Electronic scattering in half-Heusler thermoelectrics from resistivity data

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Abstract

A key part of optimising thermoelectric materials is understanding the electronic scattering mechanism. For half-Heusler (HH) thermoelectrics, the dominant mechanisms are acoustic phonon scattering in pure systems and alloy scattering in highly alloyed systems. In this report, the significance of the residual resistivity $\rho_0$ is highlighted. Large $\rho_0$ values can lead to misidentification of the dominant scattering mechanism when only high-temperature $\rho(T)$ data is available. A straightforward approach to analyse $\rho(T)$ is proposed and applied to a range of HH systems. This reveals large levels of structural disorder in $\text{X}_2\text{NiSn}$, whilst $\text{X}_2\text{FeSb}$ has the strongest coupling with acoustic phonons. The electronic scattering mechanism depends sensitively on composition, with acoustic ($\rho \sim T^{1.5}$), metallic ($\sim T^1$) and alloy ($\sim T^{0.5}$) scattering observed within the main HH families. With the aid of velocity of sound, band mass and carrier concentration data, the deformation potential can be obtained, enabling quantification of the interaction between phonons and carriers, from fits to resistivity data. This work provides a route for the analysis of experimental $\rho(T)$ data that can be applied to a range of thermoelectric materials.

1. Introduction

Semiconducting half-Heusler (HH) phases are promising candidates for thermoelectric applications, boasting high power factors, mechanical stability and high abundance constituent elements [1–6]. Accurate determination of the electronic scattering mechanism is important because it can provide guidance on optimisation, by promoting phonon scattering, while charge carrier scattering is suppressed [7–9]. At present, the dominant scattering contributions to the mobility $\mu$ in HH compounds are considered to be acoustic phonon scattering (APS) and alloy scattering (AS) [10–12]. These have different temperature dependences, $\mu \sim T^{-1.5}$ for APS and $\sim T^{-0.5}$ for AS in the non-degenerate limit [13–15]. In the metallic limit APS is expected to dominate, with a $\sim T^1$ temperature dependence [14], as demonstrated by the Bloch–Grüneisen model [16]. For extrinsically doped compositions, under the assumption that the carrier concentration ($n_{HH}$) is temperature independent, the electrical conductivity ($\sigma = n_{HH}\mu_{HH}$) or resistivity ($\rho = 1/\sigma$) are directly proportional to $\mu_{HH}$ and can be used to establish the dominant carrier scattering mechanism. Here, $n_{HH}$ and $\mu_{HH}$ are the carrier concentration and mobility from Hall measurements, and $e$ is the electron charge.

Under the above assumptions of scattering behaviour, a number of methods have been employed to understand $\rho(T)$, $\mu(T)$ and the underlying scattering. The simplest approach is to use a linear fit of either $\rho(T)$ or $\mu(T)$ on logarithmic axes in order to determine the temperature exponent. Another approach uses band modelling to fit the $n_{TH}$ dependence of $\mu_{HH}$ at fixed temperature, with Matthiessen’s rule used to balance contributions of APS and AS, although this is difficult as both have identical $n_{TH}$ dependence [14, 15, 17]. Direct fitting of $\rho(T)$ is most commonly seen in low-temperature data using the Bloch–Grüneisen model in...
highly metallic samples [18, 19], with APS as the dominant scattering mechanism. Some modelling has been done to account for the effects of grain boundary scattering close to room temperature [20–22].

In this paper, the \( \rho(T) \) data of a range of degenerately doped HH materials is examined in order to examine scattering. This is convenient given the large volume of \( \rho(T) \) data available relative to \( \mu_1(T) \) data. The article starts with an overview of the \( \rho(T) \) behaviour expected in metals and degenerate semiconductors and of the typical approach taken in the literature for analysing the temperature dependence. A fitting model incorporating a residual resistivity \( \rho_0 \), either APS or AS scattering and intrinsic carrier excitations is applied to a range of HH systems, first validating it for compositions where low-temperature \( \rho(T) \) data is available and then applying it to a broad range of high-temperature data sets. Finally, deformation potential values are extracted from the fits to \( \rho(T) \) data for the samples that show semiconductor APS behaviour, enabling a straightforward estimate of the strength of the coupling of charge carriers and acoustic phonons.

2. Carrier scattering in metals and degenerate semiconductors

For metals, \( \rho(T) \) is linear at high temperatures and characterised by a limiting non-zero \( \rho_0 \) at 0 K. This is described by the Bloch–Grüneisen model [16]:

\[
\rho(T) = \rho_0 + A \left( \frac{T}{\theta_D} \right)^i \int_0^\frac{\pi}{\theta_D} \frac{x^i}{(e^x - 1)} \frac{dx}{(1 - e^{-x})}
\]

where \( i \) is used to describe the dominant scattering mechanism, with a \( T^i \) temperature dependence observable at low temperatures (\( i = 5 \) for APS, \( i = 2 \) for electron–electron scattering), before scaling linearly at higher temperatures (\( \sim T^1 \)) with an increase in phonon population. The residual resistivity \( \rho_0 \) exists due to defects present in the system (e.g. point defects, dislocations, and grain boundary effects in polycrystalline samples).

In semiconductors, three carrier scattering mechanisms are typically considered to be relevant. Ionised impurity scattering (IIS) due to interaction with charged impurities dominates at low carrier concentrations and follows \( \rho \sim T^{-1.5} \) [14, 15]. This scattering mechanism is typically not relevant to optimally doped HH materials as these have large carrier concentrations, which screen the ionised impurities [15]. The other two mechanisms have already been introduced, APS varies as \( \rho \sim T^{0.5} \), as the phonon population increases with temperature [13–15]. Finally AS is expected to have a \( \rho \sim T^{0.5} \) temperature dependence [14, 15], and should scale with \( x(1 - x) \) where \( x \) is the alloying fraction on a site [23]. In the heavily doped degenerate semiconducting limit, both IIS and AS are considered temperature independent and APS follows a \( \sim T^1 \) dependence, in line with the Bloch–Grüneisen model [14, 15].

At present, the temperature dependence of \( \rho(T) \) (or \( \sigma(T), \mu_1(T) \)) is typically treated by analysing the slope of a straight line on a logarithmic plot of the data (\( \log \rho = i \log T \)). However, this assumes that there is a negligible \( \rho_0 \), which may not be the case. As illustrated below, the presence of a substantial \( \rho_0 \) will alter the apparent temperature dependence at high temperatures. For HH systems when trying to decide between APS and AS, this can be a crucial factor to consider. The solution is to explicitly incorporate \( \rho_0 \), following the Bloch–Grüneisen model for metals:

\[
\rho(T) = \rho_0 + BT^{1.5}.
\]

In this model, \( \rho_0 \) and \( B \) are related to temperature independent electronic scattering and the strength of APS, respectively. As for the Bloch–Grüneisen model, \( \rho_0 \) is linked to imperfections in the material and can be taken to be a measure of disorder. Dividing \( \rho_0/B \) gives a measure of the relative impact of structural disorder and APS on the electronic carrier scattering. If there is a substantial \( \rho_0 \) contribution, the increase in \( \rho(T) \) will appear reduced from a \( T^{1.5} \) dependence when plotted on a log–log plot.

Figure 1 shows examples of equation (2) with increasing \( \rho_0 \) and fixed \( B \). Panel (a) shows data over the full 0 K–1000 K range and the \( T^{1.5} \) temperature dependence is clear at high temperatures, with \( \rho(T) \) simply shifted upwards by \( \rho_0 \). Panel (b) shows a logarithmic plot of the 300 K–1000 K data. Using the slope to estimate \( i \) leads to an increasing underestimate of the true temperature dependence. For example, the sample with the largest \( \rho_0 \) is estimated to have \( i \sim 0.5 \), but in fact has \( i = 1.5 \) with a large \( \rho_0 \).

At high temperatures, many materials experience a decrease in \( \rho(T) \) due to the thermal excitation of intrinsic carriers. In this case there are two parallel conduction channels and equation (2) can be modified to include an Arrhenius term:

\[
\rho(T)^{-1} = (\rho_0 + BT^{1.5})^{-1} + \left( A e^{\frac{-\mu_i}{k_B T}} \right)^{-1}.
\]
Figure 1. Modelled electrical resistivities using fixed APS \((B = 1 \times 10^{-4} \mu \Omega \text{ m K}^{-1.5})\) and increasing residual resistivity \((\rho_0 = 0 \rightarrow 4 \mu \Omega \text{ m})\). Panel (a) shows \(\rho(T)\) over a wide temperature range from 2 K to 1000 K. Panel (b) shows the same data between 300 K and 1000 K on logarithmic scales and the linear fits (dashed lines) commonly used to assign the carrier scattering mechanism. Panel (c) plots \(\rho(T)\) normalized with respect to \(\rho_{300 \text{ K}}\) and includes the predicted pure APS \(T^{1.5}\) (dashed) and AS \(T^{0.5}\) temperature dependences. The upwards curvature in plot (c) shows that \(\rho(T)\) approaches \(T^{1.5}\) as \(T \rightarrow \infty\) and that \(\rho(T)\) is increasingly limited by APS.

To check how an alloying model compares, the following closely related equation can be used:

\[
\rho(T)^{-1} = \left(\rho_0 + CT^{0.5}\right)^{-1} + \left(Ae^{-E_{\text{g}}/k_BT}\right)^{-1}.
\]  

The final panel of figure 1 shows 300 K normalised data, \(\rho(T)/\rho_{300 \text{ K}}\), on a logarithmic plot. This normalisation was chosen to have a standard method of presenting data that focusses on temperature dependence but is not obscured by differences in magnitude. As can be seen in panel (c), the pure APS and
AS trends (i.e. \( \rho_0 = 0 \)) remain linear with logarithmic axes. As \( \rho_0 \) is increased, the line is pushed further below the ideal APS dependence but is never linear on the logarithmic plot. It is this absence of a linear regime that signals the presence of a significant \( \rho_0 \) contribution. This is true whether or not the scattering mechanism turns out to be APS or AS: the absence of a linear domain implies a substantial \( \rho_0 \). At elevated temperatures, the upwards curvature is due to the slope approaching \( T^{1.5} \) (or \( T^{2.5} \) for AS) as \( T \to \infty \). In situations with moderate \( \rho_0 \) (or sufficiently high temperature data) it is therefore possible to inspect for a slope \( i > 0.5 \) at high temperatures, which would indicate APS. A final possibility is a transition from AS to APS with increasing temperature, which is not unrealistic given the stronger temperature dependence of APS. In a pure dual mechanism system, two linear regions (\( T^{0.5} \) and \( T^{1.5} \)) are expected, separated by a curved region as dominance shifts from AS to APS. A significant \( \rho_0 \) would lead to curvature in both AS and APS domains. In this case equation (2) can be extended to include a \( CT^{0.5} \) term, which should be adequate to describe such a transition in a degenerate system.

In the above models, it is assumed that either APS or AS is present, but not at the same time. In the analysis below, it was never necessary to include both scattering mechanisms in order to achieve an adequate fit to the data and it was considered that including too many fitting parameters would reduce the overall significance of the values obtained. In principle, the two scattering mechanisms could be used in parallel by appropriately weighting \( BT^{1.5} \) and \( CT^{0.5} \) terms using Matthiessen’s rule.

### 3. Validation of the model using temperature resistivity data

Although not commonly collected, low-temperature \( \rho(T) \) data is available for the main HH families. In case of ZrNiSn, both single crystal and polycrystalline data has recently been reported [11]. The samples digitised for this manuscript have \( 7.3 \times 10^{18} \text{ cm}^{-3} < n_{\text{th}} < 2.6 \times 10^{21} \text{ cm}^{-3} \), which covers the typical range for optimal thermoelectric performance (figure 2). These samples are all degenerate semiconductors with \( \rho(T) \) described well by equation (2), indicating APS with a substantial \( \rho_0 \) contribution (table 1). Figure 2(c) plots \( \rho_0/B \) from which two key observations can be made. Firstly, \( \rho_0/B \) decreases with increasing doping, consistent with stronger APS at higher \( n_{\text{th}} \) [12]. Secondly, \( \rho_0/B \) is larger for polycrystalline samples (at a given \( n_{\text{th}} \), consistent with the larger intrinsic disorder compared to single crystals.

No other single crystal data is available, but a number of reports contain low- and high-temperature data on polycrystalline samples. \( \rho(T) \) for selected members of the n-type \( X_{\text{IV}}\text{NiSn}, X_{\text{VII/IV}}\text{CoSb} \) and p-type \( X_{\text{IV}}\text{FeSb} \) families are shown in figure 3. The \( \text{Tl}\text{NiCo}_{0.025}\text{Sn} \) sample in panel (a) shows good agreement with equation (2) up to 700 K, above which intrinsic carriers begin to contribute. The \( \text{X}_{\text{IV}}\text{NiSn} \) samples in panel (b) show much better agreement with the Bloch–Grüneisen model, as noted in the original papers [18, 19], rather than equation (2) and hence have \( \rho \sim T \) at high-temperature. The reported \( n_{\text{th}} \) values (\( 8-10 \times 10^{19} \text{ cm}^{-3} \)) are comparable to the most highly doped \( \text{ZrNiSn}_{1-x}\text{Sn}_x \) samples in figure 2, which follow standard semiconductor APS. The change from \( T^{1.5} \) to \( T^1 \) is therefore not only associated with carrier concentration. The consistent feature amongst all \( \text{X}_{\text{IV}}\text{NiSn} \) samples, including those discussed below is that they have a very significant \( \rho_0 \), making up at around 50% of the total resistivity at 800 K.

Figure 3(c) shows data for \( \text{X}_{\text{VII}0.8}\text{CoSb} \) (\( X_{\text{VII}} = \text{V, Nb, Ta} \)) samples, which have a linear temperature dependence in keeping with Bloch–Grüneisen behaviour. This is consistent with the very large metallic \( n_{\text{th}} \), approaching \( 1 \times 10^{22} \text{ cm}^{-3} \) for these samples [24, 25]. One immediate comparison that can made with respect to the \( \text{X}_{\text{IV}}\text{NiSn} \) family is that relative to \( \rho_0 \), the temperature dependence of \( \rho(T) \) is much stronger. Both systems are expected to be highly disordered: \( \text{X}_{\text{IV}}\text{NiSn} \) is famous for high concentrations of interstitial Ni known to suppress \( \mu_{\text{H}} \) [26], while \( \text{X}_{\text{VII}0.8}\text{CoSb} \) is famous for a partially vacant \( \text{X}_{\text{VII}} \)-site [24, 25]. Both might be expected to lead to large \( \rho_0 \) values, but the strong temperature dependence shows that the impact is less significant in the \( \text{X}_{\text{VII}0.8}\text{CoSb} \) family.

The final set of data presented in figure 3(d) is for \( \text{Nb}_{0.8}\text{Ti}_{0.2}\text{FeSb} \) with \( n_{\text{th}} \sim 2.2 \times 10^{21} \text{ cm}^{-3} \) [27]. \( \rho(T) \) is in agreement with equation (2) above 300 K, signalling the presence of dominant APS. The increase in \( \rho(T) \) is large compared to \( \rho_0 \), suggesting that residual disorder is less important than coupling with acoustic phonons. Despite the strong temperature dependence, the magnitude of \( \rho_0 \) is comparable to the other systems: e.g. \( \rho_0 \sim 0.8 \mu\Omega \text{ m} \) for \( \text{Nb}_{0.8}\text{Ti}_{0.2}\text{FeSb} \) and to \( \rho_0 \sim 0.7 \mu\Omega \text{ m} \) for \( \text{ZrNiSn}_{1-x}\text{Sn}_x \) with similar \( n_{\text{th}} \). This indicates that the strength of the coupling with acoustic phonons is very different in the \( \text{X}_{\text{IV}}\text{NiSn} \) and \( \text{X}_{\text{IV}}\text{FeSb} \) families. Below 300 K, \( \rho(T) \) has a \( T^2 \) temperature dependence (figure 3(d)), which has been attributed to magnetic effects [27].

From the HH samples examined, it is clear that \( \rho_0 \) is a significant fraction of the total temperature dependence of \( \rho(T) \) for the \( \text{X}_{\text{IV}}\text{NiSn} \) family. By contrast, the \( \text{Nb}_{0.8}\text{Ti}_{0.2}\text{FeSb} \) sample shows a much stronger temperature dependence and has a much lower relative impact of \( \rho_0 \) (only \( \sim 10\% \) of \( \rho_{800\text{K}} \) compared to \( \sim 50\% \) for \( \text{TlNiCu}_{0.025}\text{Sn} \)). This strong temperature dependence is significant for the thermoelectric properties, with the power factor, \( S^2/\rho \) typically decreasing with temperature in the \( \text{X}_{\text{IV}}\text{FeSb} \) system, whereas
Figure 2. Digitised 4 K–300 K literature electrical resistivity data for ZrNiSn$_{1-x}$Sb$_x$ samples [11]. Panels (a) and (b) show polycrystalline and single crystal samples. Solid lines are fits to the APS model (equation (2)). Panel (c) shows the expected decrease of $\rho_0/B$ with carrier concentration, as the relative strength of APS increases (table 1).

they increase in the X$_4$NiSn family [21, 28, 29]. The samples in figure 3 either have a $T^4$ or $T^{1.5}$ dependence of $\rho(T)$. Both are consistent with APS, with the smaller temperature dependence (Bloch–Grüneisen) usually linked to highly degenerate systems. There is no clear crossover between these different behaviours based on doping level. This demonstrates that carrier scattering depends on subtle details of the chemical composition and can show considerable variation within each family.

4. Analysis of high-temperature resistivity data for a range of half-Heusler (HH) systems

High temperature normalised $\rho(T)/\rho_{300K}$ data for selected compositions from the main HH families are plotted in figure 4. Normalisation of the data allows for the temperature dependence to be examined
Overview of parameters used to fit electrical resistivity data for a range of HH families. The $\rho$, $B$, and $A$ parameters are defined in the text.

The deformation potential ($\rho$) was obtained using equation (8). The deformation potential ($\rho_m$) was obtained using equation (8). The deformation potential ($\rho_m$) was obtained using equation (8).

| Material | $\rho_m$ (\$\Omega m$) | $B$ (${\text{G/cm}}$) | $A$ (\$\text{G m}^{-1}$) | $\rho$ (\$\Omega m$) | $\rho_m$ (\$\Omega m$) | $B$ (${\text{G/cm}}$) | $A$ (\$\text{G m}^{-1}$) |
|----------|------------------------|----------------------|----------------------|------------------------|------------------------|----------------------|----------------------|
| $\text{T}_{1-x}\text{Ta}_{x}\text{Sb}_{0.95}\text{Sn}_{0.05}$ [30] | 0.01 | 1.52 | 0.26 | 4.36 | 0.01 | 1.52 | 0.26 | 4.36 |
| $\text{T}_{1-x}\text{Nb}_{x}\text{Sb}_{0.95}\text{T}_{0.05}$ [30] | 0.02 | 1.52 | 0.26 | 4.36 | 0.02 | 1.52 | 0.26 | 4.36 |
| $\text{ZrSb}_{0.95}\text{Sb}_{0.1}$ [31] | 0.03 | 1.52 | 0.26 | 4.36 | 0.03 | 1.52 | 0.26 | 4.36 |
| $\text{Ti}_{1-x}\text{Ta}_{x}\text{Sb}_{0.95}\text{Sn}_{0.05}$ [30] | 0.04 | 1.52 | 0.26 | 4.36 | 0.04 | 1.52 | 0.26 | 4.36 |
| $\text{ZnSb}_{0.95}\text{Sb}_{0.1}$ [32] | 0.05 | 1.52 | 0.26 | 4.36 | 0.05 | 1.52 | 0.26 | 4.36 |
| $\text{Ni}_{1-x}\text{Zr}_{x}\text{FeSb}$ [28] | 0.06 | 1.52 | 0.26 | 4.36 | 0.06 | 1.52 | 0.26 | 4.36 |
| $\text{ZnSb}_{0.95}\text{Sb}_{0.1}$ (PC) [33] | 0.07 | 1.52 | 0.26 | 4.36 | 0.07 | 1.52 | 0.26 | 4.36 |
| $\text{Ti}_{1-x}\text{Ta}_{x}\text{Sb}_{0.95}\text{Sn}_{0.05}$ (PC) [34] | 0.08 | 1.52 | 0.26 | 4.36 | 0.08 | 1.52 | 0.26 | 4.36 |
| $\text{ZnSb}_{0.95}\text{Sb}_{0.1}$ (PC) [35] | 0.09 | 1.52 | 0.26 | 4.36 | 0.09 | 1.52 | 0.26 | 4.36 |

(Continued.)
Table 1. (Continued.)

|                  | $\rho_0$ ($\mu\Omega$ m) | $B \times 10^{-4}$ ($\mu\Omega$ m K$^{-1.5}$) | $A$ ($\mu\Omega$ m) | $\rho_0/B$ (K$^{1.5}$) | $n_0$ ($\times 10^{30}$ cm$^{-3}$) | $m_0^*$ ($m_e$) | $m_{DoS}^*$ ($m_e$) | $E_{def}$ (eV) |
|------------------|-------------------------|---------------------------------|-----------------|-----------------------|---------------------------------|----------------|-------------------|---------------|
| (Nb$_{1-x}$Ta$_x$)$_{0.6}$Ti$_{0.4}$FeSb [42] | $x = 0.24$ | 0.41 | 2.15 | 0.01446 | 1910 | 26.8 | 1.73 | 6.9 | 12.5 |
|                  | $x = 0.32$ | 0.24 | 2.57 | 0.07242 | 921 | 25.7 | 1.73 | 6.9 | 13.5 |
|                  | $x = 0.36$ | 0.16 | 2.88 | 0.14168 | 559 | 25.2 | 1.73 | 6.9 | 14.2 |
| Hf$_{0.6}$Zr$_{0.4}$NiSn$_{0.9}$Sb$_{0.1}$ +xW% W [43] | $x = 0$ | 7.47 | 1.83 | 0.43068 | 40710 | 1.85 | 1.35 | 2.8 | 4.0 |
|                  | $x = 2$ | 7.17 | 1.49 | 0.42426 | 40666 | 2.08 | 1.35 | 2.8 | 3.9 |
|                  | $x = 5$ | 7.97 | 1.26 | 0.44996 | 47737 | 2.79 | 1.35 | 2.8 | 4.1 |
| (Zr$_{1-x}$Hf$_x$)$_{0.8}$Nb$_{0.1}$CoSb [8] | $x = 1$ | 6.45 | 2.77 | 0.01406 | 23257 | 16.2 | 3.12 | 6.5 | 5.4 |
|                  | $x = 0.6$ | 5.51 | 3.22 | 0.04646 | 17127 | 16.3 | 3.12 | 6.5 | 5.9 |
|                  | $x = 0.3$ | 6.31 | 3.30 | 0.04624 | 19104 | 15.0 | 3.12 | 6.5 | 5.8 |
| Nb$_{0.3}$Ti$_{0.7}$FeSb [27] | $x = 0$ | 0.26 | 2.54 | 0.05711 | 1023 | 23.0 | 1.73 | 6.9 | 13.4 |
| TiNiCu$_{0.2}$Sn | $x = 0$ | 3.98 | 1.98 | 0.14447 | 20101 | — | — | — | — |

$^a$ A bandgap, $E_g = 0.5$ eV was used for samples with intrinsic carrier excitations.

$^b$ Calculations use different $m_0^*$, because it is not established if total degeneracy $N_\nu = 6$ or $N_\nu = 3$, with $m_{\text{DoS}}^2 = N_\nu^2 m_0^*$, $m_0^* = 4.5 m_e$. $N_\nu = 6$ leads to better agreement of $m_0^*$ and hence $E_{def}$ with the other $X_{10}$NiSn phases.
Figure 3. Fits to electrical resistivity ($\rho(T)$) data using either APS (equation (2)) or metallic Bloch–Grüneisen (equation (1)) models. Panel (a) shows data collected on TiNiCu$_{0.025}$Sn with Cu interstitials, which agrees well with APS up to around 700 K. Panel (b) is a similar chemical system, digitised from [18, 19], but has better agreement with the Bloch–Grüneisen model. Panel (c) shows measured data for V$_{1-x}$CoSb and Nb$_{1-x}$CoSb, which are in good agreement with metallic Bloch–Grüneisen behaviour. Panel (d) shows data on Nb$_{0.8}$Ti$_{0.2}$FeSb (digitised from [27]), which again shows APS above 300 K but deviates below room temperature.

independently of the doping. All datasets were fitted to either the APS or AS model allowing for intrinsic carrier excitations where needed (equation (3) or (4)). All fit parameters are summarised in tables 1 and 2.

Figure 4(a) shows the Ti$_{1-x}$Ta$_x$Ni$_{0.92}$Sn series [30], which immediately illustrates the complication of intrinsic behaviour in $\rho(T)$. The most highly doped samples ($x = 0.025, 0.03$ and $0.05$) agree well with an APS temperature dependence. The $x = 0.01$ sample has a weak temperature dependence and shows a crossover to semiconducting behaviour due to intrinsic carrier excitations. The fits reveal a gradual decrease in $\rho_0/B$ consistent with increasing $n_H$. Figure 4(b) confirms the dominance of APS for TiNiSn based materials, with TiNiSn$_{1-x}$Sb$_x$ showing a significant $\rho_0$ contribution and a moderate temperature dependence [31].

The heavily alloyed Zr$_{0.35}$Hf$_{0.65}$Ni$_{1-x}$Pt$_x$Sn$_{0.98}$Sb$_{0.02}$ system in figure 4(c) is less clear cut [12]. The data lie below the AS curve, which can be achieved when $\rho_0$ is added to either APS or AS models. The blue fit curve assumes an AS model (equation (4)) and the fit results are given in table 2. Furthermore, this system shows some evidence of intrinsic carrier contributions, making the behaviour much harder to untangle. Table 2 also shows the results of trial fits to the APS model (equation (3)), which can also describe the data. However, given the presence of alloying on all three atomic sites, the dominance of AS is not unreasonable. Collection of data below 300 K is needed to make an unambiguous assignment of the dominant scattering mechanism. The fitted $\rho_0$ increases with Pt/Ni alloying (table 2), suggesting that the impact of alloying is partially incorporated in the temperature independent term.

The V$_{0.955}$-yTi$_{y}$CoSb [32] and Nb$_{1-x}$CoSb [24] systems are shown in figures 4(d) and (e). The V system is consistent with APS with a significant $\rho_0$ contribution and a strong intrinsic contribution above 700 K. In the Nb system, the dependence on intrinsic carriers is apparent, with a stronger intrinsic contribution in less highly doped samples. The strong temperature dependence in each sample confirms that both are dominated by APS. Like the data presented in figure 3(c), the temperature dependence is more consistent with a metallic Bloch–Grüneisen temperature dependence.
Figure 4. Log–log plot of 300 K normalized electrical resistivities ($\rho(T)/\rho_{300 \text{ K}}$) for a range of HH systems. Solid black lines denote perfect $T^{1.5}$ APS behaviour; dashed black line denote perfect $T^{0.5}$ AS behaviour. Arrows indicate decreases in $\rho(T)$ due to intrinsic carrier excitations. Blue lines are fits to the data with the fitting model indicated in each panel. Fit parameters and references are given in tables 1 and 2.

The Zr$_{0.5}$Hf$_{0.5}$CoSb$_{1-x}$Sn$_x$ system (figure 4(f)) is another likely example of AS dominance [33]. These samples lie slightly above the AS line, suggesting that they are dominated by AS with a small $\rho_0$. Alternatively, the data could be interpreted as APS with a substantial $\rho_0$ over a wide temperature range. This is another case where low temperature data is needed to clarify the precise scattering mechanism.

The ZrCoBi$_{1-x}$Sn$_x$ system is shown in figure 4(g) [34]. At first glance all samples are in good agreement with equation (3), suggesting semiconducting APS and intrinsic carrier excitations. However, due to the large
intrinsic contribution, there is no temperature range where a large upturn in $\rho(T)$ exists that would explicitly
support a $T^{1.5}$ temperature dependence, as opposed to a $T^1$ dependence. This is another system where low
temperature data is needed to clarify the carrier scattering mechanism and confirm $\rho_0$, which points to an
increase in residual disorder with Bi/Sn alloying, similar to the Zr$_{0.35}$Hf$_{0.65}$Ni$_{1-x}$Pt$_x$Sn$_{0.98}$Sb$_{0.02}$ system.

The Nb$_{1-x}$Hf$_x$FeSb samples shown in figure 4(h) [28], match well with the APS model (equation (2))
with a small $\rho_0$ contribution (table 1). This is similar to the Nb$_{0.8}$Ti$_{0.2}$FeSb sample presented in figure 3.

To summarise, the X$_{10.8}$CoSb materials display metallic APS behaviour ($T^1$), the X$_7$FeSb system
consistently behaves as regular semiconductor ($T^{1.5}$). The X$_{IV}$NiSn family has been found to show dominant
Bloch–Grüneisen, APS and AS scattering. There is a stark contrast in temperature dependence between the
X$_V$FeSb and X$_{IV}$NiSn systems: the latter have small $B$ and relatively large $\rho_0$, whilst the former materials have
large $B$ compared to $\rho_0$.

In the following section, $B$ will be defined in terms of an effective deformation potential ($E_{def}$), which
quantifies the strength of electron–phonon scattering.

5. Evaluation of deformation potential from the $B$ parameter

The deformation potential ($E_{def}$) characterises the strength of the coupling between acoustic phonons
and electronic charge carriers. This can be evaluated from the temperature dependence of the mobility, $\mu$
[13, 35]:

$$\mu = \frac{8\pi^2 e^4 v_l^2 \rho_d}{3E_{def} m_b^* \hbar^4 (k_B T)^2}$$

(5)

here, $v_l^2 \rho_d$ is an approximation for the elastic constant [12], where $v_l$ is the longitudinal sound velocity, $\rho_d$ is
the crystal density, and $m_b^*$ is the band effective mass of the charge carriers. This expression has the same
temperature dependence as the APS model (equation (2)). After subtraction of the disorder contribution
($\rho_0$), leaving the temperature dependent term ($BT^{1.5}$) this yields:

$$1/\mu = n_H \mu_H = \frac{1}{BT^2}$$

(6)

and from substitution and rearrangement in equation (5):

$$E_{def} = \left[ \frac{8\pi^2 e^4 \hbar^4 B n_H v_l^2 \rho_d}{3k_B^2 m_b^*} \right]^{0.5}.$$  

(7)

This equation is reasonable with larger $E_{def}$ being correlated to larger $B$ and hence stronger APS. As noted
previously [12], $\mu_H$ decreases with $n_H$, which if uncorrected would lead to a large $n_H$ dependence of $E_{def}$. To
account for this, the following correction valid at 300 K is applied [36]:

$$\mu_H = \mu_0 \left[ 1 + \left( \frac{n_H}{2D m_{\text{DoS}}^*} \right)^2 \right]^{-\frac{3}{2}}$$

(8)

where $D = 1.5 \times 10^{20} \text{ cm}^{-3}$ is a constant, which slightly differs from the original methodology [36] due to
the difference between chemical carrier concentration $n$ and Hall concentration $n_H$. $m_{\text{DoS}}^*$ is the density of
states effective mass and $\mu_0$ is the mobility in the limit of $n_H \rightarrow 0$.

For cases where a $T^{1.5}$ dependence describes $\rho(T)$, $E_{def}$ can then be determined. The calculated values are
summarised in table 1. This shows that ZrNiSn based materials have $E_{def} \sim 5–8 \text{ eV}$, TiNiSn materials have

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
$z$ & $\rho_0$ ($\mu\Omega$ m) & $B \times 10^{-4}$ ($\mu\Omega$ m K$^{-1.5}$) & $A$ ($\mu\Omega$ m) & $E_d$ (eV) & $\rho_0$ ($\mu\Omega$ m) & $C$ ($\mu\Omega$ m K$^{-0.5}$) \\
\hline
0 & 3.69 & 1.25 & 0.44 & 0.5 & 1.46 & 0.162 \\
0.05 & 4.21 & 1.78 & 0.44 & 0.5 & 1.20 & 0.223 \\
0.1 & 5.34 & 1.55 & 0.38 & 0.5 & 2.98 & 0.183 \\
0.15 & 7.52 & 2.11 & 0.28 & 0.5 & 4.38 & 0.243 \\
\hline
\end{tabular}
\end{table}
slightly higher $E_{\text{def}} \sim 7–9$ eV, ZrCoBi$_{1–x}$Sn$_x$ has $E_{\text{def}} \sim 7.5–9$ eV, TaFeSb based materials have $E_{\text{def}} \sim 10$ eV and NbFeSb based materials have $E_{\text{def}} \sim 12–14$ eV. These values are in good agreement with literature values obtained using single parabolic band analysis [4, 10, 12, 21].

As is clear from the values given, even with the $n_{\text{eff}}$ correction, a range of $E_{\text{def}}$ values are found. In case of lightly doped samples, this may be linked to an underestimation of $B$ due to the difficulty of disentangling degenerate from intrinsic contributions. This may occur in Ti$_{1–x}$Ta$_x$Ni$_{0.92}$Sn$_{0.08}$, where $E_{\text{def}}$ increases from 7.1 to 8.9 eV. A similar trend is seen in the ZrCoBi$_{1–x}$Sn$_x$ series. However, there are other systems where this cause can be excluded. For example in both single crystal and polycrystalline ZrNiSn$_{1–x}$Sb$_x$, $E_{\text{def}}$ increases from 6.8 to 7.9 eV, despite the absence of intrinsic carrier effects. This suggests that the introduction of even small amounts of Sb has a substantial impact on the coupling with acoustic phonons.

6. Discussion

Fitting $\rho(T)$ provides a straightforward way to obtain insight into the carrier scattering mechanism of HH thermoelectrics. The common approach of plotting logarithmic axes and straight-line fitting is not appropriate due to the presence of large $\rho_0$ contributions in HH materials. This leads to a weaker apparent temperature dependence, potentially leading to misassignment of the dominant carrier scattering mechanism. An alternative approach is proposed for systems where only high-temperature data is available. This uses $\rho(T)$ normalised with respect to $\rho_x$ at temperature $X$. Combined with fitting $\rho(T)$ this provides a promising way to establish the dominant carrier scattering mechanism, although in all cases low-temperature data is needed to reach unambiguous conclusions. Fitting of a range of $\rho(T)$ data covering the main HH families shows that APS is the dominant scattering mechanism with not many clear examples of AS based on the temperature dependence of $\rho(T)$. Both semiconducting ($\sim T^{1.5}$) and metallic ($\sim T^4$) APS temperature dependences are observed, without a clear link to $n_{\text{eff}}$, as might have been expected from the basic scattering models [14, 15]. In all cases a substantial temperature independent $\rho_0$ term is found. This signals the presence of substantial disorder in the HH materials. The precise origin of this disorder is not known, but the HH literature shows the existence of a wide range of point defects (e.g. interstitials, vacancies, carrier dopants and alloying) and various forms of phase segregation [1]. The presence of a large $\rho_0$ is not unexpected for highly doped samples, because the common non-APS mechanisms, including IFS and AS are predicted to become temperature independent in the degenerate limit [14, 15]. This means that all non-APS is captured by $\rho_0$, as it is in the Bloch–Grüneisen model. We observe a similar situation for samples that have semiconductor APS. In most cases AS scattering appears to be incorporated in $\rho_0$, and does not give rise to a different temperature dependence, as predicted in the non-degenerate limit [14, 15]. Nevertheless, there are some systems that do show an AS ($\sim T^{0.5}$) temperature dependence. However, even in these cases a significant $\rho_0$ is found. The data therefore suggests that AS can manifest both in $\rho_0$ and in the temperature dependence. The most unambiguous confirmation of AS is to establish a $x(1-x)$ composition dependence, which would enable separation from other disorder effects that contribute to $\rho_0$. Further investigations aimed at disentangling possible contributions to $\rho_0$ are of considerable interest.

Figure 5 gives an overview of the relative strength of residual disorder and temperature dependent scattering ($\rho_0/B - n_{\text{eff}}$) for the HH families that have dominant semiconductor APS. This shows that the X$_{1–x}$FeSb materials consistently have lower $\rho_0/B$, which is largely due to a large $B$. For all other families, $\rho_0/B$ is higher and spans a relatively narrow range (8–20 × 10$^{-5}$ R$^{-1.5}$ covers most samples) reflecting larger inherent structural disorder and weaker coupling with acoustic phonons. In the X$_{1–x}$NiSn system, the large $\rho_0$ could be linked to the interstitial Ni defect, which has been shown to reduce $\mu$ and cause reduced lattice thermal conductivities [26]. Minimising interstitial Ni to levels observed in the X$_{1–x}$FeSb family (X$_{1–x}$NiSn = 0.92, Ta$_x$ < 1% Fe) [29] is likely to significantly increase the electronic performance. The temperature dependence of $\rho(T)$ in the X$_{1–x}$NiSn and X$_{1–x}$FeSb families is fundamentally different due to the larger $E_{\text{def}}$ in the X$_{1–x}$FeSb materials, up to 14 eV, where n-type ZrNiSb based compositions have $E_{\text{def}}$ as low as 5 eV, leading to a weak temperature dependence in the latter. The other materials systems investigated have intermediate $E_{\text{def}}$ values.

To conclude, the temperature dependence of the electrical resistivity for all the major HH families has been analysed using a modified approach that explicitly considers a temperature independent residual resistivity. This suggests that most HH materials have APS limited electronic transport but often accompanied by large temperature independent contributions due to structural disorder.

7. Methods

Data from the literature was digitised using the Engauge Digitizer software [37]. Source references are acknowledged in tables 1 and 2, and throughout the manuscript text.
Figure 5. A plot of $\rho_0/B$ against carrier concentration $n_H$ for a range of HH systems that have dominant semiconductor APS. The $X_V$FeSb samples have low $\rho_0$ and relatively large $B$ values, leading to a clear separation from the other HH families. The fitted values for $\rho_0$ and $B$ and source references are given in table 1.

Original data on TiNiCu$_{0.025}$Sn, V$_{1-\delta}$CoSb and Nb$_{1-\delta}$CoSb samples are shown in figure 3. The synthesis and high-temperature properties of the X$_V$$_{1-\delta}$CoSb samples was reported previously [25]. The TiNiCu$_{0.025}$Sn sample was prepared by arc-melting elemental pieces of Ti, Ni, Sn and Cu (all Alfa Aesar, >99.9%). Approximately 3 g of material was arc-melted in a MAM-1 arc-melting furnace under Ar atmosphere with Zr getter, flipped over and melted again. A bar was cut from the ingot using a diamond saw and annealed in an evacuated silica ampoule (with the bar wrapped in Ta foil) at 900 °C for 7 d. The basic structural and thermoelectric properties of the TiNiCu$_{y}$Sn series prepared using a powder route can be found in [38, 39]. The high temperature electrical resistivity of the three samples were measured using a Linseis LSR-3 apparatus. Low temperature data were collected using Quantum Design PPMS-9 apparatus.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

There are no conflicts of interest to declare.

Author credit statement

R J Q and J W G B designed the study and wrote the paper. R J Q undertook the data analysis. G B G S assisted with low-temperature resistivity data collection.

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