Enhanced Thermoelectric Properties of Semiconductor Nanowire Networks

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Abstract

To examine thermoelectric (TE) properties of a semiconductor nanowire (NW) network, we propose a theoretical approach mapping the TE network on a two-port network. In contrast to conventional single-port (i.e., resistor) network model, our model allows for a large scale calculations showing convergence of TE figure of merit, $ZT$, with increasing number of junctions. Using this model, the numerical simulations are performed for the Bi$_2$Te$_3$ branched nanowire (BNW) and Cayley tree NW (CTNW) network. We demonstrate that the phonon scattering at the network junctions plays dominant role in enhancing the network $ZT$. Specifically, random BNW and CTNW demonstrate $ZT$ enhancement factor of 20% – 150%. The simulations results suggest formation of preferential TE pathways in CTNW which effectively behave as BNW. To provide connection with experiment, we show how the model parameters can be related to the observables available in TE measurements.
The environmental concerns and demands to explore alternative energy sources have been currently motivating the search for new efficient thermoelectric (TE) materials. TE efficiency is characterized by the dimensionless figure of merit, \( ZT = \sigma_{eh}S^2T / (\kappa_{eh} + \kappa_{ph}) \), which depends on the temperature, \( T \), electrical conductivity due to electrons and holes, \( \sigma_{eh} \), Seebeck coefficient, \( S \), and thermal conductivity associated with the charge carriers, \( \kappa_{eh} \), and phonons, \( \kappa_{ph} \). Accordingly, enhanced performance of TE materials requires high power factor, \( \sigma_{eh}S^2 \), and at the same time suppressed thermal conductivity. Nanostructuring is a promising way to achieve this goal. Reduction in dimensionality of the nanomaterials can be exploited to quantize their electron structure, e.g., density of states, in order to enhance the power factor. The surface and interfaces facilitate phonon scattering subsequently decreasing associated thermal conductivity.

Semiconductor nanowires (NWs) are suitable candidates for reaping the TE benefits of reduced dimensionality. Experimental measurements show that bulk TE performance of technologically favorable Si is weak, \( ZT < 0.01 \), while Si NW with diameter of 20 nm, exhibits enhanced \( ZT \approx 1 \) at \( T \sim 200 \) K. Simulations show that further improvement in the TE performance of these NWs can be achieved via surface faceting. Surface-disordered Ge-Si core-shell nanostructures promise to enhance \( ZT \) up to 2 at \( T=300 \) K. Theoretical calculations, for 5 nm in diameter, lead chalcogenide (PbS, PbSe) NWs, and PbSe/PbS superlattice NW provide \( ZT = 0.2, 0.36, \) and \( 0.65, \) respectively, at \( T = 77 \) K. For comparison, experimental measurements on bulk PbSe show \( ZT < 0.1 \) at the same temperature. Bulk doped \( \text{Bi}_{x-1}\text{Te}_x \) is currently among the most efficient and commercially used TE materials with \( ZT \sim 1.0 \) at \( T \sim 300 \) K. Theory predicts that ultra thin (i.e., 0.5 nm in diameter) \( \text{Bi}_2\text{Te}_3 \) NW is capable to demonstrate \( ZT = 14 \) at \( T = 300 \) K. However, this value rapidly drops to \( ZT \sim 1 \) with the diameter increased to \( \sim 4 \) nm. Experimental measurements are available for \( \text{Bi}_{x-1}\text{Te}_x \) NWs of larger diameters (\( \sim 50 \) nm) and report low value of \( ZT \sim 0.1 \) at \( T \sim 400 \) K. The authors attribute such low values to a large level of NWs doping.

Use of NWs in TE devices calls for scaling-up their remarkable TE properties to the macroscopic level via assembling them into functional blocks. One example of \( \text{Bi}_2\text{Te}_3 \) NW assembling is a method of direct electro-deposition into porous alumina. Another reported approach to growing ultra-thin (\( \sim 8 \) nm in diameter) \( \text{Bi}_2\text{Te}_3 \) NWs with subsequent fabrication of their bulk pellets implements the spark plasma sintering method. The TE characterization of the NW pellets shows enhanced peak \( ZT \sim 0.96 \) at room temperature.
These experimental studies call for theoretical examination of scaling up TE properties of individual NWs to the macroscopic device level. Initial step in bridging these well separated length-scales is to consider the TE properties of the mesoscopic NW assemblies, which can subsequently be used as the building blocks of macroscopic devices. In this letter, we examine the TE properties of doped Bi$_2$Te$_3$ NW networks, which could be fabricated by growing branched NW trees. Such networks can also be considered as an approximation to the mesoscale fragments of the bulk NW pellets discussed above.

Large number of junctions in branched NW mesostructures makes conventional atomistic calculations not feasible, thus, calling for approximate theoretical models. In one example, atomistic calculations were combined with an averaging procedure to examine the effect of a single ultra-thin (≲ 2 nm in diameter) Si NW decoration with either Si branches or chemically bound alkyl molecules. The authors demonstrate that for 100 branches, ZT acquires almost four fold increase as a result of enhanced phonon scattering. To address similar computation issues in modeling the NW networks, we propose a generalized approach by mapping a NW network onto corresponding network of TE two-port elements and taking advantage of efficient electric-circuitry simulation techniques.

**NW Network Model.** Let us consider a TE NW network. For the temperature range of interest (250 – 400 K) both charge carriers and thermal transport occur in the diffusive regime leading to small local variations of electrochemical potential and temperature across the network. Therefore, we can partition the network into segments whose sizes are larger than the charge carriers and phonon mean free paths. Each segment is terminated by hot and cold junctions with other segments and/or electrical contact as shown in Fig. 1 (a). Thus, we assign the difference in electrochemical potential, $\Delta V = V_H - V_C$, and temperature, $\Delta T = T_H - T_C$ to each segment resulting in electric, $J_{eh}$, and thermal, $J_Q$, currents. In this case, the linear response theory yields $J = YV$ with the column vectors $J = \begin{pmatrix} J_{eh} \\ J_Q \end{pmatrix}$ and $V = \begin{pmatrix} \Delta V \\ \Delta T/T \end{pmatrix}$ representing the TE current and TE potential, respectively. Taking into account the two-component nature of these vectors, we implement the circuit analysis approach to treat segments of a network as TE two-port elements. This identifies the matrix $Y$ as the TE two-port admittance, and its inverse, $Z = Y^{-1}$, as the TE two-port impedance. In such a network any two segments connected in series satisfy the sum rule.
FIG. 1: (a) NW segment terminated by hot and cold junctions. (b) The segment representation as three serial connected two-port elements. (c) BNW of $N - 1$ RUs and a single NW segment at site $n = 1$. Dotted boxes mark BNW portions described by the admittance matrices $\tilde{Y}_1, \ldots, \tilde{Y}_{n-1}, \tilde{Y}_n$. (d) Associated representation of $n$-th RU in terms of two segments from panel (a) with the admittances $Y_{n,1}$ and $Y_{n,2}$. (e) CTNW of $N$ generations each containing $2^{g-1}$ RUs, where $g$ is the generation index. Dotted boxes mark the network portions each characterized by a set of admittance matrices, i.e., $\{\tilde{Y}_{N,n}\}_{n=1}^{2N-1}$, $\{\tilde{Y}_{g+1,n}\}_{n=1}^{2g}$, and $\{\tilde{Y}_{g,n}\}_{n=1}^{2g-1}$. (f) $n$-th RU from generation $g$ modeled by two NW segments from panel (a) with the admittance matrices $Y_{g,n,1}$ and $Y_{g,n,2}$.

for the impedance matrix $Z = Z_1 + Z_2$ and the segments connected in parallel satisfy the sum rule for the admittance matrix $Y = Y_1 + Y_2$.

The TE admittance matrix can be represented in terms of transport coefficients, for electrons, $L^e_i$ and holes, $L^h_i$, where $i = 0, 1, 2$. By defining $L_0 = L^e_0 + L^h_0$, $L_1 = L^e_1 - L^h_1$,
We represent the admittance matrix as

\[
Y = \begin{pmatrix}
e^2 f_{eh}(\eta) L_0 & ef_{eh}(\eta) L_1 \\
e f_{eh}(\eta) L_1 & f_{eh}(\eta) L_2 + f_{ph}(\eta, \xi) \kappa_{ph} T
\end{pmatrix},
\]

where, \( e \) denotes electron charge; \( T = (T_H + T_C)/2 \) is the averaged temperature, and \( \kappa_{ph} \) is the phonon thermal conductivity. Analytical expressions for \( L_i^e \) and \( L_i^h \) used in our numerical calculations are given in Appendix A. Equation (1) accounts for the branching induced drop in the electrical and thermal conductivities via the reduction functions \( f_{eh}(\eta) \) and \( f_{ph}(\eta, \xi) \), respectively.

Shown in Fig. 1(b) network segment (denoted by a set of indices \( s \)), is a serial connection of three two-port elements. The central element describes homogeneous part of the segment with \( f_{eh} = f_{ph} = 1 \). The right and left elements account for identical admittance drop at the junctions. Associated reduction functions are \( f_{eh}(\eta_s) = 1 - \eta_s \) and \( f_{ph}(\eta_s, \xi_s) = 1 - \xi_s \). Implementing serial connection rule, we find the following segment reduction functions

\[
f_{eh}(\eta_s) = \frac{1}{3} - \frac{2}{9} \eta_s, \tag{2}
\]

\[
f_{ph}(\xi_s, \eta_s) = \frac{1}{3} - \frac{2}{9} \xi_s - \frac{4}{9} \frac{\eta_s \xi_s (L_1^2 - L_0 L_2)}{L_1^2 - L_0 (L_2 + e^2 \kappa_{ph} T)}. \tag{3}
\]

Retaining only the linear term in Eq. (3) yields identical functional form for \( f_{eh} \) and \( f_{ph} \). This makes the electron/hole and phonon TE channels uncoupled and the network can be modeled using single-port elements. In this case \( \eta_s \) and \( \xi_s \) can be directly related to the junction impedance as shown in Appendix B. In the numerical calculations, the cross-term is retained to account for the mixed electron/hole and phonon TE channels.

First, we introduce branched NW (BNW) shown in Fig. 1(c). BNW contains \( \Gamma \)-shaped repeat units (RU) denoted by index \( n = 2, \ldots, N \) and a single NW segment at the site \( n = 1 \). All cold contacts (blue dots) are grounded. The admittance of BNW portion containing \( n - 1 \) RUs (dotted box) is denoted by \( \tilde{Y}_{n-1} \). According to panel (d), each RU contains two segments, denoted by index \( m = 1, 2 \) and is characterized by the admittance matrix \( Y_{nm} = Y(\eta_{nm}, \xi_{nm}) \) with the reduction functions given by Eqs. (2) and (3) where \( s \equiv \{n, m\} \). By taking into account that segment \( m = 2 \) of the \( n \)-th RU has parallel connection with the rest of the network containing \( n - 1 \) RUs and segment \( m = 1 \) is further attached via serial connection, we introduce the admittance of BNW portion of \( n \) RUs via

\[
Y_{nm} = Y(\eta_{nm}, \xi_{nm}),
\]

where \( \eta_{nm} \) and \( \xi_{nm} \) are the reduction functions for \( m = 1 \) and \( m = 2 \) segments, respectively.
the following relationship

\[ \tilde{Y}_n = \left( \left( \tilde{Y}_{n-1} + Y_{n,2} \right)^{-1} + Y_{n,1}^{-1} \right)^{-1}. \]  \hspace{1cm} (4)

Starting with the initial condition \( \tilde{Y}_1 = Y_{1,1} \) and performing \( n = 2, \ldots, N \) subsequent iterations according to Eq. (4), one can calculate total BNW admittance \( \tilde{Y}_{BNW} = \tilde{Y}_N \).

The network examined in this letter is binary Cayley Tree NW (CTNW) shown in Fig. 1 (e). The network contains \( N \) generations each denoted by index \( g \). Each generation is formed from \( \Lambda \)-shaped RUs denoted by index \( n = 1, \ldots, 2^{g-1} \). For the network portion containing generations \( g + 1 \) through \( N \) (dotted box), we introduce a set of admittance matrices \( \{ \tilde{Y}_{g+1,n} \}_{n=1}^{2^g} \). According to panel (f), \( n \)-th RU of generation \( g \) contains two segments, denoted by index \( m = 1, 2 \), each with admittance \( Y_{gmn} = Y(\eta_{gmn}, \xi_{gmn}) \), where the reduction functions are given by Eqs. (2) and (3) with \( s \equiv \{ g, n, m \} \). By taking into account that both segments in each RU of generation \( g \) has serial connection with the attached portion of the network (i.e., generations \( g + 1 \) through \( N \)), we introduce the admittance matrix \( \tilde{Y}_{g,n} \) as

\[ \tilde{Y}_{g,n} = \left( \left( Y^{-1}_{g,n,1} + \tilde{Y}^{-1}_{g+1,2n-1} \right)^{-1} + \left( Y^{-1}_{g,n,2} + \tilde{Y}^{-1}_{g,2n+1} \right)^{-1} \right). \]  \hspace{1cm} (5)

Starting with the initial conditions \( \tilde{Y}_{N,n} = (Y_{N,n,1}^{-1} + Y_{N,n,2}^{-1}) \) where \( n = 1, \ldots, 2^{N-1} \) and subsequently applying Eq. (5) for generations \( g = N - 1 \) through \( g = 1 \), one can calculate total CTNW network admittance \( \tilde{Y}_{CTNW} = \tilde{Y}_{11} \).

Finally, we express the TE figure of merit in terms of the TE admittance matrix as

\[ ZT = \frac{(\tilde{Y})_{12}^2}{\det \tilde{Y}}, \]  \hspace{1cm} (6)

where \( (\tilde{Y})_{12} \) denotes the off-diagonal matrix element of \( \tilde{Y} = \tilde{Y}_{BNW} \) or \( \tilde{Y} = \tilde{Y}_{CTNW} \). This expression can be verified by using general relations between transport coefficients and the electrical conductivity, \( \sigma_{eh} = e^2 L_0 \), the Seebeck coefficient, \( S = L_1/(eT L_0) \), and the electron/hole contribution to thermal conductivity \( \kappa_{eh} = L_2/e^2 T - L_1^2/(e^2 T L_0) \).

**Numerical Results.** The numerical simulations are performed for the networks made of \( n \)-doped Bi₂Te₃ NWs. Each segments is modeled by a rectangular NW elongated in the [015] crystalline direction with the cross-section of \( 8 \times 8 \) nm². The electronic structure is calculated
using six-valance-band and six-conduction-band effective mass model accounting for the band-gap temperature dependence. Cold and hot reservoirs are modeled as infinite Bi$_2$Te$_3$ NWs. The moments $L_i$ are evaluated using constant relaxation time model. Calculations of the thermal conductivity, $\kappa_{ph}$, account for the NW boundary specularity. More details on the model parameterization are provided in Appendix A.

The reduction parameters have complex dependence on the junctions structure (e.g., lattice mismatch in the branching points). Lack of necessary microscopic parameters does not allow for their direct evaluation for Bi$_2$Te$_3$ NWs. Our estimate of the transmission coefficient for Si NW junctions (Appendix B2) yields the charge carrier reduction parameter $\eta_s \sim 0.01$ and phonon thermal conductivity reduction parameter $\xi_s \sim 0.15$. Accordingly, branching strongly suppresses the phonon assisted thermal conductivity and keeps the electrical conductivity almost intact. We adopt the same order of magnitude for the reduction parameters in Bi$_2$Te$_3$ NW networks as starting point in our simulations.

Below, the following two kinds of BNW and CTNW are examined: (i) *Ordered* BNW/CTNW in which all junctions have identical reduction parameters $\eta_s = 0.05$ and $\xi_s = 0.20$. (ii) *Disordered* BNW/CTNW with each junction reduction parameter initialized according to the Gaussian distribution with the mean values $\bar{\eta}_s = 0.05$ and $\bar{\xi}_s = 0.20$ and 10% standard deviation.

Figure 2 (a) presents ZT dependence on the chemical potential, $\mu = (V_H + V_C)/2$, for the ordered CTNW (thick lines) containing $N = 5$ generations. As the chemical potential and associated carriers concentration increase, the Seebeck coefficient drops while the conductivity grows resulting in a well known ZT maximum. Similar plot for the disordered CTNW of $N = 100$ generations is shown in panel (b). ZT variation for single NW segment is plotted in panels (a) and (b) by thin lines for comparison. It shows that branching produces about 2% and 20% enhancement in ZT peak values for the ordered and disordered CTNWs, respectively. Ordered and disordered BNWs with 5 and 100 junctions have absolutely the same ZT behavior as their CTNW counterparts.

In Fig. 2 (c), we plot ZT enhancement factor, $\left[ \max_{\mu} \left( ZT_{BNW/CTNW} \right) - \max_{\mu} \left( ZT_{NW} \right) \right] / \max_{\mu} \left( ZT_{NW} \right)$, for the ordered/disordered BNW and CTNW depending on the number of junctions and generations, respectively. The ordered BNW/CTNW demonstrate identical ZT enhancement for all values of junctions/generations and saturate to $\sim 2\%$ enhancement value merely at 5 junc-
FIG. 2: ZT as a function of chemical potential calculated for (a) the ordered CTNW of $N = 5$ generations and (b) the disordered CTNW with $N = 100$ generations (thick lines). Thin lines in both panels present corresponding behavior of single NW segment. (c) ZT enhancement factor calculated at $T=300$ K using two-port (TP) network model for ordered/disordered BNW as a function of number of junctions (i.e., RUs$-1$) and for the ordered/disordered CTNW as a function of number of generations. (c) ZT vs. number of junctions in the disordered BNW calculated using single-port network model.

tions/generations. The disordered BNW/CTNW reach close ZT values at around five junctions/generation and continue to grow together. Our calculations (not shown in the plot) provide saturation of the enhancement factor to $\sim 20\%$ after the number of junctions/generations exceeds 100. Identical variation of ZT values for BNW and CTNW with increasing number of junctions and generations, respectively, suggests that within CTNW there is a preferential pathway for electrical and thermal transport. This pathway can effectively be considered as BNW whose number of junctions naturally coincides with
FIG. 3: The enhancement factor for ordered/disordered BNW and CTNW containing 100 junctions and generations, respectively, as a function of phonon reduction parameter $\xi$. For disordered BNW and CTNW the mean value of $\xi$ is varied while the standard deviation stays 10%. The electron reduction parameter is fixed at $\eta_s = 0.05$ and $T = 300$ K.

Transport properties of TE networks and devices are typically modeled by considering the electric and thermal currents independently. This allows for mapping a TE network on electrical and thermal single-port (i.e., resistor) independent networks. In particular this approach has been used to examine ZT growths with increased number of junctions for decorated Si NWs.\(^{[17]}\) To compare the proposed two-port model with conventional single-port one, Fig. 2 (c) presents ZT enhancement factor vs. number of junctions in the disordered Bi$_2$Te$_3$ BNW network calculated using both models. The plot shows that both models yield the same ZT behavior for a small (about 5) number of junction. After that point single-port network model shows much steeper growth than the two-port one. Our analysis shows that in the limit of infinite number of junctions ZT calculated with the help of single-port network diverges. Thus we argue that the single-port network model is a good approximation for small networks whereas modeling of extended mesoscale networks should be performed using proposed two-port network approach. More details on applicability of the single-port network approximation are given in Appendix B.\(^{[1]}\)

Fig. 3 shows how the enhancement factor for 100-generations (100-junctions) ordered and disordered CTNW (BNW) changes with the increase of the phonon reduction parameter. While for disordered network this value can reach 150% and higher, the ordered network shows no more than 20% enhancement. This plot clearly demonstrates that the disordered
FIG. 4: Temperature vs chemical potential phase diagram. Dashed lines show constant values of the ratio $\kappa_{eh}/TS^2\sigma_{eh}$.

network outperforms its ordered counterpart about an order of magnitude in ZT enhancement.

Accurate modeling of TE NW networks requires precise knowledge of the junction reduction parameters. These parameters can be determined using experimentally obtained values of electrical and thermal conductivities for equal length single NW and a three segment T-junction (Fig. 1 (d), $N = 2$). As derived in Appendix B, the junction reduction parameters assume simple form $\eta = 2 (\sigma_{eh} - \bar{\sigma}_{eh}) / (2\sigma_{eh} - \bar{\sigma}_{eh})$, $\xi = 2 (\kappa_{ph} - \bar{\kappa}_{ph}) / (2\kappa_{ph} - \bar{\kappa}_{ph})$, where $\kappa_{ph} (\bar{\kappa}_{ph})$ and $\sigma_{eh} (\bar{\sigma}_{eh})$ are measured single NW (the NW T-junction) thermal and electrical conductivities, respectively. Use of the proposed expressions assumes that $\kappa_{eh} < TS^2\sigma_{eh}$. Such a regime can be reached for a specific range of the chemical potential and temperature shown as blue region in Fig. 4.

In conclusion, we have developed a two-port network model to describe the TE properties of the NW networks. We argue that our model provides better approximation for mesoscale networks containing large amount of elements compared to conventional single-port (resistor) network model. The simulations performed for Bi$_2$Te$_3$ BNW and CTNW demonstrate that the disordered networks show about order of magnitude higher ZT enhancement compared to their ordered counterparts. For considered disordered BNW and CTNW, calculated ZT values show enhancement in the range of $20 - 150\%$ compared to a single NW segment.
Observed similarity in ZT growth with the number of junctions and generations for the same kind BNW and CTNW, respectively, suggests that preferential transport pathways form in CTNW effectively acting as BNWs. Precise determination of the reduction coefficients can be performed from a set of experimental measurements.

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Appendix A: Microscopic Expressions of Thermoelectric Admittance Matrix Elements

In this section, we present microscopic expressions for the transport coefficients entering the thermoelectric (TE) admittance matrix given by Eq. (1) in the Letter. These moments describe the charge carrier contributions to the electrical and thermal conductivity and the Seebeck coefficient. Representation for the phonon-assisted thermal conductivity entering the TE admittance matrix is provided as well. Finally, we discuss details of the model parameterization used to describe a homogeneous Bi$_2$Te$_3$ nanowire (NW).

1. Transport Coefficients

The transport coefficients for the charge carriers in an isolated NW are

$$L^i_j(\mu, T) = \frac{2}{\hbar} \int_{-\infty}^{\infty} \mathcal{T}_j(E) (\pm E \mp \mu)^i \left( -\frac{\partial f}{\partial E} \right) dE,$$

where $\mathcal{T}_j(E)$ is the energy dependent transmission function and $f(E, \mu) = \left\{ \exp[(E - \mu)/k_BT] + 1 \right\}^{-1}$ is the Fermi-Dirac distribution depending on the averaged chemical potential, $\mu$, and averaged thermal energy, $k_BT$. Here and below, the upper sign stands for the conduction band electrons ($j = e$), and the lower one for the valance band holes ($j = h$). The
prefactor 2 accounts for the spin degeneracy. In the constant relaxation time approximation (valid at \( T > 200K \)), the Drude conductivity model yields \(^{24,25}\)

\[
L_0^j = C_j \sum_{\alpha,\beta} \mathcal{F}_{-1/2}(\mu_{\alpha\beta}^j), \\
L_1^j = C_j k_B T \sum_{\alpha,\beta} \{ 3 \mathcal{F}_{1/2}(\mu_{\alpha\beta}^j) + \mu_{\alpha\beta}^j \mathcal{F}_{-1/2}(\mu_{\alpha\beta}^j) \}, \\
L_2^j = C_j (k_B T)^2 \sum_{\alpha,\beta} \{ 5 \mathcal{F}_{3/2}(\mu_{\alpha\beta}^j) + 6 \mu_{\alpha\beta}^j \mathcal{F}_{1/2}(\mu_{\alpha\beta}^j) + \mu_{\alpha\beta}^j \cdot \mathcal{F}_{-1/2}(\mu_{\alpha\beta}^j) \},
\]

where the integer indices \( \alpha, \beta \) describe the quantum numbers associated with the size quantization across the NW. The prefactor \( C_j = (2e\mu_j m_{j,y}^* / \pi Ah) \sqrt{2m_{j,y}^* k_B T} \) contains the NW cross-section, \( A \), carriers effective mass along the NW axis (identified as \( y \)-axis) \( m_{j,y}^* \), and the carriers mobility \( \tilde{\mu}_j \). The latter quantity is evaluated according to the Matthiessen’s rule, \( 1/\tilde{\mu}_j = (1 + (\Lambda/\sqrt{A/\pi})(1-p)/(1+p))/\tilde{\mu}_j^b \), using as parameters bulk carrier mobility, \( \tilde{\mu}_j^b \), mean free path \( \Lambda \), and surface specularity \( p \). \(^{14}\) In Eqs. \((A2)\)–\((A4)\), \( \mathcal{F}_m(\mu) = \int_0^\infty \frac{x^m dx}{\exp(x+\mu)+1} \)

is the Fermi-Dirac fractional integral whose argument is the reduced chemical potential, \( \mu_{\alpha\beta}^j = (\mu - E_{\alpha\beta}^j(0))/k_B T \), depending on the carriers energy at the band edge of associated dispersion curve, \( E_{\alpha\beta}^j(0) = E_{\alpha\beta}^j(k = 0) \), characterized by the carriers wave vector, \( k \), along the NW direction. Finally, summation over all degenerate electron/hole pockets must be carried out in Eqs. \((A2)\)–\((A4)\).

To model the electronic structure of Bi\(_2\)Te\(_3\) NW, we adopted the effective mass \( k \cdot p \) approach. Specifically, rectangular Bi\(_2\)Te\(_3\) NW grown along [015] crystallographic direction is considered. \(^{16}\) As mentioned above, the NW axis is aligned along \( y \)-direction so that the \( (x, z) \)-plane contains the NW cross-section. The sides of the rectangle are set to be identical, \( a_z = a_x = 8 \text{ nm} \). According to this model the electron/hole energy at the band edge is

\[
E_{\alpha,\beta}^j = \pm E_g(T)/2 \pm \frac{\hbar^2 \pi^2}{2} \left( \frac{\alpha^2}{m_{j,x}^* a_x^2} + \frac{\beta^2}{m_{j,z}^* a_z^2} \right).
\]

Here, zero energy is set at the middle of the bulk band gap. The temperature dependent values of the effective masses \( m_{j,n}^* \) with \( j = e, h \) and \( n = x, y, z \) are adopted from the literature. \(^{25}\) The band gap temperature dependence is \( E_g(T) = 150.0 - 0.0947T^2/(T + 122.5) \) meV. \(^{25}\) Finally, the bulk mobilities are set to \( \tilde{\mu}_e^b = 652.8 \text{ cm}^2/\text{Vs} \) and \( \tilde{\mu}_h^b = 345.9 \text{ cm}^2/\text{Vs} \) and scale with the the temperature as \( \tilde{\mu}_e^b \sim T^{-1.7} \) and \( \tilde{\mu}_h^b \sim T^{-2.0} \). \(^{25}\) Adopted specularity parameter is \( p = 0.95 \) and the mean free path of the charge carriers is set to \( \Lambda \approx 40 \text{ nm} \). \(^{14}\)
2. Phonon Conductivity

The phonon conductivity is calculated using the following general expression

$$\kappa_{ph} = \frac{\hbar^2}{2\pi k_B T} \int_0^\infty d\omega \omega^2 \mathcal{T}_{ph}(\omega) \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2},$$ (A6)

where $\mathcal{T}_{ph}(\omega)$ is the phonon transmission function. The boundary roughness described by the specularity parameter $p$ is crucial for the phonon transport in Bi$_2$Te$_3$ NWs. To account for the specularity effect, we complimented the solution of the Boltzmann equation with the corresponding boundary condition. This along with the Drude conductivity in place of $\mathcal{T}_{ph}(\omega)$ results in

$$k_{ph} = \left(\frac{k_B}{\hbar}\right)^3 \frac{k_B T^3 \Lambda_{ph}}{2\pi^2 v^2} (1 - G(p)) \frac{\Theta_D/T}{\int_0^{\epsilon_D} \epsilon^4 \exp(\epsilon) d\epsilon (\exp(\epsilon) - 1)^2},$$ (A7)

where the specularity function is

$$G(p) = (1 - p)^2 \sum_j j^3 p^{j-1} \int_0^1 \int_0^{\pi/2} \exp\left(-\frac{2jx}{\Lambda_{ph} \sin\theta}\right) \cos^2\theta \sin\theta d\theta dx. $$ (A8)

Here $v$ is the average value of the acoustic phonon group velocity weighted by the phonon population factor, $\Lambda_{ph}$ is the phonon mean free path, $\epsilon = \hbar\omega/k_B T$ is normalized phonon energy, and $\Theta_D$ is the Debye temperature. For the narrow wires ($\Lambda_{ph} \leq \sqrt{A}$), the group velocity and the mean free path become functions of $\epsilon$ due to quantization of the phonon energy. However, here we consider the situation in which $\sqrt{A} \gg \Lambda_{ph}$ so that the size quantization of phonons becomes negligible and effect of the specularity becomes dominant.

In the numerical simulations of Bi$_2$Te$_3$ NWs the following parameters are used: The transverse, longitudinal, and twisting branches of the acoustic phonons are characterized by their group velocities $v = 8.47 \times 10^5$, $5.34 \times 10^5$, and $3.95 \times 10^5$ cm/s, respectively. The phonon mean free path is set to $\Lambda_{ph} \approx 2.5$ nm and the Debye temperature is chosen so that $\kappa_{ph} \approx 450/T$ for $T > 200K$ and $p = 0$.

Appendix B: Electric and Phonon Reduction Parameters

The network effect on the TE admittance matrix (Eq. (1) in the Letter) is accounted for via the electric (i.e., electron and hole), $f_{eh}(\eta_s)$ and phonon, $f_{ph}(\eta_s, \xi_s)$, reduction functions.
As shown in the Letter for a single junction, these functions can be represented as

\[ f_{eh}(\eta) = 1 - \eta, \quad (B1) \]
\[ f_{ph}(\xi) = 1 - \xi, \quad (B2) \]

where \(0 \leq \eta \leq 1\) and \(0 \leq \xi \leq 1\) are the electric and phonon reduction parameters, respectively. For further consideration the subscript \(s\) labeling junction position within a network is not important, therefore, we omit it in Eqs. [B1] and [B2]. Using this representation, we clarify the physical meaning of these key variables in the case of a single junction and discuss their connection with the microscopic quantities introduced in Section A for T-junction.

1. Connection with Single Junction Impedances

We restrict our model to the regime of uncoupled electric and phonon channels facilitating single-port (resistor) network approximation. This approximation is valued under the conditions

\[ eL_1 \ll e^2 L_0, \quad (B3) \]
\[ eL_1 \ll \kappa_{ph} T, \quad (B4) \]
\[ L_2 \ll \kappa_{ph} T, \quad (B5) \]

simplifying the admittance matrix (Eq. (1) in the Letter) to the following diagonal form

\[ Y = \begin{pmatrix} e^2 f_{eh}(\eta) L_0 & 0 \\ 0 & f_{ph}(\xi) \kappa_{ph} T \end{pmatrix}. \quad (B6) \]

Accordingly, the electric and phonon impedances of a NW (i.e., \( f_{eh}(\eta) = f_{ph}(\xi) = 1 \)) can be defined as \( Z_{eh} = (Y^{-1})_{11} = (e^2 L_0)^{-1} \) and \( Z_{ph} = (Y^{-1})_{22} = (\kappa_{ph} T)^{-1} \), respectively. For a single junction, the corresponding impedances become defined as \( \tilde{Z}_{eh} = (\tilde{Y}^{-1})_{11} = (e^2 f_{eh}(\eta) L_0)^{-1} \) and \( \tilde{Z}_{ph} = (\tilde{Y}^{-1})_{22} = (f_{ph}(\xi) \kappa_{ph} T)^{-1} \). Substitution of the reduction functions in the form of Eqs. [B1] and [B2] into these expressions immediately results in the following expressions for the reduction parameters

\[ \eta = 1 - \frac{\tilde{Z}_{eh}}{Z_{eh}}, \quad (B7) \]
\[ \xi = 1 - \frac{\tilde{Z}_{ph}}{Z_{ph}}. \quad (B8) \]
FIG. 5: Temperature vs chemical potential phase diagram. Lines separating areas marked with different shades of blue represent constant values of the parameter $\alpha$ defining the scaling of the inequalities (B3)–(B5), i.e., $eL_1 < \alpha L_0 e^2$, $eL_1 < \alpha \kappa_{ph} T$, and $L_2 < \alpha \kappa_{ph}$.

Equations (B7) and (B8) provide connection between the reduction parameters and associated NW and junction electric and thermal phonon-assisted impedances clarifying the reduction parameters physical meaning. In principle, these quantities can be determined experimentally by measuring the impedance matrix in the uncoupled channels regime. The boundaries of this regime for Bi$_2$Te$_3$ NW examined in the Letter are shown in Fig. 5. According to the plot, values of the chemical potential of $\mu \approx 200 \, \mu$eV and the temperature ranging between $T=250$-$350$K corresponding to the maximum ZT (see Fig. 2 of the Letter) do not correspond to the desired uncoupled regime. Therefore, more complex T-junction configuration allowing experimental determination of the reduction parameters via measuring electrical and thermal conductivities is considered below.

2. Connection with T-junction Conductivities

Here, we examine a T-shaped junction made of three identical NWs. For such a junction, we denote the electrical conductivity $\tilde{\sigma}$, thermal electron/hole-assisted conductivity $\tilde{\kappa}_{eh}$, thermal phonon-assisted conductivity $\tilde{\kappa}_{ph}$, and the Seebeck coefficients $\tilde{S}$. By using general
relations\textsuperscript{23,24} between transport coefficients and the electrical conductivity, \(\bar{\sigma}_{eh} = e^2 \bar{L}_0\), the
Seebeck coefficient, \(\bar{S} = \bar{L}_1/(e T \bar{L}_0)\), and the electron/hole-assisted thermal conductivity
\(\bar{\kappa}_{eh} = \bar{L}_2/e^2 T - \bar{L}_1^2/(e^2 T \bar{L}_0)\), we represent the T-junction admittance matrix (Eq. (1) in the
Letter) as
\[
\Ybar_2 = \begin{pmatrix}
\bar{\sigma}_{eh}/e^2 & T \bar{S} \bar{\sigma}_{eh}/e \\
T \bar{S} \bar{\sigma}_{eh}/e & T^2 \bar{S}^2 \bar{\sigma}_{eh} + T \bar{\kappa}_{eh} + T \bar{\kappa}_{ph}
\end{pmatrix}.
\] (B9)

Here, \(e\) is the absolute value of the electron charge. Note that the effect of the junction is
already included into the transport coefficients \(\bar{L}_i, i = 0, 1, 2\) and no reduction functions
are needed in Eq. (B9).

On the other hand, introducing similar parameters for each NW forming the T-junction
as \(3\bar{\sigma}_{eh} = e^2 L_0, S = L_1/(e T L_0), 3\bar{\kappa}_{eh} = L_2/e^2 T - L_1^2/(e^2 T L_0)\), and \(3\bar{\kappa}_{ph}\textsuperscript{34}\) and further
applying Eq. (4) from the Letter for the T-junction (i.e., \(N = 2\)) along with the reduction
functions in the form of Eqs. (B1) and (B2), one obtains
\[
\Ybar_2 = \begin{pmatrix}
\frac{2 \bar{\sigma}_{eh}(\eta-1)}{e^2(\eta-2)} & \frac{2ST\bar{\sigma}_{eh}(\eta-1)}{e(\eta-2)} \\
\frac{2ST\bar{\sigma}_{eh}(\eta-1)}{e(\eta-2)} & \frac{2ST^2\sigma_{eh}(\eta-1)}{\eta-2} + \frac{2T(\kappa_{ph} + \kappa_{eh})}{\eta(\eta-1)\kappa_{ph}}
\end{pmatrix}.
\] (B10)

Comparing the admittance matrix elements in Eq. (B9) with Eq. (B10), one arrives at the
following expression for the reduction parameters in terms of the introduced electrical and
thermal conductivities
\[
\eta = \frac{2(\bar{\sigma}_{eh} - \bar{\sigma}_{eh})}{2\bar{\sigma}_{eh} - \bar{\sigma}_{eh}},
\] (B11)
\[
\xi = 2 + \frac{2\kappa_{eh}\sigma_{eh}}{2\kappa_{ph}\sigma_{eh} - \kappa_{ph}\bar{\sigma}_{eh}} + \frac{2(\kappa_{ph} + \kappa_{eh})^2}{\kappa_{ph}(\bar{\kappa}_{ph} + \bar{\kappa}_{eh} - 2(\kappa_{ph} + \kappa_{eh}))}.
\] (B12)

Deriving this expression, we used the fact that the junction does not change the Seebeck
coefficient, i.e., \(S = \bar{S}\textsuperscript{35}\). Accordingly, this quantity does not enter Eqs. (B11) and (B12).

To uncouple the electron-assisted and phonon-assisted effects on thermal conductivity, we
impose a requirement that \(\kappa_{eh} \ll S^2 T \sigma_{eh}\). This condition eliminates \(\bar{\kappa}_{eh}\) and \(\kappa_{eh}\) in the
matrix element \((\Ybar_2)_{22}\) of Eq. (B9) and (B10), respectively. Subsequently, one can set \(\bar{\kappa}_{eh} = \kappa_{eh} = 0\) in Eq. (B12) resulting in
\[
\xi = \frac{2(\kappa_{ph} - \bar{\kappa}_{ph})}{2\kappa_{ph} - \bar{\kappa}_{ph}}.
\] (B13)

Obtained Eqs. (B11) and (B13) are used in the Letter to provide connection with experiment.
The parameters in the right hand side of Eqs. (B11)-(B13) can be calculated microscopically using general expressions for the transport coefficients given by Eqs. (A1) and (A6). Section A contains details on how those expressions are parameterized to describe a homogenous NW. However, junction parametarization can be done in a different way: Key quantities in Eqs. (A1) and (A6) are charge carriers and phonon transmission functions, $T_j(E) \ (j = e, h)$ and $T_{ph}(\omega)$, respectively. Branching results in their reduction that can be evaluated by combining the non-equilibrium Green function method with atomistic electronic structure calculations. Challenging part of such calculations is determination of the Tersoff empirical potential matrix required to evaluate the phonon-assisted thermal conductivity. Usually, this matrix is evaluated with the help of General Lattice Utility program (GULP, http://projects.ivec.org/gulp/) working well for small unit cells that allowed us to evaluate the reduction parameters for Si NW. However, for the alloys (e.g., Bi$_2$Te$_3$) such a task becomes increasingly complex and requires a separate study going beyond the scope of this Letter.

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For Bi$_2$Te$_3$ the mean free path for electrons is 40...61 nm defined by the electron-phonon and impurities scattering mechanisms$^{14}$. The phonon mean free path is typically less than that for the charge carriers.

If the electron-phonon interaction is included$^{31}$ the proposed TE two-port model should be extended to a three-port with the extended admittance matrix.

The factor of 3 comes from the fact that each segment of the NW has three times large conductivity than the whole NW.

An assumption that the reduction parameter of a junction does not depend on energy gives

\[
\tilde{S} = \frac{\tilde{L}_1}{(eT\tilde{L}_0)} = \frac{f_{eh}(\eta)L_1}{(eTf_{eh}(\eta)L_0)} = \frac{L_1}{(eTL_0)} = S.
\]