between the \(X\) valleys and the \((\Gamma, L)\) valleys should be reduced and high mobility is expected to be maintained.\(^5^4\)

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**Fig. 5**  
(a) DOS of Bi\(_{2}\)Sb\(_2\)Se\(_3\) and Bi\(_2\)Se\(_3\), illustrating the structural transition-induced valley convergence in Bi\(_{2}\)Sb\(_2\)Se\(_3\); inset is the Fermi surface for Bi\(_{2}\)Sb\(_2\)Se\(_3\) (the upper one) and Bi\(_2\)Se\(_3\) (the lower one). Reproduced with permission.\(^7^4\) Copyright 2016, Royal Society of Chemistry.  
(b) Schematic diagram for the reduction of crystal-field splitting energy due to the pseudo-cubic structure in tetragonal chalcopyrites\(^7^5\)

**Fig. 6**  
(a) The schematic diagram for GaAs-AlAs superlattice;  
(b) energy offset of specific valleys in GaAs-AlAs superlattice;  
(c) layer thickness dependence of energy for different conduction valleys relative to the valence band maximum (superlattice period is fixed, \(d_{GaAs} + d_{AlAs} = 40 \text{Å}\); \(L_1\) and \(L_0\) refer to the pertinent conduction valleys in longitudinal and oblique orientations relative to [111] direction. Reproduced with permission.\(^1^2^8\) Copyright 2015, Elsevier B.V.
More importantly, by controlling the width of the quantum well (tuning the layer thickness of GaAs and AlAs, noted as \(d_{GaAs}\) and \(d_{AlAs}\)), the relative positions of three conduction valleys change in energy and effectively converge when the width is around 20 Å, as seen in Fig. 6c. As revealed by theoretical calculation, the \(zT\) of the whole system is increased by a factor of four compared with the superlattice case without the contribution of the X and L valleys.92

**RESONANT LEVELS**

Resonant levels refer to certain impurity energy levels in the host band structure that will cause a delta-function-like distortion to the DOS of the host material (the background DOS).85,86 Different from the routine doping, the energy states of the resonant dopants \((E_f)\) are located well above the conduction band minimum or right below the valence band maximum, coinciding in energy with the extended states (the electronic states responsible for electronic transports).87 As the resonant states has same energy with the extended states of conduction band, the resonance of these two will build up two other extended states of conduction band, which has same energy with the extended states of conduction band, and the relaxation time is highly dependent on the energy difference between the carriers and the resonant levels.90 Therefore, the effect of resonant scattering is similar to the energy filtering effect91 in nanocomposites that helps increase the Seebeck coefficient. However, as the resonant scattering tends to diminish with increasing temperature, compared with the phonon scattering, such “energy filtering” is only effective at low temperature. Therefore, the enhanced PF in TE semiconductors involving resonant doping should be mainly ascribed to the induced delta-like distortion of DOS.92

The typical example that demonstrates how TE performance could benefit from the resonant doping includes the TI-doped PbTe92 and Sn-doped Bi\(_2\)Te\(_3\).93 For TI-doped PbTe, optical measurements reveal that there exist the TI impurity levels about 0.06 eV below the valence band maximum,94 which is a favorable energy position to form resonant levels. Theoretical band structure calculations confirm that the TI impurity states hybridizing with Te 5p states create a distinctive “hump” in DOS, the width of which is relatively broad (~0.2 eV).90 Experimental work by Heremans et al. found the enhancement of Seebeck coefficient, compared with the Na-doped PbTe without resonant state formation at given hole concentrations, and a peak \(zT\) value of 1.5 in Pb\(_{0.98}\)Tl\(_{0.02}\)Te was attained.92 In the case of Sn-doped Bi\(_2\)Te\(_3\), the experimental proof of resonant levels was from Shubnikov-de Haas measurements combined with galvanomagnetic and thermomagnetic properties measurements. Strongly increased and nearly pinned Seebeck coefficient beyond the Pisarenko prediction was found for Sn-doped p-type single crystalline Bi\(_2\)Te\(_3\) at 300 K.93 As the mobility decrease is relatively moderate, overall PF for Sn-doped Bi\(_2\)Te\(_3\) could be enhanced via this approach. In the framework of Boltzmann transport theory with the simple parabolic band model, the Seebeck coefficient enhancement at a given carrier concentration due to resonant levels can be intuitively understood by the increased \(m^*\),30 which are also found from the theoretically calculated band structure diagrams.90,95 The influence of \(m^*\) on TE performance is discussed in more details in the next section. In short, the strategy by introducing resonant levels in TE materials to obtain better valley structures would inevitably bring a tradeoff on the mobility, as larger \(m^*\) not only benefits for \(\alpha\) but also lowers \(\mu\).96 The exact physical picture is yet more complicated and rather different from the simple consideration mentioned above. Nevertheless, further study of resonant levels as an approach of manipulating valley degree of freedom to optimize PF is worth conducting.

In addition to the two examples above, extensive experimental work concerning the resonant levels in semiconductors97–99 has been attempted for different classes of TE materials in the aim of enhancing the PF, such as In-doped100 or Co-doped101 SnTe, Cr-doped PbTe,102 Al-doped PbSe,103 Pb-doped BiCuSeO,104 etc.

Though various resonant levels can be introduced in TE materials, Seebeck coefficient may not be increased if the resonant states due to impurities are too localized and thus do not contribute to the TE transport, like in the case of \(n\)-type Ti-doped PbTe.105 Besides, since the Fermi level determined from the resonant dopant alone may not be optimized, additional normal dopants are needed to adjust the carrier concentration (if possible) to optimize \(zT\).106 Thus a broad “hump” in DOS is required to allow Fermi level adjustment by co-doping. In this regard, the resonant levels induced by transition metals with their \(d\) or \(f\) orbitals coupling with the matrix states are less favorable, compared to the one with coupling from the \(s\) or \(p\) orbitals, as the former usually forms very narrow DOS peaks.

![Fig. 7](image-url)
VALLEY EFFECTIVE MASS AND BAND ANISOTROPY

The effective mass, defined as a second-order tensor, can be expressed as a scalar $m^*$ with the assumption of a single parabolic band which results in a spherical Fermi surface in $k$-space. Tuning the flatness of a single valley (adjusting $m^*$) offers us another opportunity to optimize TE properties in the framework of valleytronics. Normally, lower $m^*$ is more favorable for TE materials, which could be seen from Eq. (2) and shown by both experiments and theory. The study on $p$-type (V,Nb)FeSb-based materials, a kind of HH alloys with excellent TE materials, which could be seen from Eq. (2) and shown by both valleytronics. Normally, lower $m^*$ helps lower the optimal carrier concentration, which was too high for a given TE material. Such a situation normally arises in cation substitution for $n$-type semiconductors or anion substitution for $p$-type semiconductors, where the resultant $m^*$ would usually be increased in proportion to doping. For example, Pei’s work on La-doped $n$-type PbTe clearly demonstrates that the cation substitution strategy for $n$-type semiconductors increases the $m^*$ of carriers, and thus, unfortunately, degrades the PF. Based on a simple Kane band model, the $m^*$ for La-doped PbTe is found to be 20% larger than that for I-doped $n$-type PbTe (anion substitution), which remains almost unchanged compared to PbTe, within all the temperature range considered. The electron mobility for La-doped PbTe is so severely decreased that the optimized maximum $zT$ is 20% lower than that of the I-doped one. Similar case can also be found in Li and Ga-doped $p$-type Mg$_2$(Si,Sn), where the Ga-doped ones possess much higher $m^*$ yet worse PF than the Li-doped ones.

The enhancement for TE performance through changing the value of $m^*$ is limited due to the counteractive effects on $\alpha$ and $\mu$. Nevertheless, these effects could be decoupled when the valley anisotropy is introduced. In the real circumstances, most semiconductors have anisotropic bands around the valley extrema. To the first order, the Fermi surface of these bands is often approximated as ellipsoids, characterized with effective masses along radial direction $(m^*_{\parallel})$ and longitudinal direction $(m^*_{\perp})$. The $m^*$ for a single valley $m^*_b$ is the geometric average of effective masses along each principle direction: $m^*_b = (m^*_{\parallel} m^*_{\perp})^{\frac{1}{2}}$, that is related to the Seebeck coefficient as well as the carrier concentration. While the inertial effective mass $m^*_i$ is defined as the harmonic average $m^*_i = \frac{1}{2}(m^*_{\parallel} + 2m^*_{\perp})^{\frac{1}{2}}$ and relates to the electronic transport behavior through mobility. Generally, the valley anisotropy is quantitatively defined as $K = m^*_b/m^*_i$. And a $K$-value larger than 10 is necessary to bring significant difference to the overall TE performance, as shown in Fig. 9.

The benefit of valley anisotropy can be understood in two aspects: on the one hand, with the increased degree of valley anisotropy (larger $K$-value), the Fermi surface in the Brillouin zone tends to elongate in certain directions to get both light and heavy channels, and the charge carriers would prefer to drift in the direction with lighter effective mass, gaining carrier mobility compared to that in an isotropic band. On the other hand, the original ellipsoid morphology turns to either “needle-like” or “plate-shaped”, which contributes low-dimensional transport feature and results in large $\alpha$, like the case in 2D superlattice quantum wells or 1D nanowires. Consequently, the anisotropic valley offers another possibility for decoupling $\mu$ and $\alpha$. The comparison between $n$-type PbTe and PbSe exemplifies the advantage of valley anisotropy to some extent. While the $m^*_b$ for both compounds is similar, the conduction valley of PbTe ($K = 8$) is more anisotropic than that of PbSe ($K = 2$), resulting in a higher $\mu$ and PF. Other TE materials that obviously benefit from this anisotropic valley morphology include $n$-type layered cobaltites, $n$-type rock-salt IV-VI compounds, etc.

To date, the efforts of manipulating the valley anisotropy to realize an enhanced TE performance are still limited to theoretical calculations. For example, in Fe$_2$VAl full Heusler semiconductor, the conduction valley at X point is mainly contributed by the $e_{g}$ states with dispersive band feature, above which exists another band with high anisotropy contributed by the $e_{g}$ states. First principles calculations find it possible to move the dispersive band at X point upper through substitutions of V and Al atoms, thus enabling the highly anisotropic valley dominate the electron transport. The PF values of 4–5 times larger than that in classical TE materials at room temperature are predicted for Fe$_2$TiSn ($K \approx 87$) and Fe$_2$TiSi ($K \approx 450$) with good thermodynamic stability. AgBiSe$_2$, known for intrinsically low thermal conductivity and multiple phase transitions with changing temperature, was found to have large valence valley anisotropy with one-dimensional “plate-shaped” carrier pockets based on recent DFT calculation on the

![Fig. 8 Hole concentration dependence of $\alpha$ Seebeck coefficient and $\mu$ mobility for Ti-doped V$_{0.8}$Nb$_{0.2}$FeSb with different $m^*_b$. The inset is the schematic of band structures of VFeSb (red solid line) and NbFeSb (blue dotted line). Reproduced with permission. Copyright 2015, Royal Society of Chemistry](image)
room temperature phase of hexagonal AgBiSe₂, for which a high $zT$ value of 0.7 at 300 K is also predicted. Further, high valley anisotropy can also be applied as a guideline in high-throughput calculation screening for new potential TE materials.\textsuperscript{114}

Valleytronics, which study the influence and manipulation of the band (or valley) morphology on the TE performance, could be a powerful tool in terms of searching new promising TE materials, understanding complex mechanism of carrier transport, and optimizing TE performance.

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AUTHOR CONTRIBUTIONS
J.Z.X. and Y.L.T. drafted this review. Y.T.L. offered important idea of the figures. X.B.Z. and H.G.P. gave essential criticisms and suggestions. T.J.Z. created the central idea of this review, constructed the framework, and revised it critically. All authors contributed to the writing of the manuscript.

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REFERENCES
1. He, J. & Tritt, T. M. Advances in thermoelectric materials research: looking back and moving forward. \textit{Science} \textbf{357}, eaak9997 (2017).
2. Pichanusakorn, P. & Bandaru, P. Nanostructured thermoelectrics. \textit{Mater. Sci. Eng. R Rep.} \textbf{67}, 19–63 (2010).
3. Bell, L. E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. \textit{Science} \textbf{321}, 1457–1461 (2008).
4. LeBlanc, S., Yee, S. K., Scullin, M. L., Dames, C. & Goodson, K. E. Material and manufacturing cost considerations for thermoelectrics. \textit{Renew. Sustain. Energy Rev.} \textbf{32}, 313–327 (2014).
5. Snyder, G. J. & Toberer, E. S. Complex thermoelectric materials. \textit{Nat. Mater.} \textbf{7}, 105–114 (2008).
6. Chasmar, R. P. & Stratton, R. The thermoelectric figure of merit and its relation to thermoelectric generators. \textit{J. Electron. Control} \textbf{7}, 52–72 (1959).
7. Nolas, G. S., Sharp, J. & Goldsmid, H. J. (eds) in \textit{Thermoelectrics: Basic Principles and New Materials Developments}, Ch. 2 (Springer, Berlin, Heidelberg, 2001).
8. Hicks, L. D. & Dresselhaus, M. S. Effect of quantum-well structures on the thermoelectric figure of merit. \textit{Phys. Rev. B} \textbf{47}, 12727–12731 (1993).
9. Mao, J., Liu, Z. & Ren, Z. Size effect in thermoelectric materials. \textit{Npj Quantum Mater.} \textbf{1}, 16028 (2016).
10. Sales, B. C. Electron crystals and phonon glasses: a new path to improved thermoelectric materials. \textit{MRS Bull.} \textbf{23}, 15–21 (1998).
22. Rittner, E. S. & Neumark, G. F. Theoretical bound on the thermoelectric figure of merit in SnTe crystals. Nature 508, 373–377 (2014).

24. Rycerz, A., Tworzydlo, J. & Beenakker, C. W. J. Valleytronics and thermoelectricity in the momentum Hilbert space. J. Phys. Condens. Matter 29, 415201 (2017).

25. Popescu, A. & Woods, L. M. Valleytronics, carrier filtering and thermoelectricity in bismuth: magnetic field polarization effects. Phys. Rev. Lett. 113, 226602 (2014).

26. Schäibley, J. R. et al. Valleytronics in 2D materials. Nat. Rev. Mater. 1, 16055 (2016).

27. Tong, W.-Y. & Duan, C.-G. Electrical control of the anomalous valley Hall effect in antiferroelectric bilayers. Nat. Quantum Mater. 2, 47 (2017).

28. Herring, C. Transport properties of a many-valley semiconductor. Bell Syst. Tech. J. 34, 237–290 (1955).

29. Bardeen, J. & Shockley, W. Deformation potentials and mobilities in non-polar crystals. Phys. Rev. 80, 72–80 (1950).

30. Pei, Y., Wang, H. & Snyder, G. J. Band engineering of thermoelectric materials. Adv. Mater. 24, 6125–6135 (2012).

31. Wang, H., Pei, Y., LaLonde, A. D. & Jeffery Snyder, G. In Thermoelectric Nano-materials: Materials Design and Applications (eds Kouno, K. & Mori, T.) Ch. 1 (Springer, Berlin, Heidelberg, 2013).

32. Zeitsev, V. K. et al. Highly effective Mg$_2$Si$_{1-x}$Sn$_x$ thermoelectrics. Phys. Rev. B 74, 045207 (2006).

33. Fedorov, M. I., Pshenay-Severin, D. A., Zeitsev, V. K., Sano, S. & Vedernikov, M. V. Features of conduction mechanism in n-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. Thermoelectrics, 2003 Twenty-Second International Conference on—ICT. IEEE, La Grande Motte, France, 2003.

34. Murphy-Armando, F. & Fahy, S. First-principles calculation of carrier-phonon scattering in n-type Si$_x$Ge$_{1-x}$ alloys. Phys. Rev. B 78, 035202 (2008).

35. Wang, H., LaLonde, A. D., Pei, Y. & Snyder, G. J. The criteria for beneficial disorder in thermoelectric solid solutions. Adv. Funct. Mater. 23, 1586–1596 (2013).

36. Ying, P. et al. High performance α-Mg$_2$As$_2$ thermoelectric materials for low temperature power generation. Chem. Mater. 27, 909–913 (2015).

37. Zhao, L.-D. et al. Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe. Science 351, 141–144, aad3749 (2015).

38. Norozzadeh, P. & Vashaei, D. Classification of valleytronics in thermoelectricity. Sci. Rep. 6, 22724 (2016).

39. Heremans, J. P. & Wiendlocha, B. In Materials Aspect of Thermoelectricity (ed Uhr, C. J.) Ch. 2, 39–94 (CRC Press, Boca Raton, 2016).

40. Kim, H.-S. et al. High thermoelectric performance in (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$ due to band convergence and improved by carrier concentration control. Mater. Today 20, 452–459 (2017).

41. LaLonde, A. D., Pei, Y., Wang, H. & Jeffery Snyder, G. Lead telluride alloy thermoelectrics. Mater. Today 14, 526–532 (2011).

42. Slack, C. & Hussain, M. A. The maximum possible conversion efficiency of silicon-germanium thermoelectric generators. J. Appl. Phys. 70, 2694–2718 (1991).

43. Liu, W. et al. Convergence of conduction bands as a means of enhancing thermoelectric performance of n-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. Phys. Rev. Lett. 108, 166601 (2012).
106. Fu, C. et al. High band degeneracy contributes to high thermoelectric performance in \( p \)-type FeNbSb compounds. Adv. Energy Mater., 1400600 (2014).

107. Pei, Y., LaLonde, A. D., Wang, H. & Snyder, G. J. Low effective mass leading to high thermoelectric performance. Energy. Sci. 5, 7963–7969 (2012).

108. Zhang, Q. et al. Low effective mass and carrier concentration optimization for high performance \( p \)-type Mg\(_{5-x}\)Si\(_x\)Sn\(_{1-x}\) solid solutions. Phys. Chem. Chem. Phys. 16, 23576–23583 (2014).

109. Fu, C. et al. High band degeneracy contributes to high thermoelectric performance in \( p \)-type FeNbSb compounds. Adv. Energy Mater., 1400600 (2014).

110. Young, D. P., Khalifah, P., Cava, R. J. & Ramirez, A. P. Thermoelectric properties of pure and doped FeSb\(_5\) (\( M = V, N b \)). J. Appl. Phys. 87, 317–321 (2000).

111. Fu, C., Liu, Y., Zhao, X. & Zhu, T. Are solid solutions better in FeNbSb-based thermoelectrics? Adv. Electron. Mater. 2, 1600394 (2016).

112. Zunger, A. Practical doping principles. Appl. Phys. Lett. 83, 57–59 (2003).

113. Pei, Y. et al. Optimum carrier concentration in \( n \)-type PbTe thermoelectrics. Adv. Energy Mater. 4, 1400486 (2014).

114. Gibbs, Z. M. et al. Effective mass and Fermi surface complexity factor from ab initio band structure calculations. npj Comput. Mater. 3, 8 (2017).

115. Bill, D. I., Hautier, G., Waroquiers, D., Rignanese, G.-M. & Ghozze, P. Low-dimensional transport and large thermoelectric power factors in bulk semiconductors by band engineering of highly directional electronic states. Phys. Rev. Lett. 114, 136601 (2015).

116. Parker, D., Chen, X. & Singh, D. J. High three-dimensional thermoelectric performance from low-dimensional bands. Phys. Rev. Lett. 110, 146601 (2013).

117. Hicks, L. D. & Dresselhaus, M. S. Thermoelectric figure of merit of a one-dimensional conductor. Phys. Rev. B 47, 16631–16634 (1993).

118. Kuroki, K. & Arita, R. “Puddling Mud” band drives large thermopower in NaCo\(_2\) (condensed matter: electronic structure and electrical, magnetic, and optical properties). J. Phys. Soc. Jpn. 76, 083707 (2007).

119. Chen, X., Parker, D. & Singh, D. J. Importance of non-parabolic band effects in the thermoelectric properties of semiconductors. Sci. Rep. 3, 1316 (2013).

120. Xiao, C. et al. High thermoelectric and reversible \( p-n \) conduction type switching integrated in dimetal chalcogenide. J. Am. Chem. Soc. 134, 18460–18466 (2012).

121. Parker, D. S., May, A. F. & Singh, D. J. Benefits of carrier-pocket anisotropy to thermoelectric performance: the case of \( p \)-type AgBiSe\(_2\). Phys. Rev. Appl. 3, 064003 (2015).

122. Jiang, G. et al. High performance Mg\(_5\)Si\(_x\)Sn\(_{1-x}\) solid solutions: a point defect chemistry approach to enhancing thermoelectric properties. Adv. Funct. Mater. 24, 3776–3781 (2014).

123. Kim, S. I. et al. Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics. Science 348, 109–114 (2015).

124. Shimizu, S. et al. Enhanced thermopower in Zn\(_2\)O two-dimensional electron gas. Proc. Natl Acad. Sci. USA 113, 6438–6443 (2016).

125. Zhao, W. et al. Superparamagnetic enhancement of thermoelectric performance. Nature 549, 247–251 (2017).

126. Zhang, X. & Pei, Y. Manipulation of charge transport in thermoelectrics. npj Quantum Mater. 2, 68 (2017).

127. Tan, X. J. et al. Multiscale calculations of thermoelectric properties of \( n \)-type Mg\(_5\)Si\(_x\)Sn\(_{1-x}\) solid solutions. Phys. Rev. B 85, 205212 (2012).

128. Meh dizadeh Dehkordi, A., Zebarjadi, M., He, J. & Tritt, T. M. Thermoelectric power factor: enhancement mechanisms and strategies for higher performance thermoelectric materials. Mater. Sci. Eng. R Rep. 97, 1–22 (2015).