

Validity of the scattering exponent approximation for materials with a complex electronic structure

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A common method to identify the dominant internal material electronic scattering processes that limit transport and conductivity in experimental measurements is to use the scattering exponent approximation. It assumes that the carrier relaxation time follows $\tau = \tau_0 E^r$, where r is a value that depends on a specific scattering mechanism. The exponential trend is also reflected in the temperature dependence for parameters like mobility, following $\mu \propto T^s$. Literature r and s values are defined using simplified assumptions, the most important being single-band parabolic electronic structures. Typical materials beyond simple semiconductors, however, involve complex electronic structures and many scattering processes of various strengths acting simultaneously. Here, we consider transport simulations for a series of electronic structure models, from single parabolic band models, two-band models, and the full band structure of half-Heusler materials, as well as all important scattering mechanisms such as acoustic phonons, optical phonons, polar optical phonons, and ionized impurity scattering through *ab initio* calculation methods. We show that, in general, the r values that describe transport in such complex cases do not follow the nominal literature values; thus their ability to provide transport characteristics is limited. We also explore the feasibility of using these exponents to extract thermoelectric transport characteristics from the commonly used Pisarenko relation for the Seebeck coefficient in half-Heusler materials. In this case as well, the scattering exponents used to compute the Seebeck coefficient do not correspond to the internal transport processes due to the complexity of the electronic structures. However, despite the band complexities, we have identified a significant negative correlation between the exponents and the material's optical phonon energy.

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I. INTRODUCTION

Over the last few decades, numerous new electronic materials and their alloys have been synthesized, with novel potential applications for electronics, energy generation, thermoelectrics, magnetism, optoelectronics, etc. [1–5] The ability to understand the details of their electron transport and the internal scattering processes that determine it is crucial in the design of devices and technologies out of these materials [6–8]. Traditionally, for common semiconductors, simple, empirical models have been widely used to extract material property insight from experimental results [9–11]. The trends between parameters such as electron mobility μ versus temperature T or density n , or Seebeck coefficient S versus n , can be fitted using a single parabolic band (SPB) model to extract a scattering parameter r , which represents the dominant internal transport mechanism within the material. For example, this parameter is often assumed to be $r = -\frac{1}{2}$ in the case where acoustic deformation potential phonon scattering (ADP) dominates transport [11–13]. However, in novel materials beyond common semiconductors, multiple

scattering mechanisms take place, while the electronic structures involve significant complexity with multiple, highly nonparabolic, warped bands, often with a significant degree of band mixing [14–16]. Thus, while simple fitting of measured data to scattering exponent models using a specific r value is convenient, in general, it will fail to capture the essence of the underlying scattering processes, since it is not currently understood what r , s corresponds to in these complex cases.

In this work, we use *ab initio* transport calculations to explore how the scattering exponent approximation applies to materials of larger band structure complexity compared to common semiconductors, with the additional complexity of multiple scattering processes. We follow a model-hierarchical approach, where we first examine the validity of the nominal exponent values for the different scattering mechanisms for single parabolic band materials. As a second step towards complex band structures, still within the parabolic band regime, we explore how the scattering exponents are changed in the case of two-band systems. As a third step, we compare the nominal literature scattering exponent values to the ones extracted from *ab initio* level scattering rates of complex band materials from the half-Heusler (HH) family. These are materials with many, nonparabolic/warped, and in many cases overlapping bands, and some of the most promising materials for thermoelectrics (TEs) [1, 17–19]. In this way, we are able to pinpoint where and how the nominal exponent approximations break down as band complexity evolves. Regarding TEs, we explore the feasibility of using these exponents for

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explaining the Pisarenko relation (Seebeck coefficient versus Fermi level η_F) [20,21].

The paper is organized as follows. In Sec. II, we present the standard scattering rate equations and identify how the nominal scattering exponent values are extracted. In Sec. III A, we explore the energy-dependent scattering rates $\tau \propto E^r$, as extracted from analytical rates from single parabolic band (SPB) and two-band models. In Sec. III B, the temperature dependence $\mu \propto T^s$ is explored. In Sec. IV, we explore exponents for realistic material scattering rates obtained *ab initio*, using a data set of 13 half-Heusler compounds. Finally, in Sec. V, we conclude.

II. THEORY (ENERGY-DEPENDENT RATES)

A. Transport quantities under scattering exponents

Under the Boltzmann transport equation (BTE) formalism, the electrical conductivity is given by [22,23]

$$\sigma = e^2 \int_0^\infty \Xi(E) \left(-\frac{\partial f_0}{\partial E} \right) dE \quad (1)$$

where e is the charge of the electron and $\Xi(E) = \tau(E)v(E)^2g(E)$ is the transport distribution function (TDF), consisting of the relaxation time $\tau(E)$, carrier velocity $v(E)$, and the density of states $g(E)$. f_0 is the equilibrium Fermi-Dirac distribution function.

Assuming isotropic parabolic effective mass bands, we can extract the velocities, density of states, and TDF as shown in Eqs. (A1) and (A2) in Appendix A. Then, we set the relaxation time $\tau(k)$ as

$$\tau = \tau_0 E^r, \quad (2)$$

where τ_0 and r are constants-dependent on the dominant scattering process. Using this, the electrical conductivity and drift mobility can be written as [20]

$$\sigma = \frac{e^2 (2m^* k_B)^{3/2}}{3\pi^2 m^* \hbar^3} \left(r + \frac{3}{2} \right) T^{r+3/2} \tau_0 \mathcal{F}_{r+1/2}(\eta), \quad (3)$$

$$\mu = \frac{2e(r + \frac{3}{2})T^r}{3m^*} \tau_0 \frac{\mathcal{F}_{r+1/2}(\eta)}{\mathcal{F}_{1/2}(\eta)}, \quad (4)$$

where $\mathcal{F}_{1/2}(\eta)$ is the Fermi-Dirac integral of order (1/2), solved as in Mohankumar *et al.* [24] or by direct numerical integration. Above we used the relation $\sigma = en\mu$, with the carrier density given by

$$n = \frac{1}{2\pi^2} \left(\frac{2m^* k_B T}{\hbar^2} \right)^{3/2} \mathcal{F}_{1/2}(\eta). \quad (5)$$

Notice that after this analysis, although r is the energy exponent of the scattering time as $\tau \propto E^r$, the same exponential dependence is also observed for the temperature as well, i.e., mobility is also proportional to the temperature as $\mu \propto T^r$. This temperature dependence is also used as a convenient method to extract experimentally the dominant scattering mechanism in a material [25–27], since most mobility measurements are performed as a function of temperature.

For charge transport under a thermal gradient ∇T and the corresponding role of the scattering exponents, the relevant

TABLE I. Nominal energy and temperature dependent exponents for common scattering mechanisms.

Mechanism	E^r	T^s
ADP	−0.5	−1.5
ODP	−0.5	−1.5
POP	0.5	−0.5
IIS	1.5	1.5

quantity is the thermopower S given by [23]

$$S = \frac{e}{\sigma} \int_0^\infty \Xi(E) \left(\frac{E - E_F}{T} \right) \left(-\frac{\partial f}{\partial E} \right) dE, \quad (6)$$

while when applying the energy-dependent scattering exponents, we are left with the so-called Pisarenko relation, given by [20]

$$S = -\frac{k_B}{e} \left[\frac{(5/2 + r)\mathcal{F}_{r+3/2}(\eta)}{(3/2 + r)\mathcal{F}_{r+1/2}(\eta)} - \eta \right]. \quad (7)$$

B. Scattering exponents for different mechanisms

We consider two scattering mechanisms to examine the actual scattering times and their exponents: electron-phonon scattering and electron-ionized impurity scattering. For electron-phonon scattering, we consider three types of phonon-electron interactions: acoustic phonon scattering (ADP), optical phonon scattering (ODP), and polar optical phonon scattering (POP).

When calculating the carrier scattering rates $\tau(E, k, n)$, there are no closed-form analytical expressions for real materials with complex electronic structures. For parabolic bands, however, we list below the analytical common literature expressions [22,22,28–31]. For ADP, the scattering rate is given by

$$\tau_{\text{ADP}}^{-1}(E) = \frac{\pi D_A^2 k_B T}{\hbar \rho v_s^2} g(E), \quad (8)$$

where D_A is the deformation potential, k_B is the Boltzmann constant, ρ is the material density, v_s is the speed of sound in the material, and $g(E)$ is the density of states (DOS).

For ODP, the scattering rate is given by

$$\tau_{\text{ODP}}^{-1}(E) = \frac{\pi D_O^2}{2\rho\omega_{ph}} \left(N_\omega + \frac{1}{2} \mp \frac{1}{2} \right) g(E \pm \hbar\omega_{ph}), \quad (9)$$

where D_O is the optical-phonon deformation potential, N_ω is the number of phonons at a particular frequency, evaluated using Bose-Einstein statistics, $\hbar\omega_{ph}$ is the energy of the optical phonon, and the “+/-” denote absorption and emission processes. For both ADP and ODP, the only energy dependence comes from the DOS, which leads to $r = -0.5$. Similarly, the temperature dependence T^s follows the E -dependent exponent as $s = r - 1$ [see Eq. (4)], since the scattering times are also proportional to inverse temperature (see Table I).

For polar optical phonon (POP) scattering, the scattering rates (including screening) are given by [31,32]

$$\begin{aligned} \tau_m^{-1}(E) = & \frac{m^* q^2 \omega_{ph}}{4\pi \kappa_0 \epsilon_0 p^2} \left(\frac{\kappa_0}{\kappa_\infty} - 1 \right) \left(N_\omega + \frac{1}{2} \mp \frac{1}{2} \right) \left[\frac{-\hbar}{4p} \left(\frac{\beta_{\max}^4}{\beta_{\max}^2 + \frac{1}{L_{TF}^2}} - \frac{\beta_{\min}^4}{\beta_{\min}^2 + \frac{1}{L_{TF}^2}} \right) + \frac{\hbar}{2p} (\beta_{\max}^2 - \beta_{\min}^2) \right. \\ & \left. + \left(\frac{-\hbar}{2p L_{TF}^2} \mp \frac{\omega_{ph}}{2v} \right) \ln \left(\frac{\beta_{\max}^2 + \frac{1}{L_{TF}^2}}{\beta_{\min}^2 + \frac{1}{L_{TF}^2}} \right) \right] \pm \frac{\omega_{ph}}{2v} \left(\frac{\beta_{\max}^2}{\beta_{\max}^2 + \frac{1}{L_{TF}^2}} - \frac{\beta_{\min}^2}{\beta_{\min}^2 + \frac{1}{L_{TF}^2}} \right), \end{aligned} \quad (10)$$

where ω_{ph} is the phonon frequency, κ_0 and κ_∞ are dielectric constants corresponding to the low-frequency (ionic response) and high-frequency (free electron response) limits [22,31]. Note that this is a novel derivation of screened POP from Ref. [31]. The values for $\beta_{\max}$ and $\beta_{\min}$ involve the momentum p and are given by

$$\beta_{\max} = \frac{p}{\hbar} \left(1 + \sqrt{1 \pm \frac{\hbar \omega_{ph}}{E}} \right), \quad (11)$$

$$\beta_{\min} = \frac{p}{\hbar} \left(\mp 1 \pm \sqrt{1 \pm \frac{\hbar \omega_{ph}}{E}} \right), \quad (12)$$

whereas L_{TF} is the Thomas-Fermi screening length, as

$$L_{TF} = \sqrt{\frac{2\kappa\epsilon_0 k_B T}{q^2 n} \frac{\mathcal{F}_{1/2}(\eta)}{\mathcal{F}_{-1/2}(\eta)}}. \quad (13)$$

Focusing on the energy dependence, the POP scattering time, τ_{POP} , is roughly proportional to $\tau \propto \frac{p^3}{\beta^2} \propto \frac{E^{1/2}}{(1 + \sqrt{1 + \frac{\hbar \omega_{ph}}{E}})^2}$ [using Eqs. (10), (11), and (A1)]. At energies larger than the phonon energy $E \gg \hbar \omega$, the energy dependence of the denominator becomes negligible, and the overall energy dependence follows that of the numerator, $E^{1/2}$.

For ionized impurity scattering, we use the well-established Brooks-Herring formula as [30]

$$\tau_{IIS}(E) = \frac{16\sqrt{2}\pi\kappa_0^2\epsilon_0^2}{nq^4} \left[\ln(1 + \gamma^2) - \frac{\gamma^2}{1 + \gamma^2} \right]^{-1} E^{3/2} \quad (14)$$

with $\gamma = 8m^* L_{TF}^2 E / \hbar^2$. Here the scattering times directly follow an $E^{3/2}$ trend. IIS times, on the other hand, do not have an explicit dependence on the temperature; hence, the temperature exponent on the IIS-limited mobility is only what is transferred from the energy exponent [see Eq. (4)].

The scattering rates from the different mechanisms are combined using Matthiessen's rule as

$$\tau_{TOT}^{-1}(E) = \tau_{ADP}^{-1}(E) + \tau_{ODP}^{-1}(E) + \tau_{POP}^{-1}(E) + \dots \quad (15)$$

The commonly used literature exponents of energy (E -exp) and temperature (T -exp) are given in Table I for the scattering times of all mechanisms considered. The E -exp in the center column are directly extracted from the scattering rates (for ADP and ODP, for example, this is the energy dependence of the DOS, through Fermi's Golden Rule). The T -exp in the right column appears as a byproduct of simplifying the equations for σ , μ and S in terms of Fermi integrals. When the energy E is converted into the reduced energy $E^* = \frac{E}{k_B T}$, the expressions for σ and μ acquire a temperature term of the same E -exponent, r [see Eq. (4)]. This is further modified by the details of the temperature dependence of scattering times, overall denoted as T^s . For example, the temperature-

dependent exponents for ADP, ODP, and POP scattering are a unity factor lower compared to the energy exponents, due to an additional factor of T^{-1} present in the scattering time equations [Eqs. (8)–(10)]. ADP scattering has a factor of T^{-1} directly. ODP and POP scattering rates include the phonon occupation as N_ω , which is the phonon distribution (Bose-Einstein distribution), giving $N_\omega \propto T$ at small values of $\frac{\hbar \omega_{ph}}{k_B T}$, thus, they also have an additional T^{-1} scattering time dependence.

III. PARABOLIC BAND CONSIDERATIONS

A. Energy-dependent exponent

We perform our exponent analysis by evaluating the accuracy and validity of the nominal exponents for electronic structures of increasing complexity: (i) first for a single parabolic band (SPB) model, (ii) then for a double parabolic band (DPB) model, with bands of the same polarity, but with energy separation and different effective masses, and finally for (iii) the full DFT electronic structures of the half-Heusler material group, known for its band structure complexity. While the first two are explored using analytical models, the latter utilizes fully *ab initio* transport methods. In this hierarchical approach, we aim to gradually identify when the exponents begin to fail. Although parabolic-band models are not realistic representations of real materials, their simplicity can more clearly pinpoint why the exponents start to deviate from their nominal values. The DPB model acts as an intermediate step between the SPB and the realistic band structures from the half-Heusler material group. For example, the conduction band of half-Heuslers typically consists of X valleys (i.e., NbFeSb) or, in some cases, two sets of X valleys slightly separated in energy (TiCoSb). The valence band can include Γ valleys (typically triple degenerate), or L valleys (typically a double set), W valleys (typically eight-fold degenerate, NbCoSn), and these can be separated in energy and have different masses. The DPB model can provide indications of exponent variability due to the effects of degeneracy, band energy splittings, mass variations, etc., which cannot be in the SPB model but are also hidden in the fully *ab initio* treatment of realistic band structures.

1. Single parabolic band material (SPB) exponent analysis

An SPB model was constructed using the parameters given in Table III of Appendix A. Using Eqs. (8)–(14), the scattering rates are computed, while the carrier velocities and density of states are obtained using Eqs. (A1) and (A2) in Appendix. The analytical scattering times for the different mechanisms (ADP, ODP, POP, and IIS) for this single parabolic band material are plotted in Fig. 1. The left panel's top row,

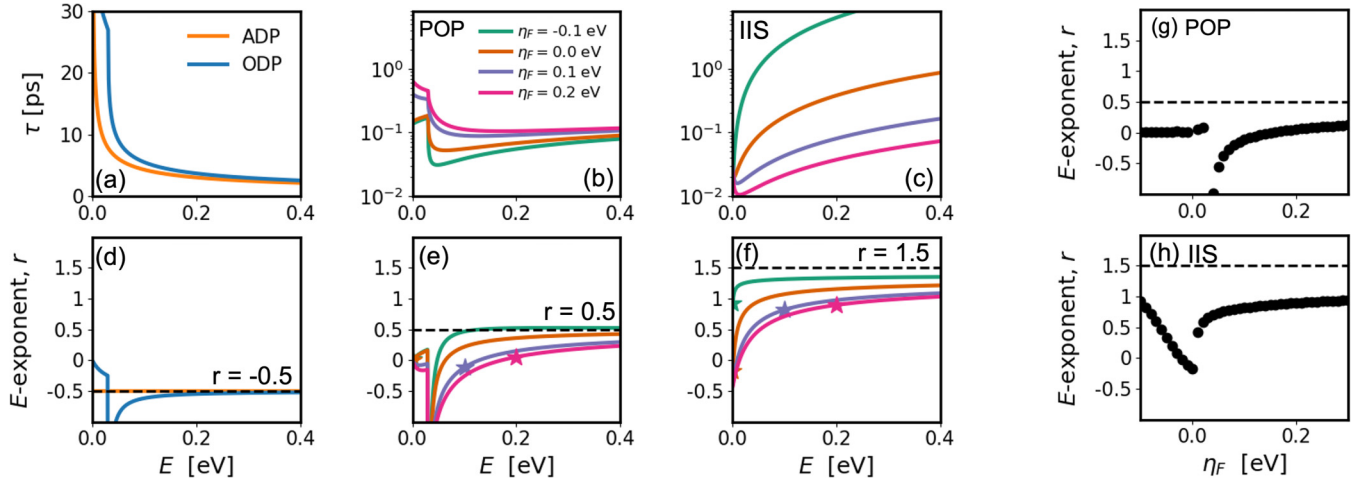


FIG. 1. [(a)–(c)] Analytical relaxation times for scattering in a single parabolic band (SPB) material. [(d)–(f)] Local scattering exponent (solid lines) with nominal values (dashed lines) for each mechanism. [(a) and (d)] ADP and ODP scattering. [(b) and (e)] POP scattering. [(c) and (f)] IIS scattering. [(g) and (h)] η_F -dependent scattering exponents for (g) POP and (h) IIS.

Figs. 1(a)–1(c), shows the scattering times, and the bottom row, Figs. 1(d)–1(f), the “local” exponent slope in energy E for all mechanisms. The dashed horizontal lines in the bottom row show the nominal exponents as listed in Table I. Note that while the nominal scattering exponents are widely employed and considered as constants, even for the SPB case their energy and Fermi level variations have not been examined—interestingly, below we show that even in this simple case, the exponents deviate significantly from nominal expectations with energy and Fermi level.

Figure 1(a) plots the ADP and ODP relaxation times, while Fig. 1(d) shows the exponent (slope). ADP scattering shows excellent agreement with the nominal exponent of $r = -0.5$. This is expected, as the only energy dependence of the relaxation times arises from the dependence of $\text{DOS}^{-1} \propto E^{-0.5}$. For ODP, on the other hand, a discontinuity is observed near the optical phonon energy (here we use $\hbar\omega \approx 0.03$ eV) due to the emission term being introduced at that phonon energy. The local energy exponent in Fig. 1(d) deviates from nominal around that region as well.

Figures 1(b), 1(e) and 1(c), 1(f) show the scattering times for POP and IIS, respectively, and their local exponents. Since screening depends on the carrier density, an η_F dependence is introduced in the scattering times and their exponents. Thus each line in these figures corresponds to a specific Fermi level and carrier density. However, the energy-local nature of the $\partial f/\partial E$ term in Eqs. (1) and (6) limits the transport energy range at each η_F . Thus, for each line, we note the position of the Fermi level, which denotes the actual relevant exponent. This is more clearly shown in Figs. 1(g) and 1(h) for the Fermi level dependent exponents of POP and IIS, respectively.

For POP, the exponent is constant around $r = 0$ for low densities [Fig. 1(g), left side], a discontinuity is observed around the phonon energy, and then the exponent asymptotically tends towards zero again at higher densities (right side). For IIS, the exponent is reduced as the carrier density increases in the low-density region. Note that for negative Fermi levels, for the exponents we take the slope at the nearest energy region, i.e. at $E = 0$ (the first relevant energy point).

The slope at that point decreases. When the Fermi level passes the band edge, a discontinuity in the exponent is observed with the exponent slightly increasing and tending towards $r = 1$, yet still lower than the nominal value. Interestingly, the nominal values are never reached for either POP or IIS cases. The respective literature values of $r = 0.5$ and $r = 1.5$ are reached for some scattering rate energy cases in Figs. 1(e) and 1(f), but these are not for the relevant Fermi level. Thus other than for ADP, the nominal values fail to describe transport even for the simplest single parabolic band model for the other scattering mechanisms.

With regard to thermoelectrics, the Pisarenko relation [Eq. (7)], typically provides information about materials’ properties such as the DOS effective mass. Deviations from the single-parabolic-band line under ADP, which is typically the basis, provide an indication of the m_{DOS} in the material of interest. However, uncertainty in the dominant scattering mechanisms and in their scattering exponent deviation from nominal values, would make such m_{DOS} identification difficult and inaccurate. We discuss this particular case in Appendix B.

2. Double parabolic band (DPB) exponent analysis

Progressing one step towards more complex band structure materials, we now explore the scattering exponent trends in a double parabolic band (DPB) system. The system is set as in Fig. 2(a): a single band of mass $m_1 = 1m_e$ is placed at energy $E = 0$ eV as the base band. A second band of arbitrary mass m_2 is placed at an arbitrary energy offset ΔE . To keep the parameters that we can vary manageable, we fix the Fermi level at $\eta_F = 0$ eV. The second band introduces an additional scattering branch at $E = \Delta E$, creating a discontinuity in the scattering times (here we consider both intra- and interband scattering as another simplification). In the example of Fig. 2, we use the values $m_2 = 3m_e$ and $\Delta E = 0.2$ eV as a basis.

We emphasize here that the two-band model we employ considers bands for the same polarity, not be confused with the typical two-band model, which is typically used in

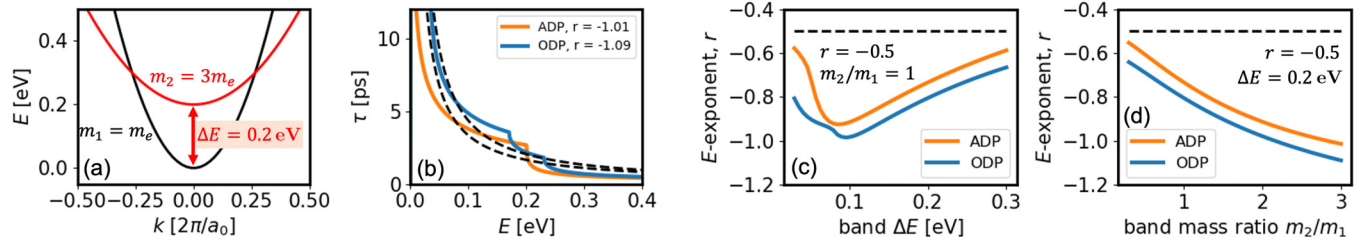


FIG. 2. Scattering exponents in a two-band system. (a) An example of the electronic structure considered, where two bands are placed 0.2 eV apart (for the upper band $m_{\text{DOS}} = 3m_e$). (b) The scattering times for ADP and ODP (solid lines) with the exponential fit (dashed lines). (c) Effect of increasing the band separation up to 0.3 eV. (d) Effect of increasing the m_{DOS} of the second band up to $3m_e$.

thermoelectrics and considers a conduction and a valence band capturing bipolar transport. What we envision is to capture the complexity of unipolar electronic structures, building our way from the SPB to the complexity of real materials. Thus, to differentiate, we refer to our model as the double parabolic band (DPB) model.

The ADP and ODP scattering times are shown in Fig. 2(b). Other parameters used for the simulation can be found in Table III in Appendix. Discontinuities appear in the energy position of the second band edge, but also due to the ODP emission/absorption processes. To extract the exponent for these scattering times, the simplified approach of using a single exponential curve that is mapped onto the scattering times line is used (dashed lines). This provides a single value for the energy exponent r . For this particular example, the scattering exponent is around $r = -1$ for both ADP and ODP. The discontinuity in the scattering times reduces the exponent, already reaching twice the nominal value for ADP and ODP scattering in absolute terms. Despite this being a simple example, what it shows is that even small additions to the band structure alter significantly the scattering exponents, and these alterations will also appear in realistic materials.

We then examine the scattering exponents for different band offsets ΔE . In this case, the band mass ratio was kept constant at $m_2/m_1 = 1$. At low ΔE , the system approaches the limit of two degenerate bands, and the exponents tend towards those of a single parabolic band for both ADP and ODP cases, as expected. For larger ΔE separation, we observe the effect of the discontinuities. Significant deviations are seen from the SPB model value, reaching values of -1 . At higher ΔE , the discontinuity is introduced too high in energy; thus, its effect becomes less prominent, resulting in exponent values closer to the nominal $r = -0.5$. Note that the Fermi level is placed near the band edge ($\eta_F = 0$ eV), only the first band contributes to the transport.

Figure 2(d) describes the effect of changing the band mass ratio m_2/m_1 at constant $\Delta E = 0.2$ eV. When the ratio m_2/m_1 is small, the DOS of the second (upper) band is low, reducing the amount of scattering it introduces on the lower energy band. Hence, the discontinuity created by the second band will be negligible, and the overall exponent will be similar to that produced by the SPB, $r = -0.5$. As the ratio m_2/m_1 increases and the effect of the second band becomes stronger, the discontinuity increases. The exponential fit must take a steeper (more negative) r value to account for the larger discontinuity, following a monotonic reduction, reaching values of $r = -1$ at typical larger ratio cases.

Overall, the energy-dependent exponent r , even for a simple two-band system, demonstrates a strong dependence on band details that makes the nominal values essentially irrelevant. (Note that we do not perform this two-band analysis for IIS or POP here, because there is no analytical formula to account for two bands and interband scattering for anisotropic scattering mechanisms. We will be discussing IIS and POP exponents for realistic half-Heusler materials later on, where we follow a fully numerical approach.)

B. Temperature-dependent exponents

Below, we examine the validity of these T-exponents (Table I) for single- and double-band material systems.

1. Single-band material T -dependent exponents

Figure 3 shows the temperature dependence of the mobility $\mu \propto T^s$ for a single parabolic band, where transport is limited by (a) ADP, (b) ODP, (c) POP, and (d) IIS. Different colors correspond to different carrier concentrations, as shown in the legend of Fig. 3(a). Figures 3(e)–3(h) show the temperature-dependent exponents, each fitted by corresponding straight lines in the data of the first row, against carrier density n . The exponent s corresponding to the lines of the top row is marked with like-colored stars in the second column, while the black lines are a fit to the data points. The gray-dashed lines show the nominal values for the temperature-dependent exponents for each mechanism.

In the case of ADP-limited transport, the temperature-dependent exponents are in general agreement with the nominal literature values. ODP-limited transport has a temperature exponent that is somewhat lower compared to the nominal value (at around $s = -2$ rather than $s = -1.5$). POP-limited transport has an exponent that deviates as well; it is lower compared to the nominal value in the entire density range ($s = -1$, compared to $s = -0.5$). The T -dependent exponent for IIS-limited transport starts close to the nominal value at low densities, but it reduces as the density increases, towards the degenerate regime. At higher densities, Coulombic screening typically makes scattering rates more isotropic, and exponents will thus drop towards ADP/ODP values.

2. Two-band material T -dependent exponents

To examine the T -dependent exponents for a two-band material, we consider a basic band structure as shown in Fig. 4(a). In this case, the first band is positioned at $E = 0$ eV and has mass $m_1 = 1m_e$. The second band is positioned at

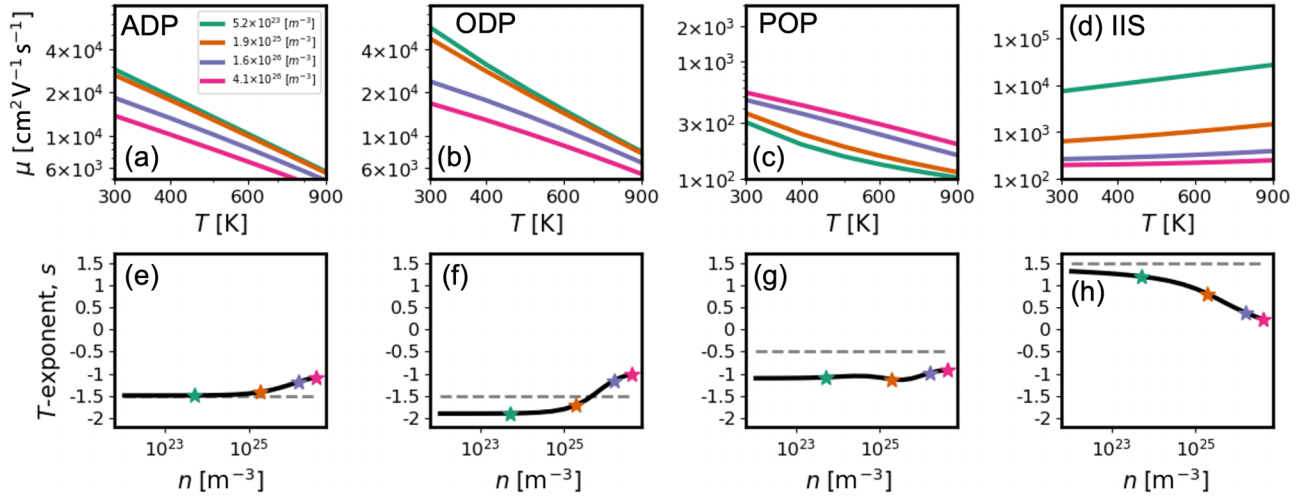


FIG. 3. Temperature-dependent exponent, s , for a single parabolic band (SPB). Four scattering mechanisms (ADP, ODP, POP and IIS) are considered, columnwise. [(a)–(d)] Mobility μ vs temperature T . [(e)–(h)]. T -exponent, s , vs charge density n . The T -exponents are the slopes of the lines in the first column as indicated by the colored stars (following the same color-code as the lines), while the solid line is a numerical fit.

$E = 0.1$ eV and has mass $m_2 = 3m_e$. We only consider ADP scattering limited transport. Both intra- and interband scattering are considered, with a common deformation potential for the scattering rates of $D_{\text{ADP}} = 1$ eV. Figure 4(b) shows the temperature dependence of the mobility, alongside the T^s . The different colored lines correspond to different initial Fermi level, η_F , positions at 300 K (different carrier densities), as shown in Fig. 4(a). For each case, as the temperature increases from 300 K, the material is assumed to retain a constant charge density accordingly by adjusting the Fermi level, η_F . The T -dependent exponents in 4(b) at low n are significantly lower than the nominal value of $s = -1.5$, reaching $s = -2.46$, explained through the E -dependent exponent decreases for multiband systems shown earlier in Fig. 2(c). At higher n (elevated Fermi levels), the system enters the degenerate regime beyond any band crossings, and the temperature dependence converges to T^{-1} , as is the case for single-band ADP as well [Fig. 3(e)]. We also note that we studied the effect of band separation: as the band separation decreases, then the single-band behavior is resumed (no extra discontinuities in the scattering times). As the separation increases significantly, again the single-band behavior is resumed, since only the lowest band is occupied. It is only in the intermediate ΔE

region that the discontinuities affect the scattering and reduce the exponents.

The basic conclusion from the SPB and DPB analysis is that even for these simple examples, other than for ADP, the T -dependent exponents deviate from nominal. The expectation is that for realistic complex band materials and scattering mechanisms, these deviations would be even larger and more complex in nature, as it will be shown below.

IV. HALF-HEUSLER MATERIALS' EXPONENTS: *AB INITIO* BAND STRUCTURES AND SCATTERING

A. Computational method

We now examine the exponents of the scattering rates of real materials. For this, we use DFT extracted electronic structures and full-band *ab initio* numerical considerations for the scattering rates and the BTE extracted transport properties, using the ELECTRA code [33]. We use half-Heusler (HH) materials as examples. Half-Heuslers are known for their strong durability and high thermoelectric performance [34], originating precisely from their complex electronic structures. The first subsection, as an example, investigates scattering exponents in NbFeSb, a HH alloy with particularly high thermoelectric power factor performance [12,35–37]. We then examine 12 more HH materials (13 in total), seeking to identify a scattering exponent that can holistically describe the scattering and transport behavior in this family of materials, but also by extrapolation the exponents in complex band structure materials in general, and TE materials in particular. The electronic structures of typical half-Heuslers, which demonstrate the band complexity, are shown in Fig. 11 in Appendix C. For example, the conduction band of HHs typically consists of X valleys (i.e., NbFeSb) or, in some cases, two sets of X valleys slightly separated in energy (TiCoSb). The valence band can include Γ valleys (typically triple degenerate), or L-valleys (double set), W valleys (eightfold degenerate, NbCoSn), and these can be separated in energy and have different masses. In a sense, the VB of HHs is the most complex system we consider.

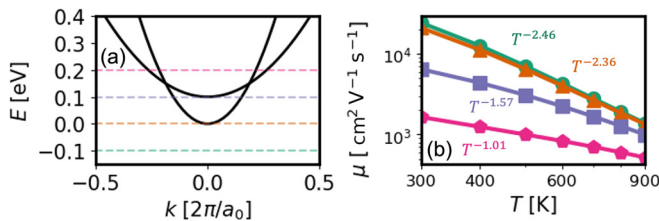


FIG. 4. (a) Band structure for a two-band system with $m_1 = 1m_e$, $m_2 = 3m_e$ and $\Delta E = 0.1$ eV. Dashed lines: The considered Fermi levels, η_F , at the initial temperature of 300 K. (b) Mobility μ versus temperature, T , for four different charge densities, each corresponding to the Fermi level (and color coding) in panel (a). The T -dependent exponent, T^s , is noted for each charge density.

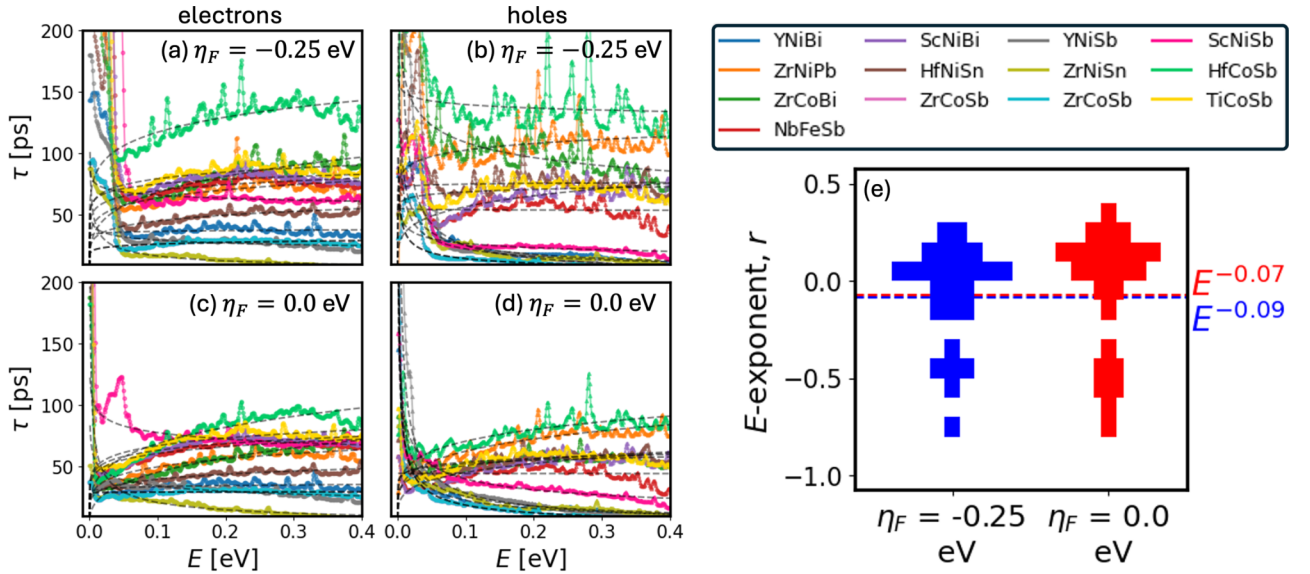


FIG. 5. [(a)–(d)] Relaxation time τ and the exponential fit for 13 half-Heuslers for both their polarities and different Fermi levels: (a) n -type at $\eta_F = -0.25$ eV, (b) p -type at $\eta_F = -0.25$ eV, (c) n -type at $\eta_F = 0$ eV and (d) p -type at $\eta_F = 0$ eV. (e) Histograms for the exponents from (a)–(d), with the average E -exponent for each case shown to the right.

The band structures are obtained using Quantum Espresso, using norm-conserving Vanderbilt (ONCV) based pseudopotentials and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals [38,39]. Detailed information on the full computational formalism can be found in our previous publication in Ref. [40], from which we extracted all *ab initio* data used in this work. Here we provide the main details for completeness. We use a cutoff of 120 Ry for the wave functions, and a convergence criterion of 10^{-8} . An $81 \times 81 \times 81$ k mesh was employed for non-self-consistent calculations to obtain accurate band structures for transport calculations. The effect of spin-orbit coupling on the band structures was found to be negligible, as seen in Refs. [6,35,41], hence it was not considered in the calculations.

To obtain the electron-phonon scattering rates, we used density functional perturbation theory (DFPT), followed by Wannierization using the EPW code [42] as in Refs. [14,35,43], to obtain a highly relevant set of matrix elements near the regions that affect transport the most (band edges for all phonon modes for intra- and intervalley transitions). Using those matrix elements, we then extracted deformation potentials (D_{ADP} and D_{ODP}), which we used to compute the scattering rates. This is a highly efficient *ab initio* computational formalism that is scalable to many materials, since it requires the calculation of only 10s of matrix elements (rather than many thousands), but these are highly relevant. The IIS and POP scattering rates, which are the strongest at room temperature in these materials, are computed using the screened Brooks-Herring and Fröhlich formalisms.

For transport, we employ our BTE solver ELECTRA, which is efficiently constructed to account for the specifics of this *ab initio* method we are using. The whole formalism is validated and compared against full EPW calculations and experiments in Refs. [14,35,40,43] with excellent agreement.

Note that common BTE codes widely used such as BoltzTraP [44] are based on the constant relaxation time ap-

proximation (CRTA), and cannot be employed in this study, which specifically focuses on the energy and temperature dependence of the scattering times. As a benchmark, however, all tests that ELECTRA performs within the CRTA (in other cases) are a good match with the BoltzTraP results [33].

Once the relaxation times are obtained for all of the thousands of k points in the Brillouin zone, we find the DOS-weighted average of the data in energy to convert the scattering times into a singular function of $\tau(E)$, as

$$\tau_{\text{DOS}}(E) = \frac{\sum_{k,n} \tau_{(k,n,E)} \text{DOS}_{(k,n,E)}}{\sum_{k,n} \text{DOS}_{(k,n,E)}}. \quad (16)$$

Once this function is calculated, we fit an exponential function $\tau = \tau_0 E^r$ to obtain the E -dependent exponents.

B. Statistical analysis of scattering exponents in half-Heusler alloys

Using the numerically computed relaxation times for the 13 HHs from their realistic electronic structures (the list of these materials is provided in Fig. 5), we can obtain a distribution of a more accurate set of scattering exponents, beyond the nominal values and beyond the simple SPB and DPB values. Here we consider the scattering exponents of the scattering times for both n -type and p -type polarities of these 13 HH alloys, i.e., we examine 26 different electronic structure cases. We also consider full numerical calculations for a combination of multiple scattering mechanisms, i.e., ADP, ODP, POP, and IIS.

The total scattering relaxation times versus energy, E , for the 26 HHs for low ($\eta_F = -0.25$ eV) and high ($\eta_F = 0.0$ eV) Fermi levels, combining all scattering mechanisms, are shown in Figs. 5(a) and 5(b), respectively. The actual times are shown by the grey dot symbols and thin lines. An exponential fit is shown by the colored-dashed lines [blue in Fig. 5(a) and red in Fig. 5(b)]. For this, we only fit the long part to the right

side, and not the sharp peak near $E = 0$ eV. Here we are more interested to present the statistical distributions of the scattering times, their variations and their exponents, rather than the individual materials' times; thus we do not distinguish the individual materials' scattering time lines. Nevertheless, we provide separate figures in Appendix C that plot these data in a less crowded way and clearly distinguish the different materials.

The E -dependent exponent, obtained for each material, is shown collectively as a histogram in Fig. 5(c). The blue histogram is formed from the data in Fig. 5(a), while the red histogram from the data in Fig. 5(b). For $\eta_F = -0.25$ eV (blue histogram), the E -dependent exponent follows a rather normal distribution with the data, with an average of $r = -0.09$. However, this fit does not account for the sharp peak near $E = 0$ eV. Similar to ODP and multiband scattering, the discontinuity decreases the E -dependent exponent. Therefore, the extracted exponent at low η_F will be on average even lower. This value suggests that the dominant scattering mechanism is something in between ADP + ODP ($r = -0.5$) and POP ($r = 0.5$). This is expected, since these mechanisms have comparable strength at low energies [40], and at low energies the complexities of the electronic structures are smaller (nonparabolicities, warping, etc., begin at energies slightly higher than the band edge). For $\eta_F = 0$ eV (red histogram), the distribution has a mean value of $r = -0.07$ (with the actual value being even smaller as explained above). Here IIS is the dominant scattering mechanism [40], with a nominal value of $r = 1.5$, but the overall calculated exponents do not actually reflect this. Thus, band structure complexities can manifest as scattering exponents that suggest different dominant scattering mechanisms compared to the real situation.

C. Pisarenko relation for the Seebeck coefficient

When it comes to thermoelectrics, the E -dependent exponent ($\tau = \tau_0 E^r$) can be used to analyze the Pisarenko relation, which plots the Seebeck coefficient S , against charge density n , or Fermi level η_F . Using the SPB model, analytical expressions for S [Eq. (7)] and n [Eq. (5)] can be obtained and fitted against experimental data to extract parameters such as the DOS effective mass m_{DOS} , Fermi level η_F , and the E -dependent exponent r . Typical Pisarenko plots for the HHs are shown in Fig. 6. However, changes in m^* and r act on the Pisarenko plot in similar ways; thus, it is not easy to distinguish between them. For example, a shift in the characteristic curve (left or right) can arise from both a change in the mass m^* (which changes the charge density, n , for a specific Fermi level) and/or a change in the E -dependent exponent, r , (which changes the Seebeck coefficient). Thus, the scattering exponent is often fixed at $r = -1/2$, (transport assumed to be limited by ADP scattering) [11–13], so that the DOS effective mass, m_{DOS} , can be extracted. However, as the scattering exponents for complex materials deviate from $r = -1/2$, estimations of the m_{DOS} can be deceiving.

Here we examine the validity of the analytical Seebeck expression [Eq. (7)], which is widely used in thermoelectric materials analysis, in mapping the fully numerical Seebeck coefficients. In Fig. 6, we plot the Pisarenko relation (S vs

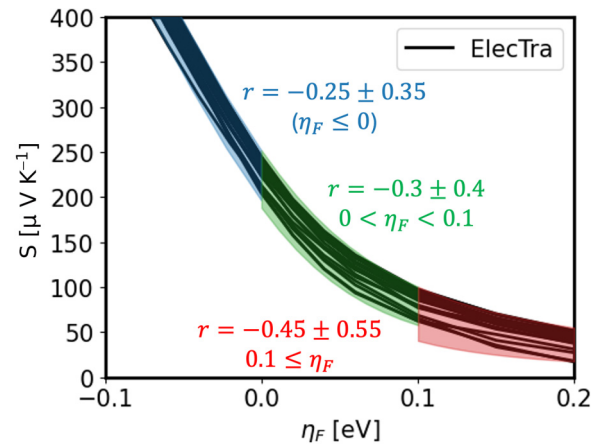


FIG. 6. Seebeck coefficient S vs η_F for 26 half-Heusler alloys (13 n -type and 13 p -type) in black lines. The highlighted regions show the range of exponents predicted by the SPB model under the scattering exponent approximation, extracted from Eq. (7). For the SPB model, the r range is denoted in each region.

η_F), using the calculated Seebeck results from the full-band ELECTRA calculation taking into account all scattering mechanisms for all of the 26 half-Heuslers (13 n -type and 13 p -type) considered (black lines). Note that plotting against the Fermi level, η_F , is equivalent to plotting against density. We then used the approximated Seebeck model from Eq. (7), and varied the E -exponent r to match the upper and lower bounds of the numerical data. A range of valid exponents to capture the variation of the actual Seebeck calculations was found to be $r = -0.25 \pm 0.35$ up to $\eta_F = 0$ (blue shaded region), $r = -0.3 \pm 0.4$ between $0 < \eta_F < 0.1$ (green shaded region), and $r = -0.45 \pm 0.55$ beyond $\eta_F > 0.1$ (red shaded region).

Compared to the E -dependent exponents obtained in Fig. 5(c) from the relaxation times themselves, the exponents extracted from the Pisarenko plot are lower. At low η_F (blue shaded region), the decrease is due to the discontinuity in the relaxation times at low energies due to emission processes in ODP and POP, as observed in Fig. 5(a). This decrease is not accounted in the fitting in Fig. 5. That peak itself contributes to a negative exponent in that region [as seen in Figs. 1(d) and 1(e) for ODP and POP]. With increasing η_F (green-red regions), more states further away from the discontinuity participate in transport. There, the transport is becoming IIS-controlled with a nominal exponent of $r = 1.5$, which is reduced by screening towards $r = 1$, further reduced by multiple bands. Moreover, higher energy band regions of larger nonparabolicity begin to participate in transport, which also reduces the characteristic exponents.

Overall, the combination of IIS and POP strength in determining the overall scattering times [40], as well as the multiband and the nonparabolic shape, reduces the characteristic exponent of these HHs to the range between $-0.6 < r < 0.1$ (at $\eta_F = 0$). Comparing this range to the exponents from the SPB model (Table I), such values suggest that transport is closer to ADP/ODP-limited. In the case of half-Heuslers, however, it is IIS and secondary POP which are limiting trans-

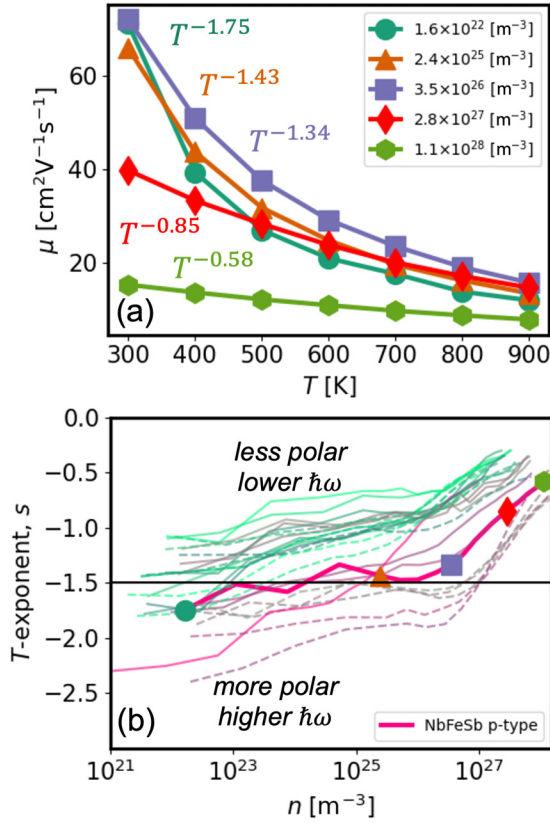


FIG. 7. (a) Mobility vs temperature for p-type NbFeSb, obtained using the full-band full-scattering ELECTRA code [33]. Each color corresponds to a different charge density, with the temperature-dependent exponent, T^s , extracted as an exponential fit, noted for each line. (b) The T -dependent exponent against charge density for 26 half-Heuslers (13 n -type and 13 p -type), each line corresponding to a different material. The symbols correspond to the T -dependent exponents extracted in (a) for n -type NbFeSb. The ADP-limited nominal value is indicated by the horizontal line at $s = -1.5$.

port at those η_F values [40], but band structure complexities obscure the resultant exponent.

D. Temperature-dependent mobility exponents for complex band half-Heusler materials

We now explore the temperature-dependent exponents of the mobility of these 13 HHs, $\mu \propto T^s$ (26 electronic structures). For instance, a mobility-temperature plot is shown in Fig. 7(a) for p -type NbFeSb for 5 charge densities. The T -dependent exponent T^s is obtained by making an exponential fit to the data points and is noted in the figure. Using this method, we then explore the T -dependent exponents for all 13 HHs.

For each material, full-band calculations are performed using the BTE code ELECTRA [33], at 20 different charge densities (or 20 Fermi levels with η_F from -0.25 to 0.35 eV as initially set at 300 K). For each charge density, the mobility μ was calculated in the temperature range of 300–900 K. Note that we keep the density constant as is physically relevant to retain charge neutrality, whereas the Fermi level changes for

each case as the temperature changes. These calculations use the same input parameters and method as in Ref. [40], but extended for higher temperatures (details for these calculations will be presented elsewhere).

Taking an exponential fit over the range of mobilities as for NbFeSb earlier, the T -dependent exponents T^s are extracted for each material and for each carrier density. The exponent results are shown in Fig. 7(b) versus charge density, with each line corresponding to a unique half-Heusler material (solid lines for n -type, dashed lines for p -type). The lines for the different HH materials are colored from green to purple, and as we explain below, the coloring ranges from less polar and/or smaller phonon energy (green), to more polar and/or larger phonon energy materials (purple). See Fig. 12 for a version where distinct colors are used for each material. In addition, see Fig. 13 for the actual mapping of each material to the corresponding color while also correlating each material to its phonon energies and polarity.

This group of 13 HHs (26 lines) starts with T -dependent exponents at low η_F ($n \approx 10^{23} \text{ m}^{-3}$), ranging from $-2.5 < s < -1.5$. As shown in Fig. 3, the values suggest strong phonon scattering (ADP, ODP, and POP) at low n . As charge density increases, their T -dependent exponents start to slightly increase to values in the interval of $-1.5 < s < -0.5$ (at $n \approx 10^{27} \text{ m}^{-3}$). This is because the contribution of IIS increases, which can be seen through the increase in the T -dependent exponent [for IIS $s = 1.5$ at low η_F and $s = 0$ at high η_F - see Fig. 3(h)]. However, the $s = 0$ value is never reached under realistic carrier density values.

A large variation can be observed for the T -dependent exponents, s , especially for low densities. One reason is the differences in electronic structures, as observed in Fig. 11, leading to different scattering profiles and hence different overall exponents. However, in a previous study, Ganose et al. found that the T -dependent exponent has a linear and negative dependence on the phonon frequency [45]. We show that this is the case here as well. Under low densities, IIS is weak, and transport is limited by the phonon processes. For weak polar materials, ADP will mostly limit transport, thus the exponents resemble more the ADP case (higher nominal exponents of around $s = -1.5$). Before the emission onset of ODP and POP, only the weaker absorption mechanisms are present, for which relaxation times are high anyway.

For strongly polar materials, the mobility at low temperatures mostly accounts for the absorption processes which have weak scattering, leading to high mobility. An increase in the temperature will populate the higher energy carriers beyond the phonon energy $\hbar\omega$, which can undergo emission. The emission onset will appear in the relaxation time plot [Fig. 1(b)], significantly increasing scattering, reducing mobility and reducing the scattering exponents. The sudden decrease in μ is reflected as a negative s value. For materials with small $\hbar\omega$, the initial Fermi distribution at low temperature accounts for the carriers which can undergo emission, having a reduced mobility from the start. Thus an increase in temperature does not result in a sudden drop in mobility. As the phonon energy increases, the higher the energy at which the emission occurs is, which is picked more distinctively as the temperature increases, making the s exponent reduction stronger. This is noted in Fig. 7(b).

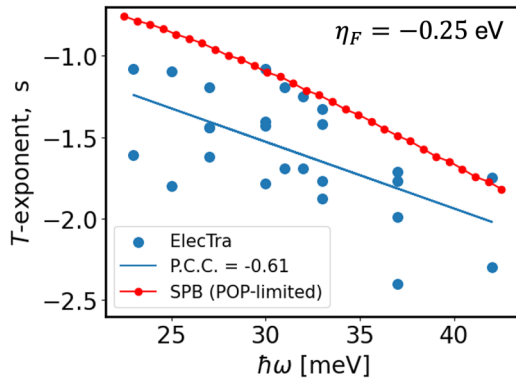


FIG. 8. T -exponent, s , vs POP energy $\hbar\omega$ at $\eta_F = -0.25$ eV for 26 half-Heuslers (blue dots) and POP-limited parabolic band (red). The line of best fit (and Pearson correlation coefficient of -0.61) is given by the blue line.

Figure 8 further explores the dependence of the scattering exponents on phonon energy by plotting s versus $\hbar\omega$ at $\eta_F = -0.25$ eV for the half-Heuslers (blue dots) and the POP-limited SPB (red line) with our standard parameters as given in Table III. The two follow similar trends, with the T -exponent decreasing with increasing $\hbar\omega$ with a Pearson correlation of -0.61 , which is significant. For this correlation to be valid, materials should have high polarity (high κ_0/κ_∞) in order to have strong POP scattering. Overall, the variance in s is caused by differences in the band structures, as well as the POP strength and its phonon energy.

Overall, by plotting the mobility exponents versus density, we observe the dominant scattering mechanism shifting from electron-phonon scattering (ADP, ODP, and POP) to ionized impurity scattering (IIS). However, the variance of the exponent distribution for this group of materials is quite large, reaching separations of $\Delta s = 1$ at different charge densities. To put this into perspective, a difference of $\Delta s = 1$ is what differentiates ADP/ODP scattering from POP, as well as POP scattering from IIS (in the SPB model). This large variance makes it difficult to extract information for individual material specifics.

E. Temperature-dependent mobility exponent from experimental measurements

Finally, we explore the temperature-dependent exponent of the mobility for HHs, extracted from experimental results using Starrydata2 [56,57]. μ versus T curves for 57 HHs were extracted from Refs. [46–55], and are shown in Fig. 9(a). A lower bound for the temperature was set to 300 K for consistency with the simulations. The mobilities for each material were normalized by their values at $T = 300$ K to allow for the comparison of trends between materials. The black dots are the data points, while the red lines are the exponential fits. The data are too numerous to distinguish individually, but we also focus on the statistical variations, rather than individual materials. Figure 9(b) plots the distribution of the extracted T -dependent exponent, s .

As we cannot obtain the charge density for each HH, we cannot make direct comparisons with the data presented in Fig. 7(b). However, since we know that HHs tend to have large

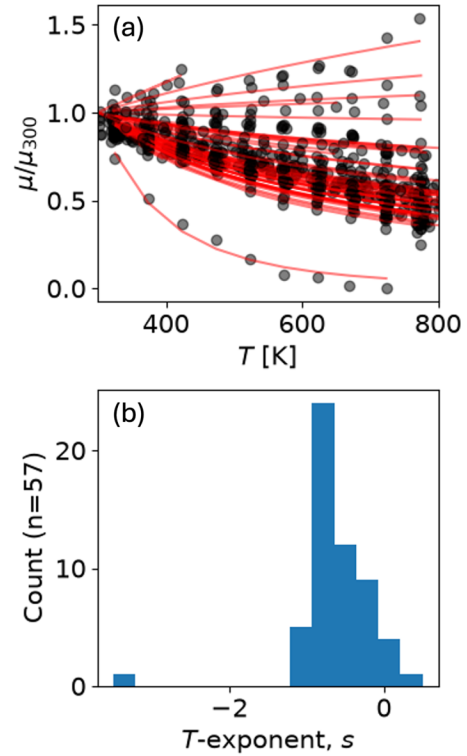


FIG. 9. (a) Experimental measurements for mobility μ against temperature [46–55]. The mobilities for each material were normalized by their values at $T = 300$ K to allow for the comparison of trends between materials. The red lines indicate exponential fits given by $\mu = \mu_0 T^s$. (b) A histogram for the T -dependent exponents s , extracted in (a).

carrier concentrations ($n > 10^{27} \text{ m}^{-3}$), a general comparison can be made. At the high n regime, the computational results indicate an exponent range of $-1.5 < s < -0.3$, while the majority of experimental results spread between the range of $-1.2 < s < 0$. The results are in decent agreement with each other. The small differences are accounted for by the presence of defects, alloying, as well as the polycrystalline nature of crystals that we do not consider in the calculations. In fact, the outlier at $s = -3$ is from a half-Heusler/full-Heusler nanocomposite, HH-FH (0.4:0.6) [49], which could lead to this anomalously large deviation.

V. CONCLUSION

In conclusion, this paper explored, for complex band materials under various scattering mechanisms, the validity of the scattering exponent approximation, which assumes exponential trends in energy (E') and temperature (T^s) for carrier transport. Nominal values exist, derived under single-band material conditions, whose validity is challenged here. Using a single parabolic band (SPB) model, we showed that only the exponent for acoustic phonon (ADP) scattering-limited transport matches the nominal value. The exponent in ODP, POP, and IIS scattering deviate due to the phonon emission onset at the phonon energy level and screening, and are typically lower than nominal. Similar conclusions are reached for the T -dependent exponents of the SPB case.

TABLE II. Comprehensive values for the Energy- and Temperature-dependent exponents E^r and T^s , for the low and high η_F (or density) cases. The table shows the nominal values, the single parabolic band (SPB) model values, the two-band model values (2PB), and the realistic overall values from the half-Heusler material family. Values for four different scattering mechanisms (ADP, ODP, POP, and IIS) are provided.

System			E^r		T^s	
			Low η_F	High η_F	Low η_F	High η_F
Nominal	ADP			−0.5		−1.5
	ODP			−0.5		−1.5
	POP			0.5		−0.5
	IIS			1.5		1.5
SPB	ADP			−0.5	−1.5	−1
	ODP		<−1	−0.5	−2 to −1	−1
	POP		0	−0.5 to 0	−2 to −1	−1
	IIS		1 to 0	0.5 to 1	1.5	0
2PB	ADP		−0.5 to −1 (band dependent)		−2.5 to −1.5 (band dependent)	
HHs	ALL	$\tau(E)$	−0.7 to 0.3	−0.7 to 0.3	−2.2 to −1	−1 to −0.2
		Pisarenko	−0.6 to 0.1	−1 to 0.1		

In the case of a two-band material system under ADP-limited transport, the introduction of a second band greatly reduces both the E - and T -dependent exponents, reaching $r = -1$ and $s = -2$ when the second band is located reasonably near the band edge.

We then investigated the scattering exponents in realistic materials. We used a group of 13 n - and p -type half-Heuslers, 26 materials in total, where electronic transport was computed fully *ab initio*. We extracted the E -dependent exponents by numerically fitting the scattering-time data, and then through fitting their Seebeck coefficients to that of a single-band material (Pisarenko relation). In the first case, the exponents are not easy to extract, as a single numerical line fit is not possible due to discontinuities in the scattering times at the onsets of phonon emission, and the band complexities that are not captured in the single band relation (e.g., additional bands, nonparabolicity, etc.). However, in both exponent extraction methods, the resulting exponents from these 26 complex band materials indicate overall lower exponents compared to the nominal values, but also a large spread in the exponents of the different materials. This suggests two things: (i) although the dominant scattering mechanism is in many cases POP and IIS (especially for the latter at higher densities), the exponents could wrongly suggest ADP/ODP-limited scattering if the nominal values are consulted. (ii) the specifics of each material with its band complexities and the scattering complexities make the use of the nominal exponent values highly inappropriate. We also show that for such materials, the exponents are determined by band complexities, but also follow a linear (and negatively correlated) trend with the optical phonon energy. Finally, a comprehensive list of the exponent values obtained is provided in Table II.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The experimental data for 57 HHs (μ versus T curves) were extracted from Refs. [46–55], obtained using Starrydata2 [56,57]. The other data are available from the authors upon reasonable request.

APPENDIX A: PARABOLIC BAND SPECIFICS

Parabolic band quantities were calculated using analytical equations as given below. The model starts by obtaining parameters for the band velocities, density of states and scattering times [$v(E)$, $g(E)$, and $\tau(E)$]. E_C is the band edge, set to 0 eV.

$$v(E) = \sqrt{\frac{2(E - E_C)}{m^*}} \quad (\text{A1})$$

$$g(E) = \frac{\sqrt{2(m^*)^3}}{\pi^2 \hbar^3} \sqrt{(E - E_C)} \quad (\text{A2})$$

Relaxation times, $\tau(E)$, are given in Eqs. (8)–(10) and (14). Once the band parameters are obtained, they are combined to create the transport distribution function (TDF), $\Xi(E)$. In the case of isotropic bands, the TDF is modified to $\Xi(E) = \tau(E)v^2(E)g(E)/3$. The factor 1/3 is used to select a unidirectional component of the velocity, as the term v^2 combines

TABLE III. The parameters in the single parabolic band (SPB) model.

Parameter	SPB
m_{DOS}	1.0
ρ (kg/m ³)	10000
v_s (m/s)	4000
D_{ADP}	1
D_{ODP}	1×10^{10}
κ_0	20
κ_{inf}	40
$\hbar\omega$ (eV)	0.03
$\hbar\omega(\text{POP})$ (eV)	0.03

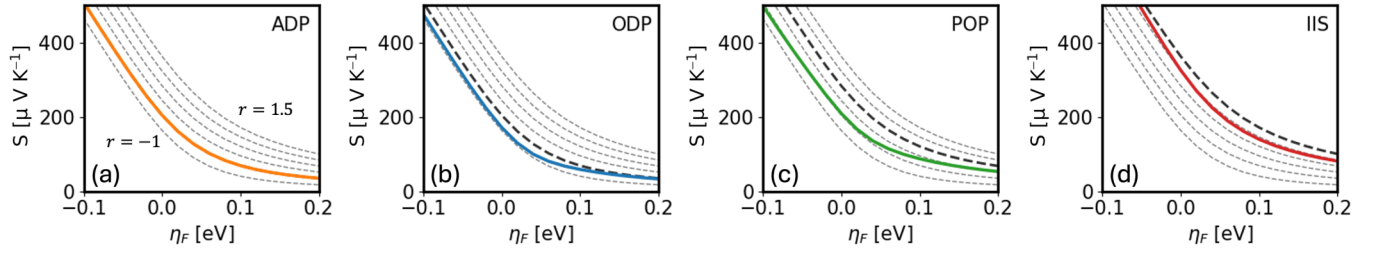


FIG. 10. Seebeck coefficient S vs Fermi level η_F using the SPB model. (a) ADP-, (b) ODP-, (c) POP-, and (d) IIS-limited transport (solid lines). Dashed lines refer to the scattering exponent model prediction [Pisarenko relation, Eq. (7)], with the lowest exponent used being $r = -1$, increasing in increments of 0.5, reaching $r = 1.5$, as denoted. Thicker dashed lines refer to nominal exponents.

the velocities from all three directions (specific for parabolic isotropic bands) and is defined as $v^2 = v_x^2 + v_y^2 + v_z^2$.

The parameters used for the single parabolic band are given below in Table III.

APPENDIX B: PISARENKO RELATION BEHAVIOR FOR THE SINGLE PARABOLIC BAND

Here we explore how different scattering cases can alter the behavior of the Seebeck coefficient in the Pisarenko relation for the single parabolic band model, using the scattering exponent approximation. Figure 10 plots the Seebeck coefficient against Fermi energy (η_F) for each scattering mechanism, with solid lines. The dashed lines are the Seebeck coefficients given by the scattering exponent approximation, calculated using Eq. (7). Each line corresponds to a characteristic exponent r from $r = -1$, increasing in increments of 0.5, up to $r = 1.5$. We note the nominal exponent lines by thick dashed lines.

Figure 10(a) shows the Seebeck coefficient for ADP-limited scattering. Clearly the full Seebeck coefficient calculation matches the one provided by the scattering exponent approximation when $r = -0.5$, as expected. The Pisarenko plot for ODP-limited scattering is shown in Fig. 10(b). At low η_F , the curve matches the exponent of $r = -1$, while at higher values of η_F , the exponent returns to the nominal value of $r = -0.5$. This is similar to the local exponent shown in Fig. 1(d), where the scattering times deviate at low energy due to the discontinuity around phonon emission, but return to the nominal value at higher energy.

Figure 10(c) shows the Pisarenko plot for POP scattering. At low η_F , the trend matches the curve with an exponent

of $r = -0.5$, while at higher η_F , the matching exponent increases, being closer to $r = 0$ (the nominal value is $r = 0.5$). The discrepancy is the same as for the local exponents of the scattering times in Fig. 1(g), where the values at low η_F deviate from nominal, since only the exponent around $E = 0$ eV is considered for all bandgap positioned Fermi levels (where the band edge begins), and a discontinuity occurs later on at the phonon energy emission onset. The Seebeck coefficient integrates over all energies; thus at high Fermi levels, beyond the discontinuity, the Seebeck will move towards the $r = 0$ exponent line in Fig. 10(c), following the exponent trend in Fig. 1.

Figure 10(d) plots the Pisarenko relation for IIS-limited scattering. The solid line is in good agreement with the $r = 1$ curve throughout η_F . Compared with the energy exponents at Fig. 1(h), there is a deviation at low η_F , due to the energy exponents not capturing the increase in r that occurs right after $E = 0$ eV, but as the Fermi level increases, the full calculation approaches what is observed in Fig. 1(h), at $r = 1$.

Thus, while the Seebeck coefficients for ADP- and ODP-limited transport have Fermi level regions where they match calculations done using the nominal exponent of $r = -0.5$, POP and IIS scattering do not follow the nominal values. This is due to the effect of Coulombic screening, which reduces the scattering at high values of η_F and lowers the exponents. In general, however, they follow what we have computed in Figs. 1(g) and 1(h).

APPENDIX C: HALF-HEUSLER SPECIFICS

The 13 half-Heusler materials considered are HfCoSb, ScNiBi, ScNiSb, TiCoSb, YNiBi, YNiSb, ZrCoSb, ZrNiPb, NbFeSb, HfNiSn, ZrNiSn, NbCoSn, and ZrCoBi. The DFT

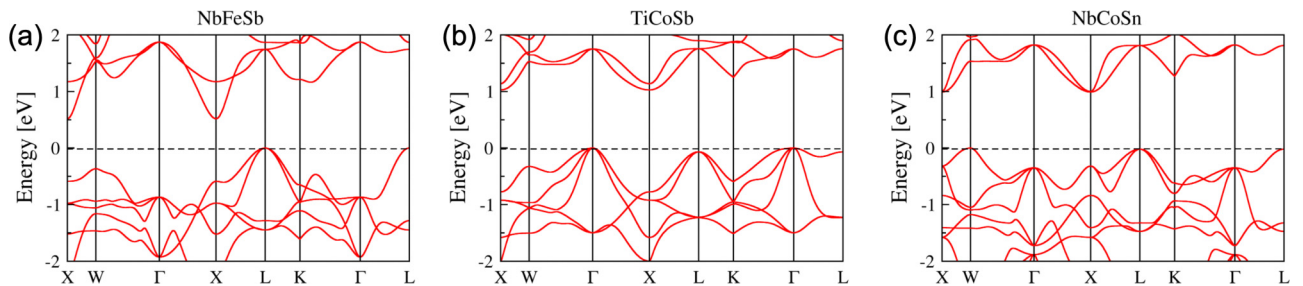


FIG. 11. Example band structures for half-Heusler materials: (a) NbFeSb, (b) NbCoSn, and (c) ZrNiSn.

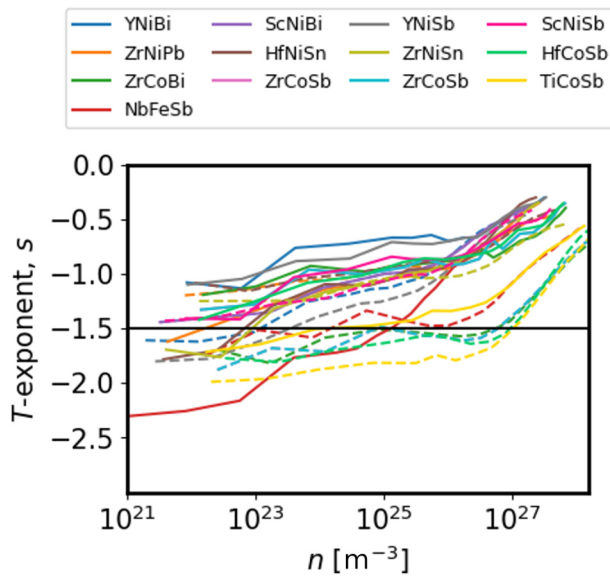


FIG. 12. The T -dependent exponent versus charge density for all 26 half-Heuslers (13 n -type in solid lines and 13 p -type in dashed lines). The different colors indicate the different materials as noted in the legend.

details are given in Ref. [40]. Examples of typical electronic structures for three of these materials are shown below in Fig. 11.

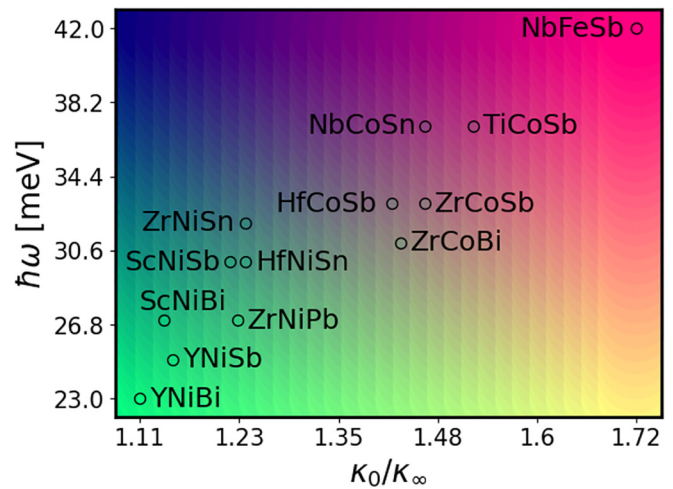


FIG. 13. Color identification for 13 half-Heuslers as plotted in the main text in Fig. 7(b). The colors were selected based on their polar optical phonon energy $\hbar\omega$ and dielectric constant ratio κ_0/κ_∞ , which determines polarity and POP strength.

Half-Heusler POP scattering strength

The 13 half-Heusler materials are assigned a color based on their polar optical phonon energy $\hbar\omega$ and dielectric constant ratio κ_0/κ_∞ . The colors used are shown in Fig. 13.

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