Thermodefect voltage in graphene nanoribbon junctions

To cite this article: Alhun Aydin et al 2022 J. Phys.: Condens. Matter 34 195304

View the article online for updates and enhancements.
Thermodefect voltage in graphene nanoribbon junctions

Alhun Aydin\textsuperscript{1,*}, Altug Sisman\textsuperscript{2}, Jonas Fransson\textsuperscript{2}, Annica M Black-Schaffer\textsuperscript{2} and Paramita Dutta\textsuperscript{2,3,4,*}

\textsuperscript{1} Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, United States of America
\textsuperscript{2} Department of Physics and Astronomy, Uppsala University, Box 516, S-751 20 Uppsala, Sweden
\textsuperscript{3} Theoretical Physics Division, Physical Research Laboratory, Ahmedabad-380009, India
\textsuperscript{4} Department of Physics, Birla Institute of Technology and Science—Pilani, Rajasthan-333031, India

E-mail: alhunaydin@fso.harvard.edu and paramita@prl.res.in

Received 12 November 2021, revised 4 February 2022
Accepted for publication 15 February 2022
Published 14 March 2022

Abstract

Thermoelectric junctions are often made of components of different materials characterized by distinct transport properties. Single material junctions, with the same type of charge carriers, have also been considered to investigate various classical and quantum effects on the thermoelectric properties of nanostructured materials. We here introduce the concept of defect-induced thermoelectric voltage, namely, \textit{thermodefect voltage}, in graphene nanoribbon (GNR) junctions under a temperature gradient. Our thermodefect junction is formed by two GNRS with identical properties except the existence of defects in one of the nanoribbons. At room temperature the thermodefect voltage is highly sensitive to the types of defects, their locations, as well as the width and edge configurations of the GNRs. We computationally demonstrate that the thermodefect voltage can be as high as 1.7 mV K\textsuperscript{-1} for 555–777 defects in semiconducting armchair GNRs. We further investigate the Seebeck coefficient, electrical conductance, and electronic thermal conductance, and also the power factor of the individual junction components to explain the thermodefect effect. Taken together, our study presents a new pathway to enhance the thermoelectric properties of nanomaterials.

Keywords: thermoelectricity, graphene, defect

(Some figures may appear in colour only in the online journal)

1. Introduction

Thermoelectricity is the phenomenon of induced electrical potential difference due to a temperature gradient and vice versa. Investigation of various junctions based on different materials has been the conventional route for thermoelectric research [1]. Following the footsteps of the pioneering works by Hicks and Dresselhaus [2, 3], subsequent efforts have established that quantum confinement can also be used to enhance the thermoelectric properties [4–15]. The contributions of nanoscale effects can be isolated and analyzed quite easily when all the components of the junctions are made of only a single material, having the same dominant charge carriers but different size or shape. Such junctions are gathered under the umbrella name of single-material unipolar thermoelectric junctions [16, 17].

The concept of single-material unipolar junctions was first introduced by Sisman and Müller in 2004 to isolate and
analyze the thermoelectric voltage generated only due to the differences of quantum size effects between the junction components [18]. Since then various single-material unipolar thermoelectric junctions formed by the combination of nano-macro [18–23] or nano-micro components have been studied [24–28], considering both classical and quantum size effects [16, 17, 29–33]. In particular, thermoelectric properties of quantum wells and nanowires using graphene-based materials have become a hot topic in material science in recent years [11, 13, 15, 16, 34–43]. In these, as well as other nano-scale systems, thermoelectric devices are made by connecting many single junctions to each other such that small nano-scale effects of many single junctions are added up to generate a usable macroscopic voltage. As a direct consequence, improving the thermoelectric properties of single junctions is essential to develop superior thermoelectric devices.

In this work, we introduce a new concept: defect-based single-material unipolar thermoelectric junctions, here consisting of one pristine and one defective nanoribbon maintained at the same temperature gradient, as shown in figure 1. Under an applied temperature gradient, we achieve an (electro-)chemical potential difference at the separated end of the junction, which is utilized as thermoelectric voltage. The voltage is generated only due to the existence of defects in one of the junction components, as all other properties of the junction materials are exactly the same, which is completely different from the conventional thermoelectric junctions. We call this junction a ‘thermodefect junction’ and the voltage a ‘thermodefect voltage’. The names are justified by the origin of the voltage i.e. the thermal gradient and defects in the system.

To establish the concept of the thermodefect voltage, we choose graphene nanoribbons (GNRs) where both GNRs have exactly the same size (both length and width) and edge configurations, the only difference being the existence of crystallographic defects in one of the GNRs. The pristine GNR then acts as the reference component with respect to the defective GNR, in order to isolate and analyze the effect of different defects on the thermoelectric properties. Note that these thermodefect junctions can also be operative when both the GNRs are made defective in different ways as it is the difference in the defective conditions of the ribbons that is essential. However, the target here is to examine the effects of various defects, particularly on the thermodefect voltage, and we, therefore, choose a pristine GNR as the reference component. Needless to say, in the absence of any defect or temperature difference, the voltage is always zero.

We here use the term defect to refer broadly to vacancies, such as single vacancy, divacancy, antidot vacancy, line vacancy, as well as impurities and dislocations. With the advancement of nanotechnology, it is nowadays possible to engineer a variety of defects in GNRs using tailored electron beam exposure technique [44–48]. In particular, by tuning the electron beam current density and the exposure time, the defect regions can be confined within a very small region of graphene [46]. Moreover, these defect regions can be probed without creating further defects [44, 49, 50]. This successful confinement of the defect regions enables the possibility of creating very specific defect structures in graphene. These already realized possibilities of engineering the disorderness [40, 41, 43, 51–56] clearly improves the potential of the present work.

For a given temperature difference we demonstrate that the thermodefect voltage is sensitive to defect configurations, degree of disorder, positions of the defects (in particular for line vacancies), widths of the ribbons, and range of chemical potential. Note that the chemical potentials can be tuned by applying a gate voltage to the leads [57, 58]. Specifically, in order to make our results comprehensive, we present the thermodefect voltage for many different defects in GNRs using three different widths of the GNRs that are characterized by either metallic or semiconducting behavior based on their edge configurations: armchair GNRs (AGNRs) and zigzag GNRs (ZGNRs). In semiconducting AGNR junctions with Stone–Wales or 555–777 defects, we find thermodefect voltages as large as 1.45 mV K\(^{-1}\) and 1.7 mV K\(^{-1}\), respectively, at room temperature. This can be compared to the conventional semiconducting [59] and ferromagnet-superconductor hybrid thermoelectric junctions [60–62] that usually produce voltages around sub-mV K\(^{-1}\) or \(\mu\)V K\(^{-1}\), showing the impressive prospects of the present work for thermoelectric applications.

In order to explain and understand the behavior of the thermodefect voltage, we also investigate the thermoelectric properties of single GNRs, both in absence and presence of various defects. In addition, these analyses allow us to identify which defects result in higher performance in terms of thermoelectricity. Specifically, in order to explore the thermoelectric properties, we compute the Seebeck coefficient of each GNR, which is the open circuit voltage developed across the junction.
Figure 2. Examples of the various defects considered for the defective GNR component of the thermodefect junction. The temperature gradient is applied along the vertical direction in each case.

Thus, the temperature difference destroys the charge homogeneity and induces an electrical field, balancing the thermal driving force and preserving the zero net current condition in the steady-state. As a consequence, the chemical potentials at the separated ends become different from each other due to the existence of defects in one of the junction components, while the connected ends of the junction maintain the same chemical potential. This established chemical potential difference is then utilized as the thermodefect voltage.

We describe each GNR of width \( W \) by the tight-binding Hamiltonian in the Wannier basis,

\[
H = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + H.c.,
\]

where the sum runs over all the nearest-neighbor sites \( \langle i,j \rangle \) and \( t \) is the nearest-neighbor hopping integral. The operator \( c_i^\dagger (c_i) \) creates (annihilates) an electron at the \( i \)th site. We use the KWANT quantum transport software package [64] to construct the tight-binding Hamiltonian and calculate the transmission function for each GNR between the two leads. We set \( t = 2.7 \text{ eV} \) as it successfully describes the electronic properties of GNRs [65–68].

It is already well-established in the literature that AGNRs of width \( W = 3n \) and \( 3n + 1 \) display semiconducting behavior, while they are metallic for widths \( W = 3n + 2 \), \( n \) being the number of dimers [68, 69]. On the other hand, ZGNRs are always semiconducting with non-dispersive edge states [68]. Throughout the rest of the work, we use the notations \( W \)-AGNR and \( W \)-ZGNR, where \( W \) is an integer defining the width of each AGNR and ZGNR junction component. We further model the defective GNRs by introducing various types of vacancies, impurities, or dislocations which create disorder in the otherwise regular lattice pattern of the GNR. For the calculations here, we consider single, double, edge, antidot and transverse and longitudinal line vacancies, as well as a result of the inhomogeneous charge distribution driven by the temperature gradient [63]. We also investigate the electrical conductance and electronic thermal conductance, which measure the ability of charge and heat transfer, respectively. Having understood the thermoelectric transport properties, we examine the performance of the GNRs in terms of the power factor as well.
as Stone–Wales and 555–777 dislocations, all illustrated in figure 2. These represent a wide variety of defects in GNRs that are all stable against the thermal vibrations even at the room temperatures [70–72].

To calculate the total density of states (DOS) in the GNRs and how defects influence it, we use the relation \( \rho(\varepsilon) = -1/(N\pi)\text{Im}[\text{Tr}[G(\varepsilon)]] \), where \( G(\varepsilon) = [(\varepsilon + i\eta)\mathcal{I} - \mathcal{H}]^{-1} \) is the Green’s function with \( \eta \) is an infinitesimal quantity, \( \mathcal{I} \) is the identity operator, and \( N \) is the total number of sites in the GNR.

In the linear regime the net current through a GNR attached to two reservoirs characterized by a temperature and chemical potential difference is given by [11]

\[
I = -GL \left( \frac{e}{\varepsilon} \frac{\partial I}{\partial \varepsilon} \right) - GSL \left( \frac{\partial T}{\partial x} \right) = -G \left( \frac{\Delta \mu}{e} \right) - GS \Delta T, \tag{2}
\]

where \( e \) is the electron charge, \( L \) is the length along the transport direction, \( G \) is the electrical conductance, and \( S \) is the Seebeck coefficient. Under zero net current condition, the thermodefect voltage can then be defined by the difference between the chemical potentials at the separated ends as

\[
V_{TD}(T_1, T_2, \mu_2) = \frac{1}{e} \left( \mu_{11}^{\text{pr}} |_{\varepsilon = 0} - \mu_{11}^{\text{def}} |_{\varepsilon = 0} \right) \tag{3}
\]

for a given chemical potential \( \mu_2 \) at the common end. We note that \( \mu_{11}^{\text{pr}} \) and \( \mu_{11}^{\text{def}} \) are to be found in the open circuit condition (\( I = 0 \)) using equation (2).

Alternatively, equation (3) can also be written in the following form

\[
V_{TD} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \left[ \left( \frac{\partial \mu_{11}^{\text{pr}}}{\partial T} \right) |_{\varepsilon = 0} - \left( \frac{\partial \mu_{11}^{\text{def}}}{\partial T} \right) |_{\varepsilon = 0} \right] dT \tag{4}
\]

which explicitly show the relation between the thermodefect voltage and Seebeck coefficients. Note that equation (4) reduces to \( (S_{\text{pr}} - S_{\text{def}})(T_2 - T_1) \) and the Seebeck coefficient also becomes \( S = -(1/e)[\mu(T_2) - \mu(T_1)]/(T_2 - T_1) \). Thus, equation (4) boils down to equation (3), since \( \mu_{11}^{\text{pr}}(T_2) = \mu_{11}^{\text{def}}(T_2) \) by construction. As a consequence, the thermodefect voltage is directly proportional to the difference in the Seebeck coefficients shown by the defective and pristine GNRs in the linear response and ballistic regime. This is already a commonly used approach to calculate thermoelectric properties of GNRs [7, 8, 16, 65, 73]. Furthermore, the thermodefect voltage is also linearly proportional to the temperature difference. However, in this study we fix it to \( \Delta T = 10 \text{ K} \) in order to focus only on the effects of defects.

To examine the Seebeck coefficients, as well as other thermoelectric transport coefficients, we employ the Landauer formalism within the linear response regime. This formalism is described in terms of the transport integrals which read [11, 74]

\[
I_{\alpha} = \int \left[ \beta(\varepsilon - \mu) \right] \beta f(\varepsilon, T)[1 - f(\varepsilon, T)]T(\varepsilon) d\varepsilon \tag{5}
\]

with \( \alpha \) being the energy moment index, \( \varepsilon \) the energy, \( T(\varepsilon) \) the transmission function, and \( f(\varepsilon, \mu, T) = 1/[\exp[\beta(\varepsilon - \mu)] + 1] \) the Fermi–Dirac distribution function with \( \beta = 1/(k_B T) \) being the inverse temperature scaled by the Boltzmann constant \( k_B \). The thermoelectric transport coefficients: electric conductance \( G \), Seebeck coefficient \( S \), and electronic thermal conductance \( \kappa_e \) are expressed in terms of the transport integrals as

\[
G = \frac{2e^2}{h} I_0, \tag{6a}
\]

\[
S = -\frac{k_B}{e} I_0, \tag{6b}
\]

\[
\kappa_e = \frac{2h}{e^2} \int \left( I_2 - \frac{I_1^2}{I_0} \right), \tag{6c}
\]

where \( h \) is the Planck constant. The factor of 2 appears due to spin degeneracy. The thermoelectric power factor \( P \) can further be obtained from the relation \( P = G \alpha S^2 \). Note that the ballistic approach allows us to express the non-equilibrium distribution function in terms of equilibrium distribution functions of the reservoirs [74, 75]. Therefore, regarding the transport integral, only the transmission function is affected by the existence of defects.

To focus on the influence of the defect difference between the GNR junction components, we assume the electrical contacts to be perfectly transmitting. Small deviations from the fully transmitting condition could make quantitative changes but should not affect the main conclusions of this work. It should also be noted that fixing the chemical potential at the hot or cold end of the junction does not change the results, because the applied temperature difference \( \Delta T = 10 \text{ K} \) is small compared to the set temperature, which is room temperature, \( T = 300 \text{ K} \).

As far as interactions are considered, thermoelectric properties are expressed as summations of diffusive (or ballistic), given by equations (6a)–(6c), and interaction terms. Note that the expression of Seebeck coefficient is the same for diffusive and ballistic approaches since it is defined under zero current condition. The contribution of interactions on thermoelectric coefficients is mainly represented by the phonon-drag effect [76, 77]. This effect causes an increment of the effective mass of electrons (or holes) as a result of electrons–phonon interactions. Increasing the effective mass decreases the mobility and the conductivity while it increases the Seebeck coefficient due to its inverse proportionality with conductivity. Therefore,
effects of phonon interactions on thermodefect voltage needs to be discussed before we continue to use equations (6a)–(6c), because the thermodefect voltage is directly proportional to the Seebeck coefficient. The phonon-drag effect depends on both electron–phonon (e–p), phonon–phonon (p–p) and phonon–boundary (p–b) interactions in general. For graphene, reference [78] provides a detailed computational study for the temperature dependency of the phonon-drag contribution on the Seebeck coefficient, $S_g$, and its comparison with the diffusive (ballistic here) contribution, $S$, equation (6b). The model of the study has been verified also by experimental data in the literature. The expression of $S_g$ is inversely proportional to the summation of p–p an p–b scattering frequencies (as a result of the Matthiessen’s rule [79]) and also contains a multiplicative term from e–p interaction in the electron relaxation process. The study concludes the following: at low temperatures, the p–p scattering rate decreases as $T^3$ and becomes negligible, while the p–b scattering rate remains almost constant. Therefore, the temperature dependence of $S_g$ is mainly due to the e–p process, which causes a temperature dependency in the form of $\exp(-\Omega_{q, \lambda}/k_B T)/T^2$ for low temperatures where $\Omega_{q, \lambda}$ is the frequency of a phonon of wavevector $q$ and branch $\lambda$. This term has a sharp increase with increasing temperature in the low-temperature regime, around 0.3–2 K. On the other hand, the $T^6$ dependency of the p–p scattering becomes dominant at relatively high temperatures (especially when $T > 10$ K) and this process contributes to $S_g$ by $T^{-3}$. Also the e–p process gives rise to $T^{-2}$ dependency at high temperatures. Consequently, $S_g$ decreases by $T^{-5}$ with increasing temperature in the high temperature regime. In the same study [78], it has been shown that the phonon-drag effect becomes negligible and the diffusive term (ballistic here) is essentially the only term contributing to the Seebeck coefficient for temperatures higher than 10 K. Practically, contributions of interactions become negligible especially when $T > 20$ K. There exist also other studies discussing the negligibility of electron–phonon coupling in graphene at room temperature [65, 73]. Since we consider room temperature, we can thus safely neglect contributions of phonons to the Seebeck coefficient as we assume that the existence of defects does not change the main mechanisms suppressing the phonon-drag effect on the Seebeck coefficient. In other words, due to the weak electron–phonon coupling in GNRs, we can ignore phonon effects at room temperature [65, 73, 80].

In the context of phonons and also nuclear vibrations, we additionally mention that effects of vibrational impurities on the electronic structure of graphene have been studied previously [81]. In particular, local vibrations may be pertinent to the vacancies and dislocations that we introduce in the GNRs. However, as was demonstrated in [81], the Friedel oscillations excited by the local vibrations are fairly short ranged and do not in a significant way distort the overall electronic structure in comparison to the Friedel oscillations already introduced through the presence of the impurities themselves. Hence, our restriction to study ballistic transport should be considered to be firmly founded in the established knowledge of graphene.

### 3. Results and discussions

With the above outline of the theoretical framework, we now present our results of thermodefect voltage and other transport coefficients in two subsections corresponding to two defect classes: vacancies and dislocations.

#### 3.1. Vacancies

We begin our discussions on thermodefect voltage by considering atomic site vacancies put in a line along the longitudinal direction with respect to the transport (see figure 2(e)) in the defective GNR of the thermodefect junction of figure 1. The effect of such a longitudinal line vacancy on the thermodefect voltage strongly depends on the position of the line vacancy relative to the edge, which is in agreement with other, non-thermal, transport results in the literature [42, 82–84]. We first in figure 3 focus on the behavior of the thermodefect voltage as a function of $\mu_2$ in the presence of longitudinal vacancies at different positions, using AGNRs in the junction. Depending on the position of the line vacancy we call it symmetrical, asymmetrical, or edge longitudinal vacancy when the vacancy line is situated in the middle i.e., $(W + 1)/2$th line, in the $(W + 3)/2$th line, or at the edge of the AGNR, respectively. Note that, exactly symmetric situation for the longitudinal vacancy is only possible when $W$ is an odd integer and an example of that is shown in figure 2(e). We can also have line vacancies of different lengths. Here, we only show results for the maximum possible length (less than the length of GNR by two atomic sites) in order to achieve the highest thermodefect voltages, but the phenomenon of thermodefect voltage is qualitatively similar, except with a reduced magnitude, for line vacancies of shorter lengths.

In figure 3 we see that there is a finite thermodefect voltage for a wide range of $\mu_2$ including a plateau region up to $\mu_2 \sim 0.4$ eV. This occurs for all three types of the longitudinal line vacancies. However, for the symmetrical line vacancy, the induced thermodefect voltage in the plateau region is much higher: 3.7 mV for 10 K, alternatively 0.37 mV K$^{-1}$ compared to the induced thermodefect voltage in the plateau region is much higher: 3.7 mV for 10 K, alternatively 0.37 mV K$^{-1}$.
to the other two line vacancy positions, and with a maxima as high as \( \sim 0.5 \text{ mV K}^{-1} \). For even larger chemical potentials, \( \mu > 0.7 \text{ eV} \), the thermodefect voltage drops substantially for all the three types of longitudinal vacancies and show damped oscillations around zero i.e., both positive and negative voltages are possible for high chemical potentials. These oscillations are associated with the degeneracy effects originated from the Fermi gas properties \([11, 85, 86]\). We note here that very high values of the chemical potential, such as \( > 1 \text{ eV} \), are difficult to utilize in practice \([37]\) and values larger than \( 2.5 \text{ eV} \) even falls outside the validity of the tight-binding model \([68]\).

To explain the phenomenon of the thermodefect voltage in the presence of longitudinal vacancies and why the horizontal position of the vacancy line matters, we draw an analogy with the classical circuit of parallel batteries. A symmetrically divided GNR similar to figure 2(e), can be seen as two identical thinner ribbons connected at the two opposite ends, setting up a parallel and short-circuited configuration of a thermosize junction \([16]\). In this symmetric configuration, the net induced voltage throughout the defective GNR is equal to the voltage of each individual thinner ribbon, since the short-circuit current is zero as a result of the same thermosize voltage induced in each identical ribbon. In the asymmetric case, however, the widths of the two thin GNRs are different, and the defective ribbon starts operating as an individual thermosize cell, which induces a non-zero voltage and short-circuit current in the defective GNR. Since the thinner ribbon has higher resistance, the voltage drop across the thinner GNR becomes higher than that in the thicker ribbon. The total voltage of this parallel and non-identical ‘battery’ circuit finally approaches the voltage of the thicker ribbon, which is smaller in magnitude (see the supplementary material \([https://stacks.iop.org/JPCM/34/195304/mmedia]\) \([87]\) for more details on this analogy).

Thus, the largest thermodefect voltage is always induced for a line vacancy causing a symmetric division of the ribbon.

So far, we have considered the thermodefect voltage only. In order to understand these results, we next plot in figure 4 the Seebeck coefficient \( S \), electrical conductance \( G \), electronic thermal conductance \( \kappa_e \), and thermoelectric power factor \( P \) as functions of the chemical potential \( \mu \) in a single 13-AGNR. We note that, unlike the thermodefect junction of two GNR components under a temperature gradient, we now consider the properties of a single GNR considering the constant chemical potential \( \mu \) for both the reservoirs attached to the two opposite ends of the single ribbon. Comparing the thermoelectric properties of defective ribbons with the pristine one gives an idea about the behavior of a thermodefect junction made by these GNRs. The longitudinal line vacancies preserve the particle–hole symmetry, so the figures show only the results for electron doping, i.e., positive chemical potential values. The zero of \( \mu \) corresponds to the charge neutrality point, above (below) which the electrons (holes) are the dominant charge carriers.

In figure 4(a), we see that the Seebeck coefficient for the pristine ribbon shows a dip for low values of the chemical potential \( \mu \). But, notably, the values of \( S \) in the presence of asymmetrical and edge longitudinal vacancies almost do not change from that of the pristine AGNR. However, the AGNR with the symmetrical longitudinal line vacancy has a considerably enhanced value of \( S \) compared to the other two defect conditions. Thus, when a symmetrical longitudinal line vacancy is present, the Seebeck spectrum changes considerably. The differences between the Seebeck profiles for the different configurations is directly reflected in the thermodefect voltage shown in figure 3, following the prediction of equation (4). This includes the voltage peak at \( V_{TD} \sim 0.5 \text{ eV} \), where the difference between the Seebeck values for the pristine and symmetrical configurations also reaches its maximum.

Note that, in figure 4(a) only plot for the regime: \( 0 < \mu < 1 \text{ eV} \), as \( S \) dies out at higher \( \mu \) values for all defect configurations. This is due to the occupancy variance window (i.e., derivative of the Fermi function \( f(\varepsilon, \mu, T) \) with respect to the dimensionless chemical potential, \( \mu/k_B T \)) in the transport integral becomes narrower at higher \( \mu \). This forces the transport integrals to decrease for any order of energy moments. However, the integrals with higher moments decrease faster than the lower ones. Therefore, \( I_1/I_0 \) decays rapidly leading to a strong decrease in the Seebeck coefficient at higher chemical potentials. The Seebeck spectrum of the pristine AGNR also display some smaller oscillations in the high chemical potential regime causing sign changes. These small oscillations can shift to other locations along the chemical potential axis with the change of the width of the AGNR \([8, 16]\).

The sign changing behavior of the thermodefect voltage occurring in the higher chemical potential regime can be understood quantitatively from these oscillations of the Seebeck coefficients, more specifically, where the Seebeck coefficients of the pristine and defective AGNRs cross each other, see figure 4(a). Whenever the magnitude of the Seebeck coefficient of the pristine GNR is smaller than the defective one, a negative
Voltage is induced and vice versa, following the relationship between the Seebeck coefficients and the thermodefect voltage in equation (4). However, this oscillatory behavior of the voltage profiles has no practical importance because they tend to occur at high chemical potentials where the thermodefect voltages drop close to zero.

Moving on to the electrical conductance $G$ in figure 4(b), we see a regular stepwise pattern for the pristine AGNR consistent with earlier work [42]. As soon as we put in a longitudinal vacancy, it starts deviating from the plateaus and resonances appear. The latter occur due to quantum interference effects caused by the vacancies in the AGNR [88]. The behavior of the thermal conductance $κ$ of the ribbon is similar to the electrical conductance profiles, as shown in figure 4(c). The behavior of both the electrical and thermal conductances in the presence of the defects thus provides information on how the transport properties are affected by the defects.

Finally, we compare the power factor $P$ between a pristine AGNR and those with different line vacancy defects in figure 4(d). The existence of large peaks for various chemical potentials indicates the range of $μ$ for which our thermodefect junction can give the maximum power output [77]. The harvestable voltage range occurs to be at lower chemical potentials corresponding to large voltage values combined with the finite (non-vanishing) conductance. As a matter of fact, the power factor captures the chemical potential ranges where conductance and Seebeck coefficient are both large enough to get power. From the power factor analysis we can find the optimal conditions for $μ$ that ensure the operation of a thermoelectric device with maximum output.

Till now, we have discussed only the longitudinal vacancies for the defective ribbon. We also investigate the thermodefect voltages for our thermodefect junction when the defective ribbon has single, double, edge, antidot or transverse line vacancy, shown in figures 2(a)–(d) and (f), and present their maximum voltage values in table 1, obtained for the same range of the chemical potential as used in figure 3. For these vacancies, changing the position of the defects inside the GNR along both the transverse and longitudinal directions (with respect to the transport direction) does not affect the thermodefect voltages much, except the edge defects. This occurs due to the lattice symmetry along the transport direction is not changing between different vacancies. We note that the transverse line vacancy may be energetically unstable due to open tips and strong affinity of carbon atoms. However, we still explore it for the sake of comparison with the other possibilities.

In order to investigate how the thermodefect voltages are sensitive to the edge configurations of the ribbon and also the existence of the band gap (finite for semiconductor and zero for metallic), we choose two different ribbon widths $W = 11$ and $13$ for metallic and semiconducting AGNRs, respectively, and $W = 12$ for ZGNR. In table 1 we see that for single, double, edge, transverse line and asymmetric longitudinal vacancies, metallic AGNR is the most suitable one in order to get larger voltages, whereas the semiconducting AGNR shows a considerably higher voltage for a symmetric longitudinal line vacancy. Other types of vacancies show more or less similar and notably smaller voltage values. Thus, on the whole AGNRs is more effective compared to ZGNRs.

As soon as a defect is introduced in a pristine GNR, it induces some quasi-localized states and destroys some extended states in the DOS spectrum, which makes the electronic structure different than the pristine one, as already studied in the literature [83, 89, 90]. We confirm this by calculating DOS and the transmission spectra but avoid providing the plots in order to focus on our main results of the thermodefect voltage. Overall, which defect type produces larger voltage depends on the number of localized states around the Fermi level as well as their degree of localization. The voltage values can be compared by analyzing the DOS and the transmission spectra for the defective ribbons.

We also compare our results for the thermodefect junctions with vacancies to that for the junctions with impurities replacing the vacancies. Vacancies have more dramatic effects on the thermodefect voltage than impurities. The voltage decreases significantly when a vacancy is replaced by an impurity, no matter its physical placement. We therefore do not include showing the impurity results in table 1 as they have relatively very low thermodefect voltages.

Throughout this work, we keep the widths of the GNR small to minimize the computational load and maximize the voltage, since the smaller the ribbon width, the larger the size effects and the higher the voltages. This is because the performances of nanoscale thermoelectric devices are enhanced, in general, as a result of the DOS modifications by the quantum confinement effects [91]. Thus, keeping the defect types same, decreasing the widths of both the junction components causes a steady increase in the voltage amplitudes.

### 3.2. Dislocations

Next we turn our attention to thermodefect junctions with dislocations in the form of Stone–Wales and 555–777 defects. For these crystallographic dislocations the lengths of all nearby bonds are affected and that in turn affects the hopping integrals [92, 93]. We therefore adjust our Hamiltonian in equation (1)
by making the hopping parameter \( t \) site-dependent, choosing values near these defects from the density functional theory results existing in the literature [94, 95]. Although the hopping values near the vacancies can change, we find the thermodefect voltage to be robust against small changes in hopping values near the defects.

We show our results on thermodefect voltages for dislocations in figure 5 using a 13-AGNR (i.e. semiconducting) junction. Here we plot the thermodefect voltage as a function of the chemical potential of the electrically connected end of the junction, within the range \(-0.5 \leq \mu_2 \leq +0.5 \) eV, as the thermodefect voltage dies out outside this range. We observe clear and large peaks at low \( \mu_2 \) for both dislocation defects, corresponding to the highest voltages highlighted (in bold) in table 1.

Interestingly, unlike vacancies, the voltage spectrum is asymmetric across the charge neutrality point (\( \mu_2 = 0 \)) for GNRs with dislocation defects. We see a similar particle–hole asymmetry exists in the DOS spectrum, plotted in the inset of figure 5. This asymmetry can be explained as follows. In a regular honeycomb lattice, nearest neighbor hopping always occurs between different sublattices (i.e., A to B or B to A, where A is denoted by blue and B is by orange color in figure 2 respectively) and forms even-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings.

Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings. Dislocations, like 555–777 and Stone–Wales defects, however, break this sublattice symmetry around the defect regions [96] and forms odd-membered (even number of bonds) rings.
In the presence of dislocation defects, the thermodefect voltage, namely, thermoelectric transport coefficients between the defective and pristine GNRs particularly large around zero energy. Following the derivation in equation (4) this directly explains the large thermodefect voltages around zero energy in figure 5. The particle–hole asymmetry also appears in the electrical $G$ and thermal conductance $\kappa_e$ profiles, shown in figures 6(b) and (c), respectively. The deviations of the conductance profiles of the GNRs with the dislocations from that of pristine GNR are similar to that of the case of vacancy. The asymmetry in the conductance spectra is transplanted also to the distinct peaks in the power factor $P$ in figure 6(d).

To summarize, for dislocations we find that the larger the difference between the transport properties of the defective GNR and the pristine one, the higher the thermodefect voltages. In other words, the more asymmetry we have in the electronic spectrum in the presence of dislocation defects, the higher thermodefect voltages that can be obtained. This is a clear clue we can provide for the defect engineering to be used in the thermodefect junctions in reality.

4. Conclusions

We introduced the concept of defect-induced thermoelectric voltage, namely, thermodefect voltage, in a junction made of two identical GNRs but with defects present in one of the ribbons. We investigated this thermodefect voltage for various defects: single vacancy, multi-vacancies (double, antidot, edge), as well as for dislocations and impurities. For vacancies we found that the thermodefect voltage can be $\sim 0.6 \text{ mV K}^{-1}$ for the case of longitudinal line vacancies, whereas it can be as high as $\sim 1.7 \text{ mV K}^{-1}$ when dislocation defects are used instead. For illustration we have shown results for mainly semiconducting AGNRs, as they are more effective in producing higher thermodefect voltages, but for completeness we also reported the thermodefect voltage values for AGNRs and ZGNRs with various widths.

In order to analyze the thermodefect voltages, we also studied the Seebeck coefficient, electrical conductance, electronic thermal conductance, and thermoelectric power factor of single AGNRs, both in pristine and defective conditions. Thermodefect voltages are related to signatures in the thermoelectric properties of the junction, the difference in the Seebeck coefficients between pristine and defective GNRs. Our results for the thermoelectric properties of a single GNR in the presence of defects are consistent with the sensitivity of the electric transport properties of GNRs to the configuration of defects as shown earlier in the literature [52, 100–105]. We also showed that vacancies and dislocations induce (quasi-)localized states by destroying the extended states of the GNRs. Combining these (quasi-)localized states with the particle–hole asymmetry produced by dislocations result in very large Seebeck coefficient differences between pristine and defective GNRs, which explain finding the largest thermodefect voltages in these setups.

Based on our results for the thermodefect voltage in many different GNR junctions we find that the performance of these thermodefect junctions is considerably better than traditional bulk systems and defects are thus able to make appreciable contributions for the enhancement of thermoelectric properties [1, 11]. Depending on the defect type, the thermodefect voltage is even of the same order as in nanoscale bipolar thermoelectric junctions [4]. It may in fact be possible to double the thermodefect voltage in a bipolar junction where both $p$ and $n$ components of the junction have exactly the same defects.

Finally, we emphasize that our concept of thermodefect voltage generation can be implemented in other nanostructured materials, beyond GNRs. Our thermodefect junction should be easy to implement experimentally. It additionally provides a varied and rich way of generating thermoelectric voltage owing to the existence of abundant defect types that can be engineered in the junction. Thus, the thermodefect effect proposed in this work may open up new efforts to further enhance the thermoelectric properties of nanostructured materials.

Acknowledgments

ABS and PD acknowledge the financial support from the Knut and Alice Wallenberg Foundation through the Wallenberg Academy Fellows program and the Swedish Research Council (Vetenskapsrådet Grant No. 2018-03488). AS wishes to extend his gratitude for the gracious hospitality and collaboration in Materials Theory Division, Department of Physics & Astronomy, Uppsala University.
Data availability statement

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

ORCID iDs

Alhun Aydin https://orcid.org/0000-0002-1130-0936
Altug Sisman https://orcid.org/0000-0002-7431-5115
Jonas Fransson https://orcid.org/0000-0002-9217-2218
Paramita Dutta https://orcid.org/0000-0003-2590-6231

References

[1] Pichanusakorn P and Bandaru P 2010 Mater. Sci. Eng. R 67 19
[2] Hicks L D and Dresselhaus M S 1993 Phys. Rev. B 47 12727
[3] Hicks L D and Dresselhaus M S 1993 Phys. Rev. B 47 16631
[4] Koutomo K and Morita T 2013 Thermoelectric Nanomaterials (Berlin: Springer)
[5] Liang G, Huang W, Koong C S, Wang J-S and Lan J 2010 J. Appl. Phys. 107 014317
[6] Ziani X 2010 Appl. Phys. Lett. 97 233106
[7] Zhou J and Yang R 2011 Appl. Phys. Lett. 98 173107
[8] Wang B, Zhou J, Yang R and Li B 2014 New J. Phys. 16 066018
[9] Zhou J and Yang R 2011 J. Appl. Phys. 110 084317
[10] Chen Y, Jayasreeka T, Calzolari A, Kim K W and Buongiorno Nardelli M 2010 J. Phys.: Condens. Matter 22 372202
[11] Pan C, Xie Z and Chen K 2014 Nanoscale Thermoelectrics ed X Wang and Z M Wang (Berlin: Springer) ch 13 p 393
[12] Gadea G, Morata A and Tarancon A 2018 Semicond. Semimet. 98 321
[13] Tran V et al 2017 Sci. Rep. 7 2313
[14] Saiz-Bretn C M, Orellana P A, Rosales L D and Domene-Garzio-Fa 2020 J. Phys.: Condens. Matter 32 275301
[15] Dollfus P, Hung Nguyen V and Saint-Martin J 2015 J. Phys.: Condens. Matter 27 133204
[16] Aydin A, Fransson J and Sisman A 2019 J. Appl. Phys. 126 104302
[17] Sisman A, Aydin A and Fransson J 2020 J. Phys.: D: Appl. Phys. 53 375510
[18] Sisman A and Muller I 2004 Phys. Lett. A 320 360
[19] Lin T, Su G, Ou C, Lin B, Le Mehaute A, Wang Q A and Chen J 2010 Mod. Phys. Lett. B 24 1727
[20] Wang H, Wu G and Chen X 2012 J. Appl. Phys. 111 024312
[21] Wang H and Wu G 2012 J. Appl. Phys. 112 084317
[22] Wang H and Wu G 2013 J. Appl. Phys. 113 054309
[23] Wang H, Wu G, Chen X and Chen D 2013 Contin. Mech. Thermodyn. 25 43
[24] Nie W and He J 2008 Phys. Lett. A 372 1168
[25] Nie W, He J and He X 2008 J. Appl. Phys. 103 114909
[26] Su G, Chen L, Lin T and Chen J 2011 J. Low Temp. Phys. 163 275
[27] Karabegolu S and Sisman A 2017 Phys. Lett. A 381 2704
[28] Nie W, Lü K, Chen A, He J and Lan Y 2018 Appl. Energy 232 695
[29] Babac G and Sisman A 2011 J. Comput. Theor. Nanosci. 8 1
[30] Sisman A and Babac G 2012 Contin. Mech. Thermodyn. 24 339
[31] Babac G and Reese J M 2014 Nanoscale Microscale Thermophys. Eng. 18 39
[32] Senay M and Kibaroglu S 2018 Mod. Phys. Lett. B 32 1850230
[33] Aydin A and Sisman A 2019 Phys. Lett. A 383 655
[34] Sevinçli H and Cuniberti G 2010 Phys. Rev. B 81 113401
[35] Nozaki D, Sevinçli H, Li W, Gutiérrez R and Cuniberti G 2010 Phys. Rev. B 81 235406
[36] Sevinçli H, Sevik C, Çağın T and Cuniberti G 2013 Sci. Rep. 3 1228
[37] Tran V-T, Saint-Martin J and Dollfus P 2015 Nanotechnology 26 495202
[38] Nozaki D, Avdoshenko S M, Sevinçli H and Cuniberti G 2014 J. Appl. Phys. 116 074308
[39] Sevinçli H and Sevik C 2014 Appl. Phys. Lett. 105 223108
[40] Harzheim A et al 2018 Nano Lett. 18 7715–29
[41] Xiao H, Cao W, Ouyang T, Xu X, Ding Y and Zhong J 2018 Appl. Phys. Lett. 112 233107
[42] Mu W L, Wu H-N, Han Y and Gong W-J 2019 Phys. Lett. A 383 264
[43] Zong P-A, Liang J, Zhang P, Wan C, Wang Y and Koutsou N 2020 ACS Appl. Energy Mater. 3 2224
[44] Hashimoto A, Suenaga K, Gloter A, Urita K and Iijima S 2004 Nature 430 870
[45] Jafr S H M et al 2010 J. Phys.: D: Appl. Phys. 43 045404
[46] Robertson A W, Allen C S, Wu Y A, He K, Olivier J, Neethling J, Kirkland A I and Warner J H 2012 Nat. Commun. 3 1144
[47] Robertson A W, Montanari B, He K, Allen C S, Wu Y A, Harrison N M, Kirkland A I and Warner J H 2013 ACS Nano 7 4495
[48] Topazlı, H., Dobrik, G., Nemes-Incze, P., Vertesy, G., Lambin, P. and Biris, L. P. 2008 Phys. Rev. B 78 233407
[49] Kelly K F and Halas N J 1998 Surf. Sci. 416 L1085
[50] Ouyang M, Huang J-L, Cheung C L and Lieber C M 2001 Science 291 97
[51] Li Z, Xiao C, Zhu H and Xie Y 2016 J. Am. Chem. Soc. 138 14810
[52] Haskins J, Knačič A, Sevik C, Sevinçli H, Cuniberti G and Çağın T ACS Nano 2011 5 3779
[53] Ohnishi M, Shiga T and Shimoi J 2017 Phys. Rev. B 95 155405
[54] Zhao C, Li Z, Fan T, Xiao C and Xie Y 2020 Research 2020 965279
[55] Anno Y, Imakita Y, Takei K, Akita S and Ariie T 2017 2D Mater. 4 020519
[56] Chen S et al 2020 ACS Appl. Mater. Interfaces 12 19664–73
[57] Chen J et al 2010 Phys. Rev. Lett. 105 176602
[58] Lin L et al 2016 Nano Lett. 16 4094
[59] Sharp J 2016 Reference Module in Materials Science and Materials Engineering (Amsterdam: Elsevier)
[60] Kolenda S, Wolf M J and Beckmann D 2016 Phys. Rev. Lett. 116 097001
[61] Dutta P, Saha A and Jayannavar A M 2017 Phys. Rev. B 96 115404
[62] Dutta P, Alves K R and Black-Schaffer A M 2020 Phys. Rev. B 102 094513
[63] Blundell J S and Blundell K M 2009 Concepts in Thermal Physics (Oxford: Oxford University Press)
[64] Groth C W, Wimmer M, Akhmerov A R and Waintal X 2014 New J. Phys. 16 063065
[65] Gunlycke D, Lawler H M and White C T 2007 Phys. Rev. B 75 085418
[66] Reich S, Maultzsch J, Thomesen C and Ordejón P 2002 Phys. Rev. B 66 053412
[67] Hancock Y, Uppstu A, Saloriutta K, Harju A and Puska M J 2010 Phys. Rev. B 81 245402
[68] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109
[69] Peres N M R, Guinea F and Castro Neto A H 2006 Ann. Phys. NY 321 1559
[70] Gong C, Robertson A W, He K, Lee G-D, Yoon E, Allen C S, Kirkland A I and Warner J H 2015 ACS Nano 9 10066
[71] Galashev A E and Rakhmanova O R 2014 Phys.-Usp. 57 970
[72] Ermakov V A, A Aferdov A V, Vaz A R, Perim E, A Fretre P A, Paupitz R, Galvao D S and Moshkalev S A 2015 Sci. Rep. 5 11546
[73] Pan C-N, Xie Z-X, Tang L-M and Chen K-Q 2012 Appl. Phys. Lett. **101** 103115

[74] Datta S 1995 *Electronic Transport in Mesoscopic Systems* (Cambridge: Cambridge University Press)

[75] Yuli Y M B and Nazarov V 2009 *Quantum Transport: Introduction to Nanoscience* (Cambridge: Cambridge University Press)

[76] Wu M W, Horing N J M and Cui H L 1996 Phys. Rev. B **54** 5438

[77] Goldsmid H J 2009 *Introduction to Thermoelectricity* 1st edn (Springer Series in Materials Science vol 121) (Berlin: Springer)

[78] Bao W S, Liu S Y and Lei X L 2010 J. Phys.: Condens. Matter **22** 315502

[79] Ziman J M 2001 *Electrons and Phonons: The Theory of Transport Phenomena in Solids* (Oxford: Oxford University Press)

[80] Ouyang Y and Guo J 2009 Appl. Phys. Lett. **94** 263107

[81] Fransson J, She J-H, Pietronero L and Balatsky A V 2013 Phys. Rev. B **87** 245404

[82] Costa Filho R N, Farias G A and Peeters F M 2007 Phys. Rev. B **76** 193409

[83] Dutta P, Maiti S K and Karmakar S N 2013 J. Appl. Phys. **114** 034306

[84] Deng H-Y and Wakabayashi K 2014 Phys. Rev. B **90** 115413

[85] Aydin A and Sisman A 2018 Phys. Lett. A **382** 1807

[86] Aydin A and Sisman A 2018 Phys. Lett. A **382** 1813

[87] See supplementary material for details.

[88] Rodrigues J N B, Peres N M R and Lopes dos Santos J M B 2012 Phys. Rev. B **86** 214206

[89] Pereira V M, Guinea F, Lopes dos Santos J M B, Peres N M R and Castro Neto A H 2006 Phys. Rev. Lett. **96** 036801

[90] Li T C and Lu S-P 2008 Phys. Rev. B **77** 085408

[91] Mahan G D and Sofo J O 1996 Proc. Natl Acad. Sci. **93** 7436

[92] Bhownik S and Waghmare U V 2010 Phys. Rev. B **81** 155416

[93] Zayye O V and Louie S G 2010 Phys. Rev. B **81** 195420

[94] Ihnatsenka S and Kirczenow G 2013 Phys. Rev. B **88** 125430

[95] Linhart L, Burgdörfer J and Libisch F 2018 Phys. Rev. B **97** 035430

[96] Kot P, Pamell J, Habibian S, Straller C, Ostrovsky P M and Ast C R 2020 Phys. Rev. B **101** 235116

[97] Tamura R and Tsukada M 1994 Phys. Rev. B **49** 7697

[98] Peres N M R, Guinea F and Castro Neto A H 2006 Phys. Rev. B **73** 125411

[99] Bischoff D, Varlet A, Simonet P, Eich M, Overweg H C, Ihn T and Ensslin K 2015 Appl. Phys. Rev. **2** 031301

[100] Lherbier A, Dubois S M-M, Declerck X, Niquet Y-M, Roche S and Charlier J-C 2012 Phys. Rev. B **86** 075402

[101] Banhart F, Kotakoski J and Krasheninnikov A V 2011 ACS Nano **5** 26

[102] Deng H-Y and Wakabayashi K 2015 Phys. Rev. B **91** 035425

[103] Han M Y, Brant J C and Kim P 2010 Phys. Rev. Lett. **104** 056801

[104] Terrones H, Lv R, Terrones M and Dresselhaus M S 2012 Rep. Prog. Phys. **75** 062501

[105] Abergel D S L, Apalkov V, Barashchevich J, Ziegler K and Chakraborty T 2010 Adv. Phys. **59** 261