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## Material descriptors for thermoelectric performance of narrow-gap semiconductors and semimetals†

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Thermoelectric (TE) cooling is an environment-friendly alternative to vapor compression cooling. New TE materials with high coefficients of performance are needed to further advance this technology. Narrow-gap semiconductors and semimetals have garnered interest for Peltier cooling, yet large-scale computational searches often rely on material descriptors that do not account for bipolar conduction effects. In this work, we derive three material descriptors to assess the TE performances of narrow-gap semiconductors and semimetals – band gap, n- and p-type TE quality factors, and the asymmetry in transport between the majority and minority carriers. We show that a large asymmetry is critical to achieving high TE performance through minimization of bipolar conduction effects. We validate the predictive power of the descriptors by correctly identifying  $\text{Mg}_3\text{Bi}_2$  and  $\text{Bi}_2\text{Te}_3$  as high-performing room-temperature TE materials. By applying these descriptors to a broad set of 650 Zintl phases, we identify three candidate room-temperature TE materials, namely  $\text{SrSb}_2$ ,  $\text{Zn}_3\text{As}_2$ , and  $\text{NaCdSb}$ . The proposed material descriptors will enable fast, targeted searches of narrow-gap semiconductors and semimetals for low-temperature TEs. We further propose a refined TE quality factor,  $B_{\text{bp}}$ , which is a composite descriptor of the peak  $zT$  in materials exhibiting significant bipolar conduction;  $B_{\text{bp}}$  can be used to compare the TE performances of narrow-gap semiconductors.

### 1. Introduction

The rising demand for cooling, including refrigeration and air conditioning, poses environmental and economic challenges. Conventional cooling systems used in homes, vehicles, industries, and data centers are based on vapor-

#### New concepts

There is a strong need for low-temperature thermoelectric (TE) materials for Peltier cooling and for powering IoT devices. Computational approaches to search and discover new low-temperature TE materials have been limited by material descriptors that do not account for bipolar conduction effects – important in narrow-gap semiconductors and semimetals commonly used for this purpose. In this work, we derive fundamental materials descriptors from Boltzmann transport theory applied to a two-band model, where bipolar conduction effects are considered. We demonstrate the efficacy of these descriptors by re-discovering well-known low-temperature TE materials as well as proposing three new Zintl phases as candidates for future investigation. The proposed descriptors will enable large-scale searches of narrow-gap semiconductors and semimetals for low-temperature TE applications.

compression cycles utilizing coolants that are a major source of greenhouse gas emissions.<sup>1–4</sup> The International Energy Agency reported that air conditioning is responsible for



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*Materials Horizons has risen in this last decade to become a prominent platform for showcasing innovative materials science research. Congratulations on this achievement! With an excellent editorial team at the helm, I am optimistic that the journal will continue on its upward trajectory. Personally, being recognized as an Emerging Investigator in 2020 provided the proverbial “pat of the back” early in my independent career. In this contribution, we propose new*

*materials descriptors that will aid in the discovery and design of low-temperature thermoelectric materials. Coincidentally, these descriptors are refined versions of those I had proposed almost a decade ago – when Materials Horizons was launched.*

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almost 20% of the electricity use in buildings globally,<sup>5</sup> with some studies estimating up to 30–40% usage.<sup>6</sup> Distributed thermoelectric (TE) cooling offers a viable solution,<sup>7</sup> with studies demonstrating TE-based air conditioning<sup>8</sup> and cooling powered by solar energy.<sup>9,10</sup> In addition, low-temperature TE materials have applications in powering Internet of Things (IoT) devices,<sup>11</sup> including low-power Arctic data sensors.<sup>12</sup> Due to their diverse applications, there is a critical need for the discovery and development of low-temperature TE materials.

Historically, narrow-gap semiconductors and semimetals have been found to exhibit good low-temperature TE performance. Bi<sub>2</sub>Te<sub>3</sub>, with a band gap of 0.14 eV, is the state-of-the-art TE material in the near-room temperature range (300–350 K).<sup>13</sup> The recent demonstration of semimetallic Mg<sub>3</sub>Bi<sub>2</sub>-based materials with a peak  $zT$  of 0.9 at 350 K<sup>14</sup> has renewed interest in low-temperature TE applications.<sup>15–17</sup> Other narrow-gap semiconductors and semimetals such as CsBi<sub>4</sub>Te<sub>6</sub>,<sup>18</sup> Bi<sub>1–x</sub>Sb<sub>x</sub>,<sup>19</sup> Cd<sub>3</sub>As<sub>2</sub>,<sup>20</sup> ZrTe<sub>5</sub>,<sup>21</sup> and correlated materials<sup>22</sup> have also been studied for TE applications at or below room temperature. However, the coefficient of performance of current TE cooling devices (10–20% of the Carnot limit) is poor compared to vapor compression technology (50% of the Carnot limit under ideal conditions).<sup>7</sup> Since the coefficient of performance increases with the TE figure of merit  $zT$ , it is important to search for new TE materials with high  $zT$ .

Computations have been instrumental in the discovery and development of new TE materials.<sup>23–28</sup> Large-scale computationally-driven discovery of TE materials requires robust and tractable performance metrics or descriptors. Several such descriptors, including the electronic fitness function,<sup>29,30</sup> Fermi surface complexity factor,<sup>31</sup> and the quality factor<sup>32,33</sup> have been proposed. In developing these material descriptors, it is typically assumed that the charge transport can be ascribed to a single carrier type (electrons or holes) and, therefore, the TE performance can be described within a single parabolic band approximation.<sup>34,35</sup> While this is a reasonable approximation for materials with band gaps that are wide enough to avoid significant bipolar conduction, or even “gapped metals” where a single charge carrier type dominates transport,<sup>36</sup> it breaks down in materials where both electrons and holes are present in high concentrations, such as narrow-gap semiconductors and semimetals.<sup>37–39</sup> Bipolar conduction increases the electrical conductivity while simultaneously decreasing the Seebeck coefficient and increasing the electronic thermal conductivity.<sup>40</sup> As such, material descriptors for predicting the TE performance of narrow-gap semiconductors and semimetals must account for effects arising from bipolar conduction. One of the co-authors of this study has developed models to estimate the quality factor  $B$  – a material descriptor for predicting TE performance.<sup>32</sup> Several high-throughput computational searches for new TE materials have been performed using  $B$  as a material descriptor.<sup>33,41–44</sup> However, the models assume charge transport is dominated by either electrons or holes, not both. In this study, we derive new material descriptors for

TE performance that account for bipolar conduction effects on charge transport properties.

Using semi-classical Boltzmann transport theory, we derive three important material descriptors for TE performance: (1) band gap, (2) n- and p-type TE quality factors, and (3) asymmetry parameter (ratio of the quality factors). We apply these material descriptors to search for new room-temperature TE materials among narrow-gap and semimetallic Zintl phases. In addition to the Zintl phases, we also calculate the material descriptors for Mg<sub>3</sub>Bi<sub>2</sub>, Bi<sub>2</sub>Te<sub>3</sub>, and Bi<sub>2</sub>Se<sub>3</sub> as benchmark materials in this study. Consistent with experiments, we show that Mg<sub>3</sub>Bi<sub>2</sub> and Bi<sub>2</sub>Te<sub>3</sub> are high-performing TE materials near room temperature, which validates the predictive power of the descriptors. Through this search, we identify three Zintl phases (SrSb<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, and NaCdSb) with promising room-temperature TE performance. Lastly, we propose a refined TE quality factor,  $B_{\text{bp}}$ , which is a composite descriptor of the peak  $zT$  that can be used to compare the TE performances of narrow-gap semiconductors with significant bipolar conduction effects.

## 2. Theory: models and material descriptors

Carrier transport is often described in the Boltzmann transport theory framework.<sup>45–47</sup> In the relaxation time approximation, the transport coefficients for isotropic bands is expressed in terms of the transport function  $\Sigma(E)$  as,

$$\Sigma(E) = \frac{e^2}{3} \sum_n \tau_n(E) v_n(E)^2 g_n(E) \quad (1)$$

where the summation runs over bands with indices  $n$ ,  $\tau(E)$  is the scattering time,  $v(E)$  is the group velocity, and  $g(E)$  is the density of states. The  $1/3$  factor in  $\Sigma(E)$  arises from averaging over the three Cartesian directions. The scattering time  $\tau$  can be expressed as a power law in  $E$  for standard scattering mechanisms:

$$\tau(E) \equiv \tau_0 \left( \frac{E}{k_{\text{B}}T} \right)^r \quad (2)$$

where  $r$  is a parameter representing the charge scattering mechanism. For example,  $r = -1/2$  represents acoustic deformation potential scattering, whereas  $r = 1/2$  represents polar optical phonon scattering.<sup>47</sup> There is a growing body of work suggesting polar optical scattering is the dominant scattering mechanism in many polar materials,<sup>48</sup> including PbTe<sup>49–51</sup> and SnSe.<sup>52</sup> As such, we present results for polar optical scattering ( $r = 1/2$ ) in the main text. We provide the analogous results for acoustic deformation potential scattering in the ESI† and show that the qualitative trends are similar regardless of the scattering mechanism. The transport coefficients, namely the electrical conductivity  $\sigma$ , Seebeck coefficient  $S$ , Lorenz number  $L$ , and electronic thermal

conductivity  $\kappa_e$ , are given by

$$\begin{aligned}\sigma &= \int \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \\ S &= \frac{k_B}{e} \frac{1}{\sigma} \int \Sigma(E) \left( \frac{E - E_F}{k_B T} \right) \left( -\frac{\partial f}{\partial E} \right) dE \\ L &= \left( \frac{k_B}{e} \right)^2 \frac{1}{\sigma} \int \Sigma(E) \left( \frac{E - E_F}{k_B T} \right)^2 \left( -\frac{\partial f}{\partial E} \right) dE - S^2 \\ \kappa_e &= L\sigma T\end{aligned}\quad (3)$$

where  $T$  is the temperature. In cases where carrier transport is dominated by majority carriers and can be described by a single parabolic band, using the power law form of  $\tau(E)$  in eqn (2), the transport coefficients are expressed as,

$$\begin{aligned}\sigma(\eta) &= \frac{8\pi e}{3} \left( \frac{2m_c k_B T}{h^2} \right)^{3/2} \mu_w \left( r + \frac{3}{2} \right) F_{r+\frac{1}{2}}(\eta) \\ S(\eta) &= \frac{k_B}{e} \left[ -\eta + \frac{\left( r + \frac{5}{2} \right) F_{r+\frac{3}{2}}(\eta)}{\left( r + \frac{3}{2} \right) F_{r+\frac{1}{2}}(\eta)} \right] \\ L(\eta) &= \left( \frac{k_B}{e} \right)^2 \left[ \frac{\left( r + \frac{7}{2} \right) F_{r+\frac{5}{2}}(\eta)}{\left( r + \frac{3}{2} \right) F_{r+\frac{1}{2}}(\eta)} - \left( \frac{\left( r + \frac{5}{2} \right) F_{r+\frac{3}{2}}(\eta)}{\left( r + \frac{3}{2} \right) F_{r+\frac{1}{2}}(\eta)} \right)^2 \right]\end{aligned}\quad (4)$$

Here,  $F_i$  is the Fermi-Dirac integral, given by

$$F_i(\eta) = \int \frac{e^{\varepsilon}}{1 + \exp(\varepsilon - \eta)} d\varepsilon \quad (5)$$

where  $\eta \equiv E_F/k_B T$  is the reduced Fermi energy and  $\varepsilon \equiv E/k_B T$  is the reduced energy.  $\mu_w$  is the weighted mobility,<sup>53</sup>

$$\mu_w = \mu_0 \left( \frac{m_{\text{DOS}}^*}{m_c} \right)^{3/2} = \frac{e\tau_0}{m_b^*} N_V \left( \frac{m_b^*}{m_c} \right)^{3/2} \quad (6)$$

where  $\mu_0$  is the intrinsic carrier mobility and  $m_{\text{DOS}}^*$  is the density-of-states effective mass, which can be expressed in terms of band effective mass  $m_b^*$  and valley degeneracy  $N_V$ . The transport coefficients in eqn (4) must be revised when accounting for the effects of both electrons and holes (two-band model) on TE transport. The theory of the two-band model has been presented in detail elsewhere,<sup>37,54–57</sup> but we briefly review it here to illustrate how the material descriptors are derived.

Here, we adopt the “majority” and “minority” carrier labels so that the theoretical expressions are applicable to both n-type (excess electrons) and p-type (excess holes) materials.<sup>58</sup> We demonstrate that TE transport in narrow-gap semiconductors and semimetals depends on the asymmetry of the majority and minority carrier transport properties. We show this by considering isotropic conduction and valence bands with different effective masses and scattering times *i.e.*, different weighted mobilities.

We can graphically understand the transport coefficients in a material with majority and minority carriers (Fig. 1). In isotropic and parabolic bands, squared group velocity varies linearly with energy  $E$  as  $v^2(E) \sim |E - E_b|$ , where  $E_b$  is the band edge. The density of states of a parabolic band is given by  $g(E) \sim \sqrt{|E - E_b|}$ , and the scattering time due to polar optical phonons is expressed as  $\tau(E) \sim \sqrt{|E - E_b|}$ . By eqn (1), the transport distribution function follows a squared energy dependence  $\Sigma(E) \sim (E - E_b)^2$  as shown in Fig. 1(d). The selection function  $-\partial f/\partial E$ , which peaks at the Fermi energy  $E_F$  (Fig. 1e), samples  $\Sigma(E)$  in both the conduction and valence bands, resulting in contributions from both bands to the transport coefficients  $\sigma$  (Fig. 1f),  $S$  (Fig. 1g), and  $\kappa_e$  (Fig. 1h). The qualitative trends in the transport coefficients are not dependent on the scattering mechanism; similar results are obtained for acoustic deformation potential scattering (Fig. S1, ESI†).

Since the transport coefficients depend on the position of  $E_F$  relative to the valence and conduction band edges, it is convenient to define a reduced Fermi energy for each band separately. If we reference  $E_F$  to the majority carrier band edge *i.e.*,  $E_F = 0$ , then the reduced Fermi energy of majority carriers ( $\eta_{\text{maj}}$ ) and minority carriers ( $\eta_{\text{min}}$ ) are given by,

$$\begin{aligned}\eta_{\text{maj}} &= \frac{E_F}{k_B T} \\ \eta_{\text{min}} &= -\eta_{\text{maj}} - \frac{E_g}{k_B T}\end{aligned}\quad (7)$$

where  $E_g$  is the band gap. For n-type (p-type), a positive  $E_F$  implies the Fermi energy lies inside the conduction (valence) band. It is important to note that the range of  $\eta_{\text{maj}}$  is bounded such that the majority carrier concentration is larger than minority carriers.

In a two-band model,  $\Sigma(E)$  is the sum of the individual  $\Sigma(E)$  of the valence (VB) and conduction (CB) bands. As a result, the electrical conductivity  $\sigma$  in a two-band model is

$$\sigma = \sigma_{\text{maj}} + \sigma_{\text{min}} \quad (8)$$

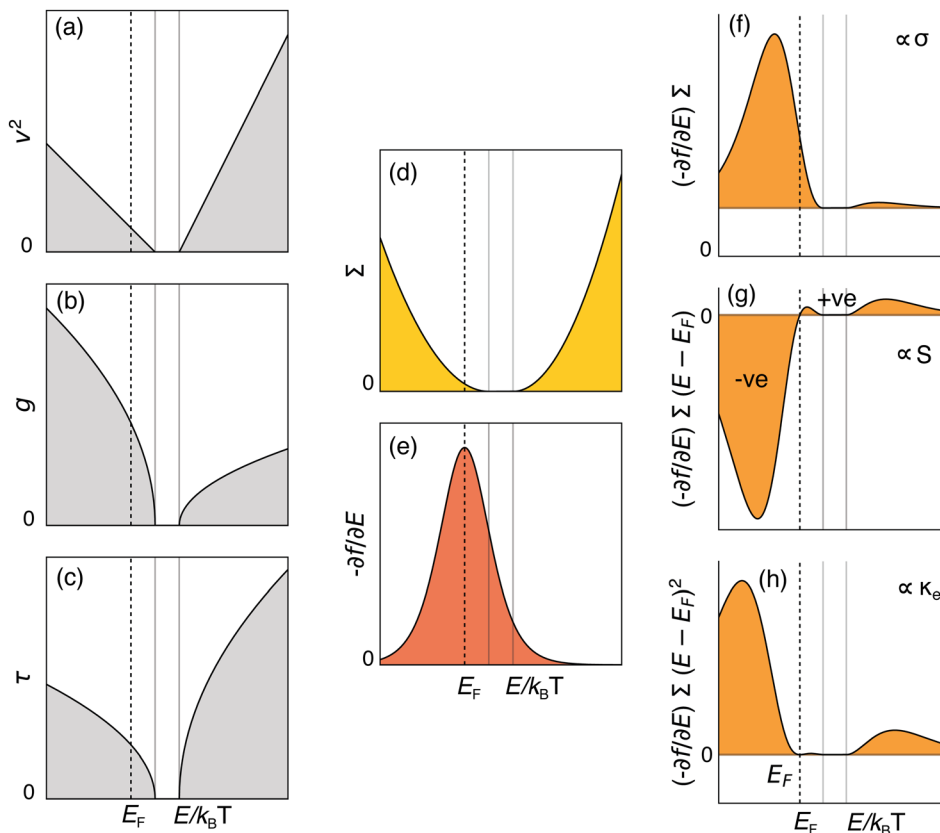
where  $\sigma_{\text{maj}}$  and  $\sigma_{\text{min}}$  are the single-band conductivities of majority and minority carriers, respectively, as defined in eqn (4). The Seebeck coefficient  $S$  is given by,

$$S = \frac{S_{\text{min}} + S_{\text{maj}} \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}}}{1 + \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}}} \quad (9)$$

where  $S_{\text{maj}}$  and  $S_{\text{min}}$  are the single-band Seebeck coefficients of majority and minority carriers, respectively. Note that, by convention, the Seebeck coefficient of holes is positive and that of electrons is negative. The Lorenz number is

$$L = \frac{[L_{\text{min}} + S_{\text{min}}^2] + [L_{\text{maj}} + S_{\text{maj}}^2] \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}}}{1 + \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}}} - S^2 \quad (10)$$

where  $L_{\text{maj}}$  and  $L_{\text{min}}$  are the single-band Lorenz numbers of majority and minority carriers, respectively. The electronic



**Fig. 1** Transport coefficients in a two-band model. The valence and conduction band edges are shown as solid vertical lines, and the Fermi level  $E_F$  is shown as a dotted vertical line. (a)–(c) The components of the transport function  $\Sigma(E) = v^2(E)g(E)\tau(E)$ , shown in (d), where  $v(E)$ ,  $g(E)$ , and  $\tau(E)$  are the energy-dependent velocity, density of states, and scattering time, respectively.  $\Sigma(E)$  is sampled by the selection function  $-\partial f/\partial E$ , shown in (e), and weighted by  $(E - E_F)^m$  to obtain (f) the electrical conductivity  $\sigma$  ( $m = 0$ ), (g) Seebeck coefficient  $S$  ( $m = 1$ ), and (h) the Lorenz number ( $m = 2$ ), which is related to the electronic thermal conductivity. The area under the curves are proportional to the magnitude of each transport coefficient at a fixed Fermi energy  $E_F$ .

thermal conductivity  $\kappa_e = L\sigma T$  is,

$$\kappa_e = \kappa_{e,\text{maj}} + \kappa_{e,\text{min}} + \underbrace{\sigma T \left( \frac{S_{\text{maj}}^2}{1 + \frac{\sigma_{\text{min}}}{\sigma_{\text{maj}}}} + \frac{S_{\text{min}}^2}{1 + \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}}} - S^2 \right)}_{\kappa_b} \quad (11)$$

where  $\kappa_{e,\text{maj}}$  and  $\kappa_{e,\text{min}}$  are the majority and minority carrier contributions to the thermal conductivity, respectively. The last summand in eqn (11),  $\kappa_b$ , is often referred to as the “bipolar thermal conductivity”, which arises due to the presence of both electrons and holes.<sup>59,60</sup> Using the two-band transport coefficients in eqn (8)–(11),  $zT$  is expressed as,

$$zT = \frac{S^2 \sigma T}{\kappa_e + \kappa_L} = \frac{S^2}{L + \frac{\kappa_L}{\sigma T}} \quad (12)$$

The term  $\kappa_L/(\sigma T)$  can be expressed in terms of the majority and minority carrier quality factors, denoted  $B_{\text{maj}}$  and  $B_{\text{min}}$  respectively:

$$\frac{\kappa_L}{\sigma T} = \frac{(k_B/e)^2}{r + \frac{3}{2}} \frac{1}{F_{r+\frac{1}{2}}(\eta_{\text{maj}})B_{\text{maj}} + F_{r+\frac{1}{2}}(\eta_{\text{min}})B_{\text{min}}} \quad (13)$$

Here, the quality factors  $B_i$  are dimensionless

$$B_i = \left( \frac{k_B}{e} \right)^2 \frac{8\pi e}{3} \left( \frac{2m_e k_B}{h^2} \right)^{3/2} \frac{\mu_{w,i} T^{5/2}}{\kappa_L}, \quad i = \text{maj, min} \quad (14)$$

where  $B_{\text{maj}}$  and  $B_{\text{min}}$  are the  $B$  values of majority and minority carriers, respectively.

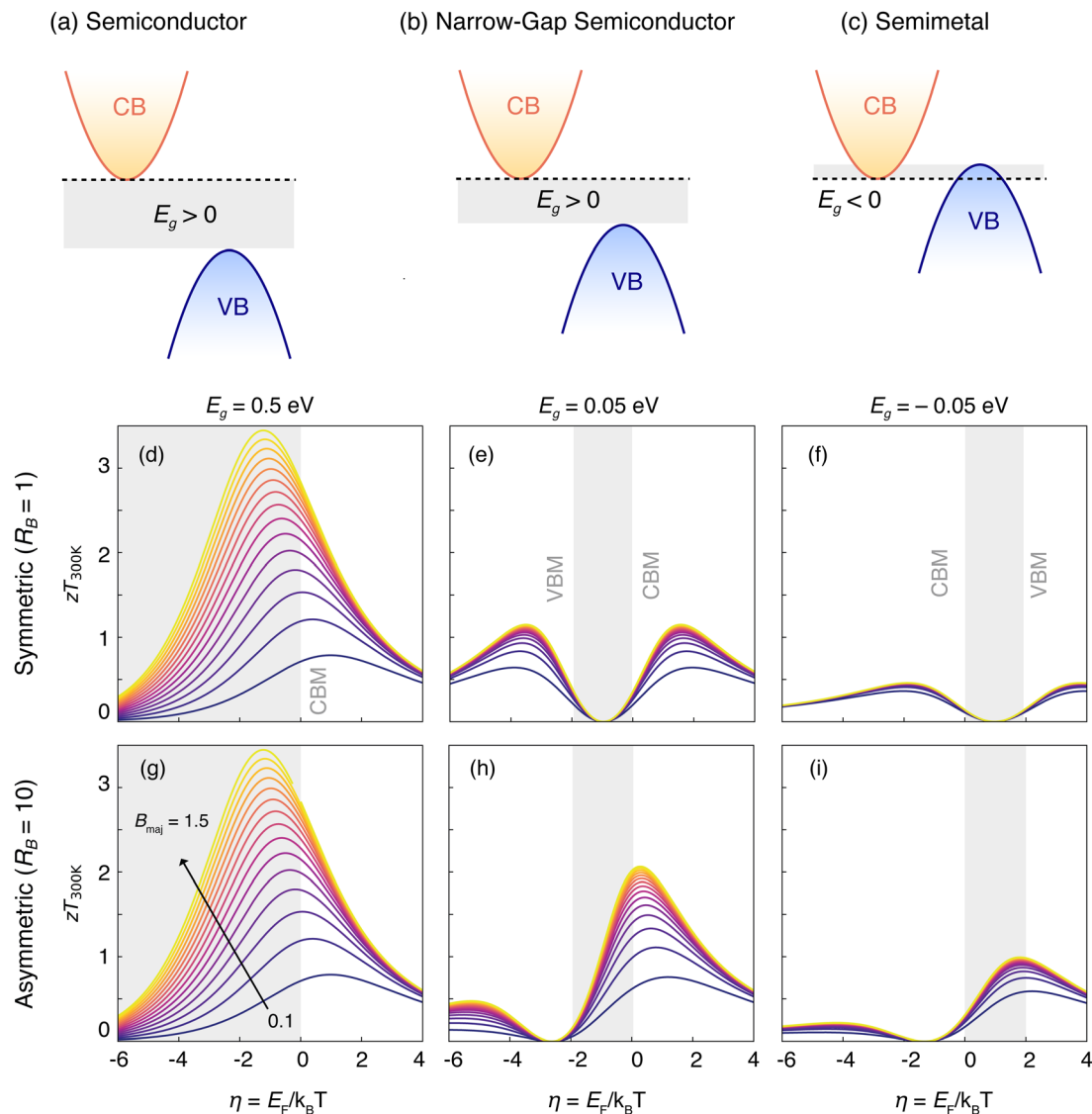
Charge transport is regulated by the conductivity ratio  $\sigma_{\text{maj}}/\sigma_{\text{min}}$ , as it appears in  $S$  (eqn (9)) and  $\kappa_e$  (eqn (11)). From the single-band model (eqn (4)), the conductivity ratio is

$$\frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}} = R_B \frac{F_{r+\frac{1}{2}}(\eta_{\text{maj}})}{F_{r+\frac{1}{2}}(\eta_{\text{min}})} \quad (15)$$

where we define a material-dependent asymmetry parameter  $R_B$ ,

$$R_B = \frac{\mu_{w,\text{maj}}}{\mu_{w,\text{min}}} = \frac{B_{\text{maj}}}{B_{\text{min}}} \quad (16)$$

which represents the relative contributions of majority and minority carriers to the overall charge transport. Note that “asymmetry” does not imply anisotropy *i.e.*, direction dependence of transport properties. As a result, bipolar conduction effects in systems with both majority and minority carriers,



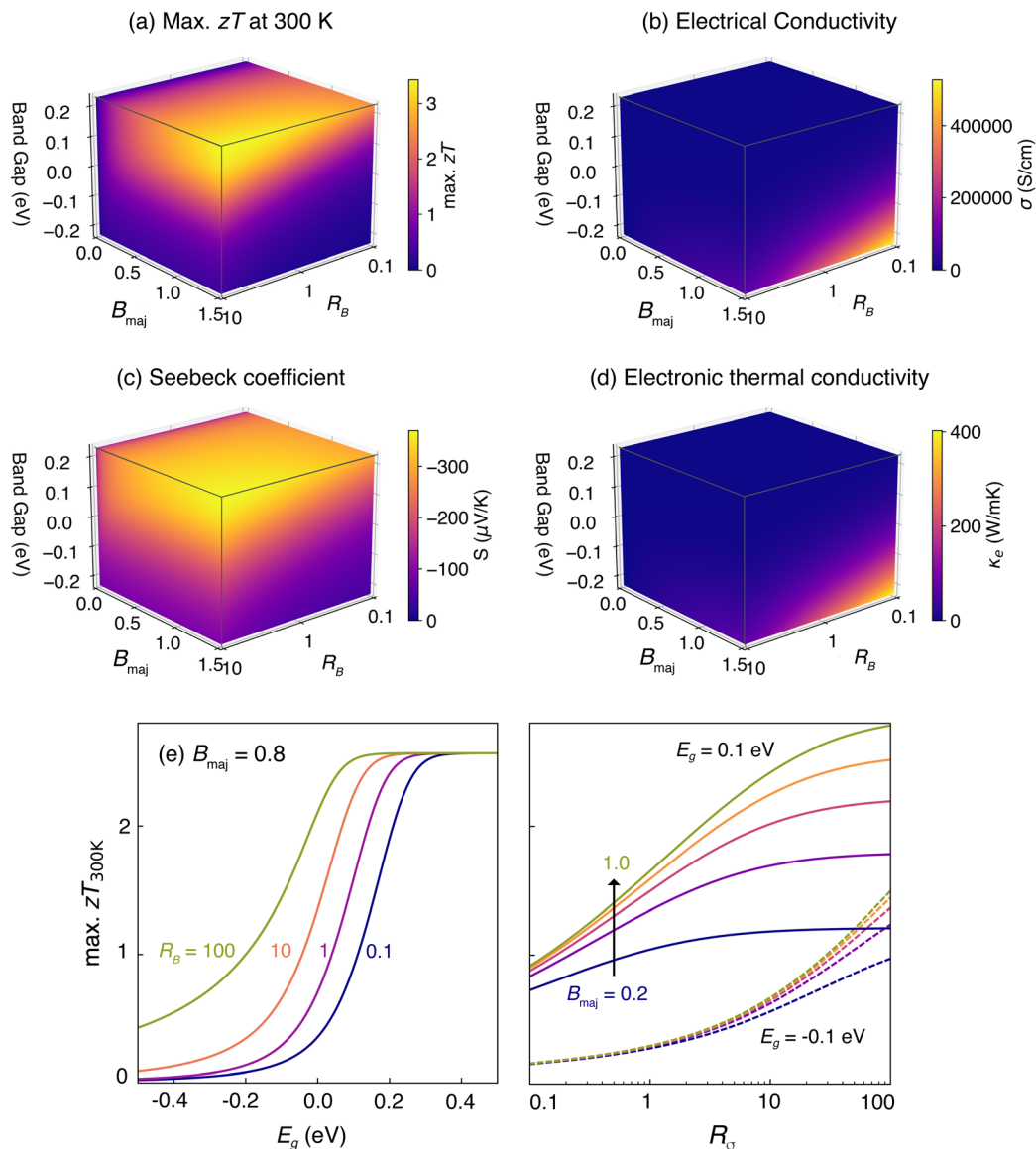
**Fig. 2**  $zT$  as a function of the reduced Fermi energy ( $\eta$ ) at 300 K for (a) semiconductors, (b) narrow-gap semiconductors, and (c) semimetals. The  $zT$  vs.  $\eta$  curves are plotted at 300 K for different  $B_{maj}$ , as defined in eqn (14), assuming majority carriers are electrons.  $B_{maj}$  values range from 0.1 (dark blue) to 1.5 (yellow) in 0.1 increments. Panels (d)–(f) for the symmetric ( $R_B = 1$ ) case, and panels (g)–(i) illustrate the case of large asymmetry ( $R_B = 10$ ). For materials with narrow or negative band gap, large  $R_B$  is favorable for TE performance due to minimization of bipolar conduction effects.

such as narrow-gap semiconductors and semimetals, are significantly affected by  $R_B$ .

We compare  $zT$  for three representative cases of  $E_g$ : a semiconductor with a wide band gap (Fig. 2a), a narrow-gap semiconductor (Fig. 2b), and a semimetal (Fig. 2c). Regardless of  $E_g$ , higher  $B_{maj}$  corresponds to higher  $zT$  for a given doping level  $\eta$  and temperature, as expected from a single-band model with no minority carriers.<sup>35,61</sup> As the band gap decreases (0.5 eV  $\rightarrow$  0.05 eV  $\rightarrow$  -0.05 eV), the maximum  $zT$  decreases due to the detrimental effects of bipolar conduction. This behavior can be understood from the individual transport coefficients in Fig. 3.  $\sigma$  is higher when the band gap is small or negative due to additive contributions from both electrons and holes (Fig. 3b). However,  $S$  decreases due to the partial cancellation of opposite

charge carrier contributions (Fig. 3c), and the higher  $\sigma$  leads to a higher  $\kappa_e$  (Fig. 3d).

Bipolar conduction effects in narrow-gap semiconductors and semimetals can be partially minimized when  $B_{min}$  is lower than  $B_{maj}$  *i.e.*,  $R_B > 1$ . We show this by contrasting  $zT$  when the quality factors are nearly the same (Fig. 2d–f) *vs.* asymmetric (Fig. 2g–i).  $zT$  is nearly unaffected by  $R_B$  when the band gap is sufficiently large (Fig. 2d and g). However, the benefit of a higher  $R_B$  is more noticeable when the band gap is smaller; in particular,  $zT$  is higher for a given doping level and temperature when  $R_B$  is higher (Fig. 2e, f, h, i). For a given  $B_{maj}$ , a higher  $R_B = B_{maj}/B_{min}$  corresponds to a lower  $B_{min}$ , meaning that we minimize minority carrier contributions to the overall TE transport.  $\sigma$  of minority carriers therefore decreases for higher  $R_B$ , leading



**Fig. 3** (a) Maximum  $zT$  at 300 K as a function of band gap ( $E_g$ ), majority carrier quality factor ( $B_{\text{maj}}$ ), and asymmetry parameter ( $R_B$ ). The electrical conductivity (b), Seebeck coefficient (c), and electronic thermal conductivity (d) are shown at the  $E_F$  where  $zT$  is maximized at 300 K. (e) Maximum  $zT$  at 300 K as a function of band gap, assuming  $B_{\text{maj}} = 0.8$ . Each curve corresponds to different  $R_B$ . (f) Maximum  $zT$  at 300 K for different  $R_B$ , shown for  $E_g = 0.1$  eV (solid) and  $E_g = -0.1$  eV (dashed). Each curve corresponds to different  $B_{\text{maj}}$ . Wide-gap materials exhibit high  $zT$ ; however, high TE performance is also achieved in narrow-gap semiconductors and semimetals with high  $B_{\text{maj}}$  and  $R_B$ .

to a decrease in the overall  $\sigma$  (Fig. 3b). However,  $\kappa_e$  is correspondingly lower (Fig. 3d) and, more notably, the magnitude of the Seebeck coefficient is higher because the cancellation of opposite charge carriers is minimized (Fig. 3c). In effect, higher asymmetry between the quality factor of majority and minority carriers mitigates the detrimental effects of bipolar conduction in narrow-gap semiconductors and semimetals. We arrive at the same qualitative conclusions regardless of the scattering mechanism, as evident from comparing Fig. 2, 3 and Fig. S2, S3 (ESI<sup>†</sup>).

It is worth noting cases where transport by majority and minority carriers are asymmetric but in favor of minority carriers, *i.e.*,  $R_B < 1$ . For a given  $E_g$ ,  $zT$  is lower when  $R_B < 1$

as illustrated in Fig. 3e and f. Since the transport properties of minority carriers in this case are favorable over those of majority carriers,  $zT$  is maximized only when the material is nearly intrinsic and the concentrations of opposite carrier types are roughly the same (Fig. S4, ESI<sup>†</sup>). The implication of  $R_B < 1$  is that the material will display better TE performance by switching the majority carrier type. For example, if  $R_B < 1$  and electrons are assumed to be the majority carriers, the material will be better as a p-type material instead when holes are the majority carrier type. This is consistent with the overall framework. In summary,

1. Semiconductors with large  $E_g$  will not suffer from bipolar conduction effects and exhibit higher maximum  $zT$ .

2. Large  $B_{\text{maj}}$  indicates high TE performance in the absence of bipolar conduction.

3.  $zT$  of narrow-gap semiconductors and semimetals is sensitive to the asymmetry parameter *i.e.*,  $R_B = B_{\text{maj}}/B_{\text{min}}$ . When the asymmetry is in favor of the majority carriers *i.e.*,  $R_B > 1$ , the material exhibits higher  $zT$  because bipolar conduction effects are minimized.

Therefore, we use  $E_g$ ,  $B_{\text{maj}}$ , and  $R_B$  as material descriptors to search for room-temperature TE materials that are narrow-gap semiconductors or semimetals. Prior studies have identified the importance of transport asymmetry to minimize bipolar conduction and achieve high power factors in narrow gap materials.<sup>62–64</sup> Our analysis is in agreement with these prior studies. However, these studies relied on either full-zone electrical transport calculations or a large number of descriptors obtained through parameter combinations. In contrast, we derive the functional dependence of TE performance on  $R_B$  from the two-band model. Also, prior work has focused on narrow-gap materials. Our proposed descriptors are applicable to both narrow-gap semiconductors and semimetals, which is important to account for well-known low-temperature TE materials such as  $\text{Mg}_3\text{Bi}_2$ .

### 3. Application: search for narrow-gap and semimetallic thermoelectric materials

#### 3.1 Computational workflow

We apply the proposed material descriptors to computationally search for room-temperature TE materials among narrow-gap and semimetallic Zintl phases. The search focuses on Zintl phases because they are known to have narrow and negative band gaps, and generally exhibit good TE performance.<sup>65</sup> The tiered computational workflow is depicted in Fig. 4. Details of the density functional theory (DFT) and other calculations, as well as the workflow, are provided in Section 6.

Out of 650 Zintl phases from the Inorganic Crystal Structure Database (ICSD), we identify 44 phases that are potentially narrow-gap semiconductors or semimetals using DFT with the semilocal PBE functional. By calculating the maximum  $zT$  at 300 K (Section 2), we identify 28 promising Zintl phases, for which we perform more accurate electronic structure calculations with a hybrid DFT functional. The computed material descriptors for these 28 phases, in addition to the benchmark materials  $\text{Mg}_3\text{Bi}_2$ ,  $\text{Bi}_2\text{Te}_3$ , and  $\text{Bi}_2\text{Se}_3$ , are reported in Table S1 (ESI<sup>†</sup>). The predicted  $zT_{\text{max}}$  at 300 K as a function of the transport asymmetry ( $R_B$ ) and band gap ( $E_g$ ) are plotted in Fig. 5a. Below, we discuss the material descriptors and predicted TE performance of  $\text{Mg}_3\text{Bi}_2$ ,  $\text{Bi}_2\text{Te}_3$ , and the three best candidate Zintl phases.

#### 3.2 Validation and materials recommendations

**$\text{Mg}_3\text{Bi}_2$ .** Recent work on  $\text{Mg}_3\text{Bi}_2$ -based materials have demonstrated their excellent room-temperature TE performance, which rivals the state-of-the-art  $\text{Bi}_2\text{Te}_3$ -based materials.<sup>66</sup> The superior

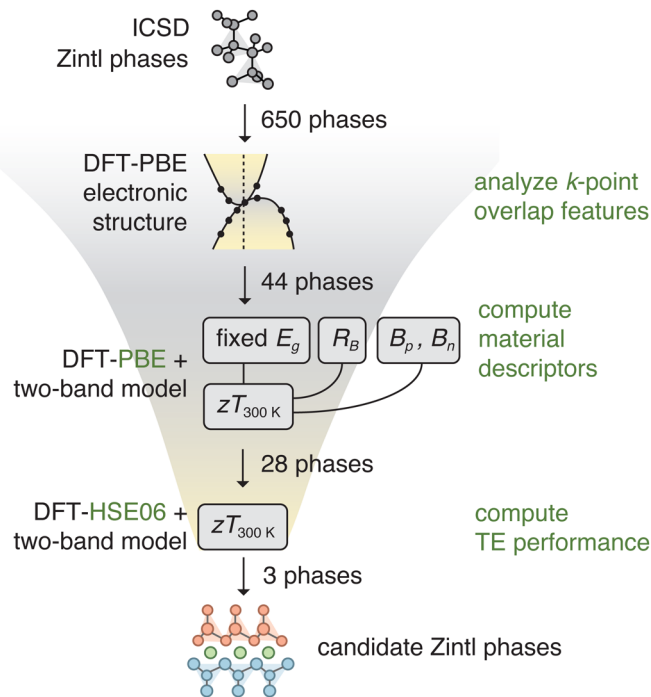
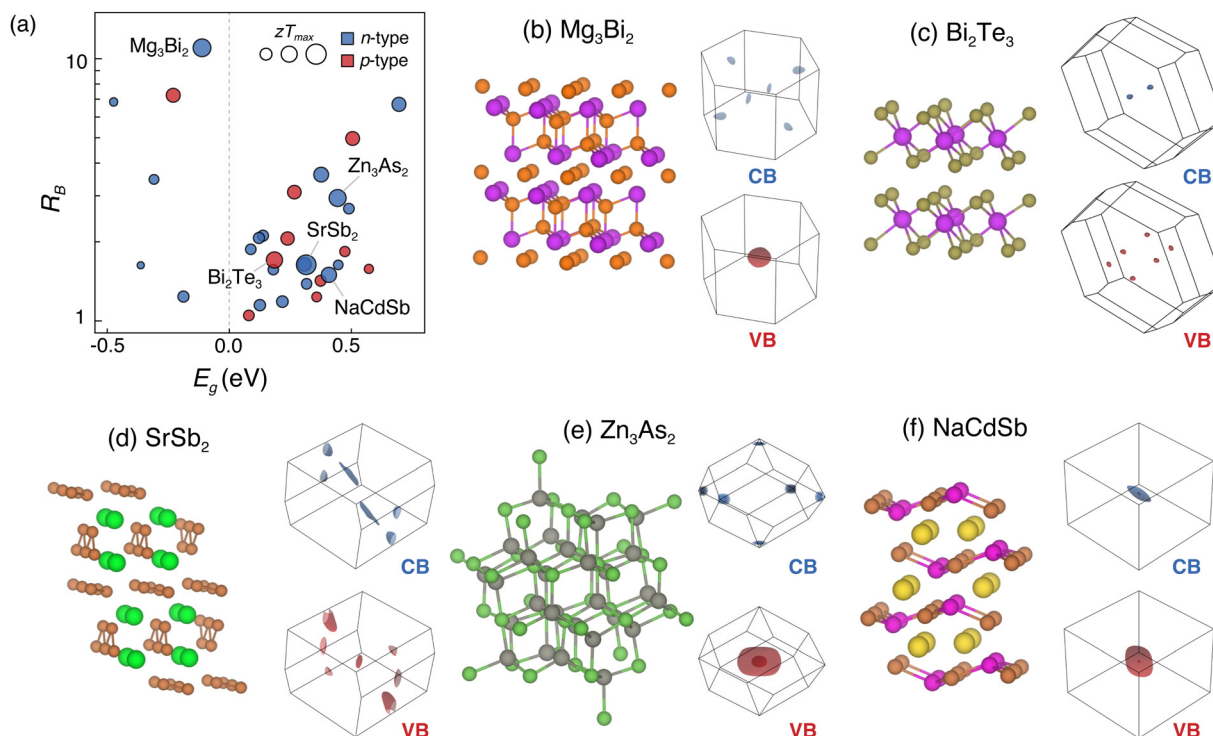


Fig. 4 Computational workflow to identify Zintl phases that are narrow-gap semiconductors or semimetals and exhibit high room-temperature thermoelectric performance.  $E_g$  is the band gap,  $R_B$  is the asymmetry parameter, and  $B_{\text{maj}}$  and  $B_{\text{min}}$  are the quality factors of majority and minority carriers. PBE and HSE06 refer to DFT functionals (see Methods).

TE performance of  $\text{Mg}_3\text{Bi}_2$  is despite the fact that it is a semimetal with a measured band gap of  $-0.1$  eV.<sup>14</sup> Recall from the analysis in Section 2 that semimetals are generally at a disadvantage due to increased bipolar conduction. Our calculated band gap (with HSE06 + SOC) of  $-0.11$  eV is in good agreement the experimentally measured value. The computed TE quality factors (Table 1) yield an  $R_B = 11$ , which is the highest among the structures calculated with the hybrid DFT functional. The large  $B_n$  and  $R_B$  is mainly a result of the high conduction band degeneracy  $N_{\text{V,CB}}$  of 6 (Fig. 5b). Based on the descriptors, we find that  $\text{Mg}_3\text{Bi}_2$  is one of the best-performing room-temperature TE material (high n-type  $zT_{300\text{K}}$ ) among the narrow-gap and semimetallic Zintl phases considered in this study (Fig. 5a). In fact, the predicted  $zT_{\text{max}}$  of 0.32 at 300 K (Table 1) is close to the experimental value when doped with Te ( $zT \sim 0.3$ ). The “rediscovery” of  $\text{Mg}_3\text{Bi}_2$  provides validation for our computational search workflow. Note that high TE performance at room temperature is achieved by alloying  $\text{Mg}_3\text{Bi}_2$  with  $\text{Mg}_3\text{Sb}_2$ .<sup>14</sup>  $\text{Mg}_3\text{Sb}_2$  also has a large conduction band degeneracy of 6,<sup>67</sup> which yields a large  $R_B$  of 7.6, and  $zT_{300\text{K}} = 0.28$  for n-type (Table S1, ESI<sup>†</sup>).

**$\text{Bi}_2\text{Te}_3$ .**  $\text{Bi}_2\text{Te}_3$ -based materials have been the state-of-the-art low-temperature TE materials for commercial devices.<sup>13</sup>  $\text{Bi}_2\text{Te}_3$  has a small band gap of 0.14 eV,<sup>13</sup> which is in agreement with our calculated value of 0.18 eV from HSE + SOC (see Table 1). Bipolar conduction effects are expected to be non-negligible in such small band gap materials. We identify  $\text{Bi}_2\text{Te}_3$  as a high-performing TE material with a maximum p-type  $zT$  of 0.26 at



**Fig. 5** (a) Predicted thermoelectric performance of 31 phases plotted as a function of the transport asymmetry ( $R_B$ ) and the band gap ( $E_g$ ). The marker size scales with the maximum  $zT$  at 300 K using the two-band model. The maximum  $zT$  are reported in Table 1. The crystal structures and Fermi surfaces of the conduction band (blue, labeled “CB”) and valence band (red, labeled “VB”) are shown for (b)  $Mg_3Bi_2$ , (c)  $Bi_2Te_3$ , and three candidate materials: (d)  $SrSb_2$ , (e)  $Zn_3As_2$ , (f) and  $NaCdSb$ .

**Table 1** Material properties and descriptors of  $Mg_3Bi_2$ ,  $Bi_2Te_3$ , and three candidate Zintl phases calculated with the hybrid HSE06 functional, including spin–orbit coupling.  $E_g$  is the band gap in eV,  $N_{V,VB}$  and  $N_{V,CB}$  are the valence and conduction band valley degeneracies, respectively,  $B_p$  and  $B_n$  are the TE quality factors of p- and n-type, respectively, and  $R_B$  is the asymmetry parameter. The maximum  $zT$  is calculated at 300 K assuming polar optical scattering ( $r = 1/2$ )

Compound	$E_g$	$N_{V,VB}$	$B_p$	$N_{V,CB}$	$B_n$	$R_B$	max. $zT_{300K}$	n-/p-type
$Mg_3Bi_2$	-0.11	1	0.002	6	0.021	11.0	0.32	n
$Bi_2Te_3$	0.18	6	0.011	2	0.006	1.7	0.26	p
$Bi_2Se_3$	0.32	1	0.003	1	0.004	1.4	0.11	n
$SrSb_2$	0.32	3	0.011	4	0.018	1.6	0.39	n
$Zn_3As_2$	0.44	2	0.004	3	0.012	2.9	0.29	n
$NaCdSb$	0.41	2	0.006	2	0.009	1.5	0.23	n

300 K, assuming polar optical scattering.<sup>68</sup> The high TE performance can be partly attributed to the intrinsically high valley degeneracy and low carrier effective mass.<sup>13</sup> In contrast, the TE performance of  $Bi_2Te_3$  is predicted to be lower with a maximum  $zT$  of 0.11 at 300 K since the valley degeneracies and, correspondingly, the TE quality factors, are low (Table 1). The identification of  $Bi_2Te_3$  as a candidate material further validates the proposed descriptors and our computational workflow.

**$SrSb_2$ .** This phase is predicted to have the highest  $zT$  at 300 K.  $SrSb_2$  crystallizes in a monoclinic structure (space group  $P2_1/m$ , no. 11) composed of infinite 1-D Sb chains interspersed

with Sr (Fig. 5d).<sup>69</sup>  $SrSb_2$  has a narrow band gap of 0.32 eV and valence and conduction band valley degeneracies of 3 and 4, respectively (Table 1). The Fermi surfaces are shown in Fig. 5d. An asymmetry parameter  $R_B$  of 1.6 results in a maximum n-type  $zT_{300K}$  of 0.39, which is  $1.22\times$  larger compared to  $Mg_3Bi_2$  and  $1.5\times$  compared to  $Bi_2Te_3$ .  $SrSb_2$  has been used as a precursor for synthesizing Sr-filled  $CoSb_3$  through arc-melting,<sup>70,71</sup> and small grains of  $SrSb_2$  have been observed in the samples.<sup>70</sup> However, detailed characterization of transport properties has so far not been reported. Our predictions make  $SrSb_2$  an interesting candidate to pursue experimentally.

**$Zn_3As_2$ .** This semiconductor ( $E_g = 0.44$  eV) adopts the  $Mn_2O_3$ -type structure (space group  $Ia\bar{3}$ , no. 206) and is one of several polymorphs of  $Zn_3As_2$ .<sup>72</sup> Several other polymorphs of  $Zn_3As_2$  are known, including the room-temperature  $\alpha$  phase ( $I4_1/acd$ ),<sup>73</sup> the high-temperature  $\alpha'$  phase ( $P4_2/nbc$ ),<sup>74,75</sup> another high-temperature  $\beta$  phase ( $Fm\bar{3}m$ ),<sup>76</sup> and the high-temperature, high-pressure  $\alpha''$  phase ( $P4_2/nmc$ ).<sup>77,78</sup> The TE properties of  $Cd_3As_2$ - $Zn_3As_2$  alloys have been studied,<sup>79–82</sup> but the transport properties of the  $Ia\bar{3}$  phase has not been measured. There are three conduction bands that are close in energy and located at the Brillouin zone edges (Fig. 5e), yielding a valley degeneracy  $N_{V,CB}$  of 3. There are two valence bands close in energy at the  $\Gamma$ -point, yielding a valley degeneracy  $N_{V,VB}$  of 2. Despite a modest  $R_B$  of 2.9, the relatively large band gap of 0.44 eV facilitates a high TE performance. The lower performance compared to  $SrSb_2$  is primarily due to the smaller  $B_n$ .



**NaCdSb.** This Zintl phase belongs to a large family of ternary *ABX* Zintl phases that adopt many different structure types.<sup>43</sup> NaCdSb crystallizes in an orthorhombic structure (*Pnma*, no. 62) with distorted square pyramidal NaSb<sub>5</sub> units, which share edges with CdSb<sub>4</sub> tetrahedra.<sup>83,84</sup> The structure can also be visualized as corrugated (CdSb)<sup>1-</sup> layers arranged in a honeycomb structure and intercalated with Na (Fig. 5f). The material is predicted to be semiconducting with a band gap of 0.41 eV. The individual TE quality factors yield an  $R_B$  of 1.5. Overall, we predict the maximum  $zT_{300\text{K}}$  of NaCdSb to be 72% of the maximum  $zT_{300\text{K}}$  of Mg<sub>3</sub>Bi<sub>2</sub>. Guo *et al.* recently reported experimentally measured  $zT_{300\text{K}}$  of 0.2 without optimizing the carrier concentration.<sup>85</sup> The highest  $zT$  of the material was found to be 1.3 at 673 K.

## 4. Thermoelectric quality factor for narrow-gap semiconductors

We identified three material descriptors that are important to describe the TE performances of narrow-gap semiconductors and semimetals: majority carrier quality factor ( $B_{\text{maj}}$ ), band gap

( $E_g$ ), and the asymmetry parameter ( $R_B$ ). We used these descriptors to efficiently search for new TE materials with narrow or negative band gaps for room-temperature TE applications. Our search methodology based on these descriptors is distinct from previous studies that assume absence of minority carrier effects.<sup>29,32</sup> In the case of single-band transport, the maximum  $zT$  of a material is solely determined by the quality factor ( $B$ ) of the majority carriers and it monotonically increases with  $B$  (Fig. S5, ESI†). Prior studies have used  $B$  as a descriptor to search for high-performing TE materials.<sup>32,86,87</sup> However, a composite descriptor that provides a measure of peak  $zT$  *i.e.*, optimized with respect to doping and temperature, for two-band transport is currently missing. To address this need, we propose a refined TE quality factor,  $B_{\text{bp}}$ , where “bp” denotes “bipolar”.

$B_{\text{bp}}$  is a useful descriptor of TE performance when both majority and minority carriers significantly contribute to charge transport, for example, in narrow-gap semiconductors. The mathematical form of  $B_{\text{bp}}$  should ideally have the following characteristics: (i) increase monotonically with peak  $zT$ , (ii) include  $B_{\text{maj}}$ ,  $E_g$ , and  $R_B$ , and (iii) be interpretable to understand the relative contribution of each parameter to peak  $zT$ . Liu *et al.* defined a parameter  $B^*$ , which describes the

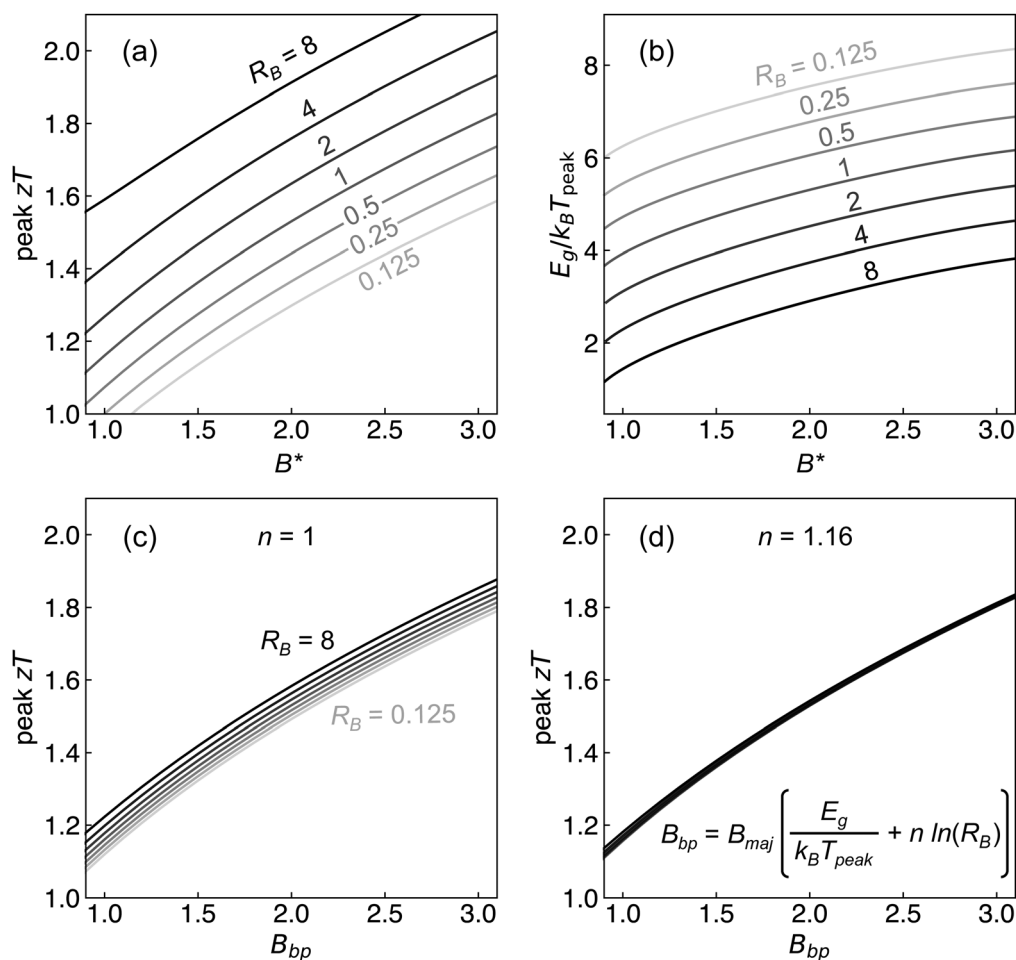


Fig. 6 (a) Peak  $zT$  and (b)  $E_g/k_B T_{\text{peak}}$  plotted against  $B^*$  (eqn (17)) for different values of  $R_B$ . Peak  $zT$  plotted against  $B_{\text{bp}}$  (eqn (18)) is shown for (c)  $n = 1$  and (d)  $n = 1.16$ .

relative contributions of two of the three descriptors,  $B_{\text{maj}}$  and  $E_{\text{g}}$ , towards the peak  $zT$ :<sup>88–90</sup>

$$B^* = B_{\text{maj}} \frac{E_{\text{g}}}{k_{\text{B}} T_{\text{peak}}} \quad (17)$$

where  $T_{\text{peak}}$  is the temperature corresponding to peak  $zT$ . Note that  $T_{\text{peak}}$  is a material property that depends on  $B_{\text{maj}}$ ,  $E_{\text{g}}$ , and  $R_{\text{B}}$ . The peak  $zT$  at a given  $R_{\text{B}}$  value monotonically increases with  $B^*$  (Fig. 6a). The  $E_{\text{g}}/k_{\text{B}}T_{\text{peak}}$  curve as a function of  $B^*$  shows a nearly-constant shift when  $R_{\text{B}}$  changes by some multiplicative factor (Fig. 6b), suggesting an additive correction to  $E_{\text{g}}/k_{\text{B}}T_{\text{peak}}$  that depends logarithmically on  $R_{\text{B}}$ . We therefore propose the following mathematical form of  $B_{\text{bp}}$ :

$$B_{\text{bp}} = B_{\text{maj}} \left[ \frac{E_{\text{g}}}{k_{\text{B}} T_{\text{peak}}} + n \ln(R_{\text{B}}) \right] \quad (18)$$

where  $n$  is a fitted parameter. As shown in Fig. 6c, with  $n = 1$ , peak  $zT$  still varies noticeably with the choice of  $R_{\text{B}}$ . We find that  $n = 1.16$  yields a satisfactory fit with only 3% spread in peak  $zT$  when  $R_{\text{B}}$  is changed by a factor of 64 (Fig. 6d). We also find that the functional dependence in eqn (18) is valid for various scattering mechanisms, which are implemented through our choice of the scattering parameter  $r$  (Fig. S6, ESI<sup>†</sup>).

We calculate  $B_{\text{bp}}$  and the corresponding peak  $zT$  for the narrow-gap Zintl phases (Fig. S7, ESI<sup>†</sup>). We find that candidate materials identified in our search (SrSb<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, and NaCdSb) have fairly high  $B_{\text{bp}}$  values, as well as other Zintl phases such as Mg<sub>2</sub>ZnAs<sub>2</sub>, NaZn<sub>4</sub>As<sub>3</sub>, and Li<sub>4</sub>Ba<sub>3</sub>As<sub>4</sub>. We note that ranking the TE performances of narrow-gap semiconductors with  $B_{\text{bp}}$  is fundamentally different from the search methodology employed in Section 3.  $B_{\text{bp}}$  is a measure of the peak performance at the corresponding  $T_{\text{peak}}$  and optimized doping level.  $T_{\text{peak}}$  need not be 300 K, which was the focus of the search presented in Section 3. On the other hand, using  $B_{\text{maj}}$ ,  $E_{\text{g}}$ , and  $R_{\text{B}}$  as separate descriptors allows us to compare the TE performances of materials at assumed temperatures or doping levels, or both. In Section 3 for example, we rank the TE performance of Zintl phases at room temperature (300 K). Using the individual descriptors ( $B_{\text{maj}}$ ,  $E_{\text{g}}$ ,  $R_{\text{B}}$ ) allow us to search for materials for specific low-temperature applications, for example, at or near room temperature for IoT sensors.<sup>11,12</sup>

## 5. Conclusions

We use an analytical two-band model to derive material descriptors for predicting the TE performances of narrow-gap semiconductors and semimetals. The proposed descriptors are obtained from simple DFT calculations, which allows reliable, high-throughput search of narrow-gap semiconductors and semimetals for low-temperature thermoelectrics. We find that the material descriptors that govern TE performance are: (1) the majority carrier quality factor ( $B_{\text{maj}}$ ), (2) the band gap ( $E_{\text{g}}$ ), and (3) the asymmetry in the transport properties of majority and minority carriers ( $R_{\text{B}} = B_{\text{maj}}/B_{\text{min}}$ ), where  $B_{\text{min}}$  is the minority carrier quality factor. As in a single-band model, materials with high quality factors tend to exhibit high TE performance when

doping is optimized. However, high TE performance in narrow-gap semiconductors and semimetals also hinges on minimizing bipolar conduction effects, which is achieved when majority and minority carrier transport is asymmetric, *i.e.*, when  $R_{\text{B}}$  is large. Using the proposed material descriptors, we assess the TE performances of a set of narrow-gap and semimetallic Zintl phases. In agreement with experiments, we correctly re-identify Mg<sub>3</sub>Bi<sub>2</sub> and Bi<sub>2</sub>Te<sub>3</sub> as high-performing TE materials for room-temperature applications. In particular, Mg<sub>3</sub>Bi<sub>2</sub> showcases the importance of transport asymmetry; despite being a semimetal, a large  $R_{\text{B}}$  ensures high room-temperature TE performance. From our search, we find three Zintl phases (SrSb<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, and NaCdSb) that exhibit high room-temperature TE performance. We further propose a refined TE quality factor,  $B_{\text{bp}}$ , which is a useful measure of the TE performance when bipolar conduction effects are significant.  $B_{\text{bp}}$  combines the individual descriptors ( $B_{\text{maj}}$ ,  $E_{\text{g}}$ , and  $R_{\text{B}}$ ) into a single metric to assess the peak  $zT$  of materials.

While the descriptors help to identify candidate TE materials, there are others factors that require careful consideration for practical applications. The temperature-dependence of  $E_{\text{g}}$  for example may affect the predicted maximum  $zT$  at 300 K. The negative  $E_{\text{g}}$  of Mg<sub>3</sub>Bi<sub>2</sub> changes by  $\sim 25$  meV within a range of 350 K,<sup>14</sup> and  $E_{\text{g}}$  of Bi<sub>2</sub>Te<sub>3</sub> changes by  $\sim 100$  meV within a range of 600 K.<sup>91</sup> We find that for Bi<sub>2</sub>Te<sub>3</sub> and the three candidate Zintl phases, maximum  $zT$  at 300 K does not change significantly if the band gap is changed by 25 meV or 100 meV (Table S2, ESI<sup>†</sup>). Maximum  $zT$  of Mg<sub>3</sub>Bi<sub>2</sub> however, owing to its negative band gap, is most sensitive to changes in  $E_{\text{g}}$ , as illustrated in Fig. 3e. Oxidation is another consideration for terrestrial applications.<sup>92</sup> Near room-temperature operation will reduce the effects of oxidation due to sluggish kinetics, but experimental verification is needed especially for materials containing alkali and alkaline-earth elements. Materials also need to be doped to optimize TE performance. Generally, narrow band gap semiconductors are more easily dopable compared to wide-gap insulators due to low concentrations of charge compensating native defects.<sup>93</sup> Future work should address these key considerations in optimizing the TE performance of the candidate materials.

## 6. Computational methodology

A schematic of the computational workflow is shown in Fig. 4. We use first-principles density functional theory (DFT) to perform structural relaxations, and to calculate electronic band structures and bulk moduli. All DFT calculations are performed with the Vienna ab initio simulation package (VASP)<sup>94,95</sup> and the projector augmented wave (PAW) method is used to describe the core electrons.<sup>96,97</sup> The wavefunctions are expanded as plane waves with an energy cutoff of 340 eV.

First, we relax the ICSD structures of 650 Zintl phases using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)<sup>98</sup> as the exchange correlation functional and an automatically-generated  $\Gamma$ -centered  $k$ -point mesh with

length factor  $R_k = 20$ . We apply on-site Hubbard  $U$  corrections on the  $d$  orbitals of certain transition metals, following the methodology in ref. 41 and 99. For the relaxed structures, we computed their electronic structures on a dense  $\Gamma$ -centered  $k$ -mesh determined by the equation  $N_{\text{atoms}} \times N_{\text{kpts}} \approx 8000$ , where  $N_{\text{atoms}}$  and  $N_{\text{kpts}}$  are the number of atoms in the primitive cell and number of  $k$ -points, respectively.<sup>43,44</sup> This translates to a  $k$ -point grid of  $14 \times 14 \times 8$  for  $\text{Mg}_3\text{Bi}_2$  and  $12 \times 12 \times 12$  for  $\text{Bi}_2\text{Te}_3$ . We include relativistic spin-orbit coupling (SOC) effects in these calculations.

Next, we analyze features of the electronic structures calculated with the PBE functional. It is well-known that semilocal DFT functionals such as GGA-PBE tend to severely underestimate the band gaps of materials, while predictions with hybrid functionals (e.g., HSE06) are generally more reliable for semiconductors and insulators.<sup>100–102</sup> However, the large computational cost associated with hybrid functionals makes them unsuitable for high-throughput calculations. Within the dataset of 650 Zintl phases, we focus on compounds that have zero or negative band gap in GGA-PBE calculations and try to identify potentially narrow-gap semiconductors and semimetals. We choose to focus on this subset of materials to demonstrate the usefulness of the descriptors in materials where bipolar conduction cannot be ignored. The specific procedure we have adopted to identify narrow-gap semiconductors and semimetals is not important because the descriptors are generally applicable irrespective of the band gap.

We analyze the band occupations to assess the extent of band overlap (nesting) near the Fermi level. In a typical semiconductor with a well-defined band gap, bands below the Fermi level are fully occupied (valence bands) and those above are unoccupied (conduction bands) at 0 K (DFT calculation). In this case, there are no partially occupied bands. In contrast, a metal is characterized by overlapping bands with partial occupancies at numerous  $k$ -points around the Fermi level. We therefore evaluate the fraction of partially-occupied  $k$ -points relative to the total number of sampled  $k$ -points. If this fraction is small, it is possible that the material is a narrow-gap semiconductor or semimetal, but less likely to be a true metal. Specifically, we calculate the ratio,

$$R = \frac{\sum_{n=n_1}^{n_2} \sum_k P(O_{n,k})}{2N_{\text{kpts}}(N+1)} \quad (19)$$

$$n_1 = \frac{n_c}{2} - N, \quad n_2 = \frac{n_c}{2} + N + 1$$

where  $n$  is the band index,  $n_c$  is the number of electrons, and  $N$  is the number of bands considered below and above the band index  $n_c/2$ , which in the case of a semiconductor will correspond to the index of the valence band maximum.  $O_{n,k}$  is the occupation of the band  $n$  at a specific  $k$ -point. Here,  $P$  is a Boolean function of  $O_{n,k}$ . For bands with indices  $n_1$  through  $n_c/2$ , if  $O_{n,k} < 2 - \delta$  (assuming doubly occupied bands),  $P = 1$  otherwise  $P = 0$ . Similarly, for band indices  $n_c/2 + 1$  through  $n_2$ ,  $P = 1$  if  $O_{n,k} > \delta$ .

We use  $N = 3$  and occupation tolerance  $\delta = 10^{-3}$  to calculate  $R$ .  $R$  varies between 0 and 1, with  $R = 0$  representing a semiconductor and large  $R$  indicating that the phase is likely a metal (Fig. S8, ESI†). We classified materials with  $0 < R \leq 0.1$  from the GGA-PBE electronic structure as potential narrow-gap semiconductors and semimetals because of the small overlap between the nominal valence and conduction bands. Among the 650 Zintl phases, we identify 44 that have  $R \leq 0.1$ .

For these 44 Zintl phases, we then estimate the maximum  $zT$  at 300 K using the two-band transport model (eqn (12)). Three independent material descriptors are necessary to estimate  $zT$ : band gap ( $E_g$ ),  $n$ - and  $p$ -type quality factors ( $B_n$  and  $B_p$ ), and asymmetry parameter ( $R_B$ ). Due to the unsystematic underestimation of the band gap in GGA-PBE calculations, we fix  $E_g$  to 0.3 eV for all 44 phases. Since larger  $E_g$  leads to higher  $zT$  (Fig. 3), fixing  $E_g$  to 0.3 eV allows us to compare the best-case-scenario  $zT$  across materials. We perform a scissor operation to adjust  $E_g$  with the assumption that the band geometry remains unchanged. The band effective mass  $m_b^*$  is an important parameter in calculating the quality factors and, therefore,  $R_B$ . We use a finite-difference method to calculate  $m_b^*$  from the electronic structure calculated on a dense  $k$ -point grid.<sup>103</sup> We also calculate the density-of-states effective mass  $m_{\text{DOS}}^*$  from  $m_b^*$  using the relation  $m_{\text{DOS}}^* = N_V^{2/3} m_b^*$ , where  $N_V$  is the valley degeneracy. The quality factors are then calculated using eqn (14), where  $\mu_0$  and  $\kappa_L$  at 300 K are calculated using semi-empirical models that are fitted to large experimental datasets (see ref. 32 and 86 for details). The bulk modulus, which is an input parameter for the semi-empirical models, is calculated by fitting the Birch–Murnaghan equation of state to a set of total energies at different volumes.<sup>104</sup> In each case, we adjust the Fermi energy to maximize  $zT$  at 300 K.

Due to the recent success of  $\text{Mg}_3\text{Bi}_2$ -based materials for low- and room-temperature TE applications,<sup>14</sup> we compare the estimated maximum  $zT$  of the 44 Zintl phases to that of  $\text{Mg}_3\text{Bi}_2$ . We find that 20 out of the 44 Zintl phases have an estimated maximum  $zT$  of more than 20% of the maximum  $zT$  of  $\text{Mg}_3\text{Bi}_2$  at 300 K. We perform higher accuracy electronic structure calculations with the hybrid HSE06 functional on the 20 phases, in addition to 8 randomly-chosen Zintl phases out of the remaining 24 phases. The exchange mixing parameter is set to 25%, and all HSE06 calculations include spin-orbit coupling effects. The structures are relaxed with HSE06 prior to calculating the electronic structure. We use the HSE06 electronic structure to calculate  $E_g$  and  $m_b^*$ , which are then used as inputs to estimate the maximum  $zT$  at 300 K. The corresponding results are shown in Fig. 5a and tabulated in Table 1 and Table S1 (ESI†).

## Author contributions

Michael Y. Toriyama: conceptualization, investigation, data curation, writing (original draft), writing (editing). Adam N. Carranco: investigation, data curation, writing (editing). G. Jeffrey Snyder: investigation, writing (editing), supervision.

Prashun Gorai: conceptualization, investigation, data curation, writing (editing), supervision, project administration.

## Conflicts of interest

There are no conflicts to declare.

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