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Unravelling the Influence of Dimensions on the Thermo-electric Properties of AHEGNR

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Abstract

The thermoelectric properties of hydrogenated edge semiconductor graphene nanoribbons (GNRs) have thus far been explored in detail. The effects of varying the sizes of zigzag hydrogenated edge graphene nanoribbons (ZHEGNRs) and armchair hydrogenated edge graphene nanoribbons (AHEGNRs) in terms of their properties were investigated in this study. This was achieved via the control of the graphene nanoribbon dimensions i.e., width and length by utilizing density functional theory in Quantum Espresso, augmented by the BoltzTraP code. Assuming a constant relaxation time, the Seebeck coefficient, electrical conductivity, and electronic thermal conductivity were calculated using Boltzmann transport theory to determine the coefficient of performance. Our findings indicate that transport properties are sensitive to sample dimensions, showing a more pronounced trend in ZHEGNRs than AHEGNRs. When the graphene sample becomes larger, there will be a larger number of low-frequency acoustic phonons that can be excited. It helps in thermal conduction and shows length dependence in thermal conductivity. The number of edge-localized phonon modes is constant at lower widths of GNRs but increases at larger widths. Hence, while the number of edge-localized phonon modes does not significantly affect the thermal conductivity with every width increase, the variation itself is too small to be registered.

Keywords: Graphene, thermo-electric properties, transport properties, nanoribbon, size dependent properties

INTRODUCTION

Modern technology in the electronics industry faces a growing challenge in thermoregulation due to reduced sizes of circuit components. Such situation has built up a great interest- so to speak, has resonated in material thermal properties; specifically, their nanostructured forms usable in electronic components and circuitry. The thermal transport properties of graphene and its derivatives, especially in terms of their size dependence, are investigated. Heat conduction in carbon-based materials, such as metals and argentite are chiefly carried out by phonons. This is basically due to sp^2 covalent bonding facilitating conduction through lattice vibrations. Computer experiments have been done to calculate electronic thermal conductivity in graphene structures.

In other words, the results obtained in the study show that conductivity is dependent on sample size, which will lead to an incentive for further investigation of these systems in terms of their transport properties. This work specifically investigates the electronic characteristics of graphene nanoribbons to explore how structural parameters, such as type, length, and width influence their behavior.

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COMPUTATIONAL MODEL AND METHOD

To investigate the size dependence of graphene nanoribbons on transport properties, we perform first-principle calculations using the density functional theory and the semi-classical Boltzmann theory, as implemented in the BoltzTraP code (Figure 1) [1].

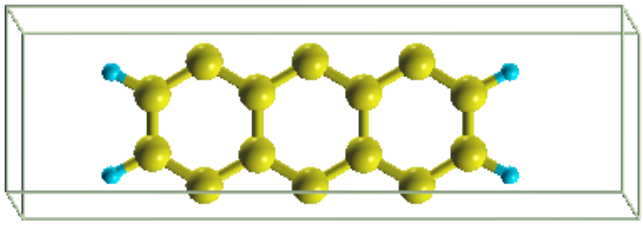

Figure 1. Primitive unit cells of a clean hydrogenated edges armchair carbon nanoribbon included 14 carbon atoms. The yellow spheres are carbon atoms and light blue spheres are hydrogen atoms.

Based on the type of edge shape, graphene nanoribbons (GNRs) are generally categorized into two groups: namely, zigzag and armchair. Hydrogenation of the edges of armchair graphene nanoribbons (HEAGNRs) makes them much more stable than the non-hydrogenated nanoribbons because the dangling bonds are passivated.

The structures for the HEAGNRs and HEZGNRs were firstly optimized by minimizing the forces acting on them. For Brillouin zone manipulation, the Monkhorst-Pack scheme was utilized, in such a way that the structures were fully relaxed. Varying energy cut-off, lattice constants, and Monkhorst-Pack grid parameters were varied after the initial restrained self-consistent calculation The optimized parameters extracted from this NSCF calculation were subsequently used for further simulations.

For transport calculation, we depend on the constant relaxation time approximation and the rigid band approximation, and the computations were performed using the BoltzTrap code, relying on smoothed Fourier interpolations [2–5].

TRANSPORT PROPERTIES

Thermal Conductivity of Armchair and Zigzag GNRS, as a Function of Length

It has been seen that, for zigzag graphene nanoribbons (ZGNRs), the thermal conductivity is a lot higher than that for armchair graphene nanoribbons (AGNRs) and pristine graphene nanosheets. The change in thermal conductivity for single-layer pristine graphene, ZGNRs, and AGNRs concerning their length is pinpointed in Figure 2.

Our simulations, done for lengths 50 nm and 70 nm, using a fixed width of 20 nm, show that thermal conductivity increases as the length of suspended graphene structure increases. This agrees with the literature existing so far and confirms the theoretical prediction [6]. Least frequency ranges allow sound acoustic phonons to be dispersed: the heat conduction becomes much more efficient for larger dimensions. Such extended confusion exists for longer wavelengths, which have a transport discussed very generally as ballistic or nearly ballistic. Large number of such ballistic phonon means more efficient thermal conductivity in these long samples. The edge in the GNRs, as shown in Figure 2, shows decreased value of the thermal conductivity, which can be attributed to the two reasons [7–16]. First, compared with that of pristine graphene, in the low-energy region there appears two edge-localized phonon modes for the GNRs, i.e., the lowest-lying optical mode and the transverse acoustic mode [17]. These two, edge-localized phonons and low-energy phonons can interact with other and thus reduce their PMFP edge effect. This would reduce the low-energy phonon contribution to thermal conductivity remarkably and is very substantial and significant for thermal transport. Second, at the edges of GNRs the boundary scattering also reduces the thermal conductivity.

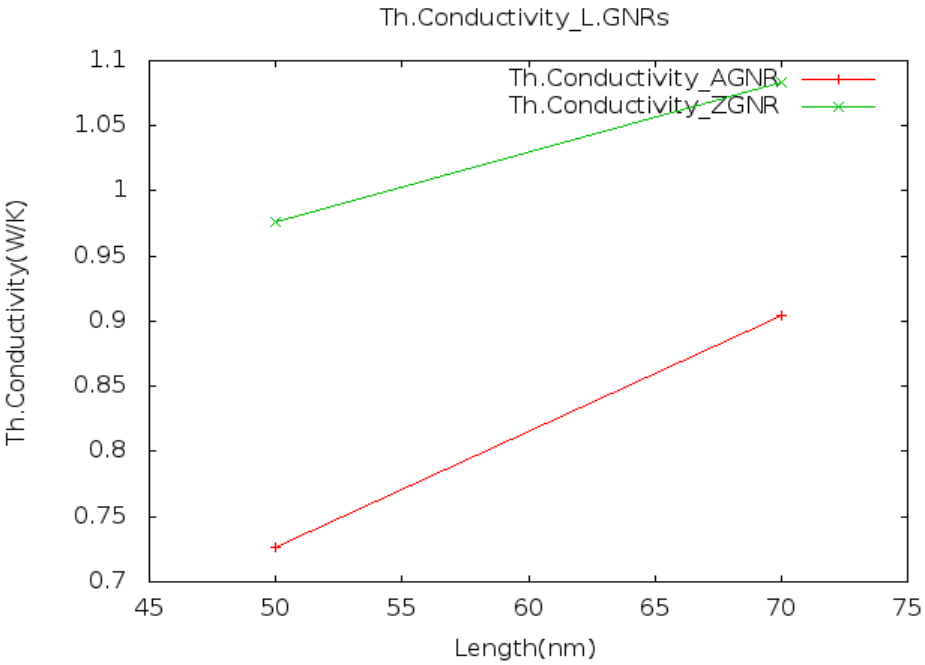

Figure 2. Simulated electronic thermal conductivity for armchair and zigzag GNRs, as a function of lengths with simulations (width 20nm), as per our calculations.

Thermal Conductivity of Armchair and Zigzag GNRS, as a Function of Widths

We analyzed the thermal conductivities of zigzag and armchair nanoribbons for larger widths, and the effects thereof. At very large widths, the thermal conductivity of the armchair form is essentially a constant, while that of the zigzag form first increases to about 30 nm, before decreasing as the width is increased further [8–10]. The simulated results of thermal conductivity of AGNRs and ZGNRs for the width changing from 10 to 30 nm are collected into Figure 3. In all the considerations done here, the lengths of the graphene and GNRs were kept constant, and the simulation parameters were held constant.

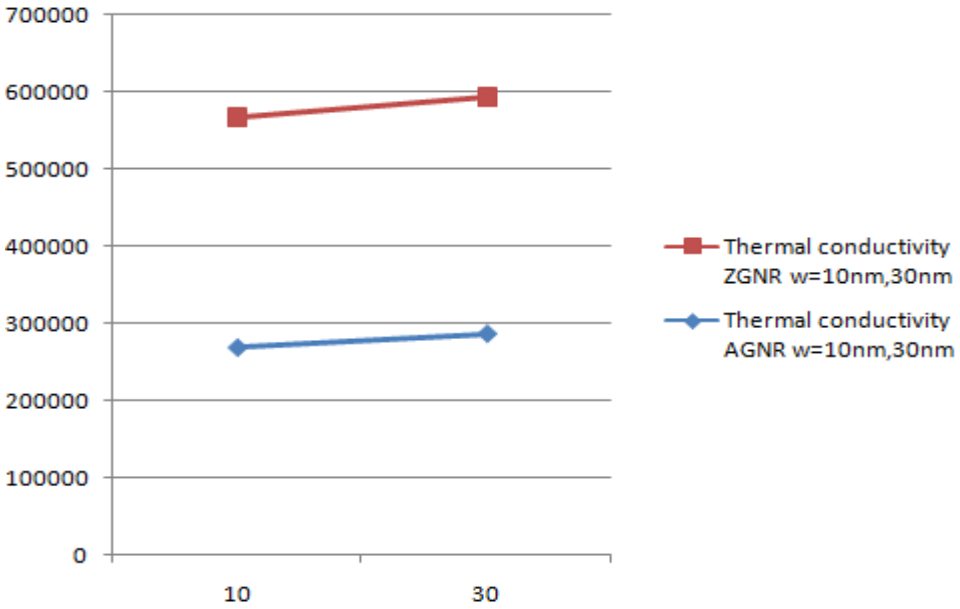

Figure 3. Simulated thermal conductivity of armchair GNR and zigzag GNR at two different widths, for fixed length value L = 40 nm, as per our calculations.

It is remarkable that the trend of thermal conductivity shows some change as the width increases from 10 to 30 nm for armchair GNR and zigzag GNR, respectively. Therefore, thermal conductivity is width dependent. The phenomenon may be explained because GNR width is increased with more edge-localized phonon modes increasing in width. For GNRs having width up to 3 nm, the slightly changing thermal conductivity with width is due to a constant number of edge-localized phonon modes. For low values of GNR width, the number of edge-localized phonon modes remains the same. Total number of edge-localized phonon modes increases with larger width. However, confident limit beyond a width by which thermal conductivity tends to saturate as the width further increases, in more and more phonon modes coupling generation or elongation, which increases the chances of Umklapp scattering [13–15].

The pure simulation of thermal conductivity for GNRs is presented in Figure 3. It is noticed that with increasing widths of GNR thermal conduction behavior got similar and compliant to that which has been discussed in literature.

RESULTS AND DISCUSSION

Thermal Conductivity Armchair and Zigzag GNRS, as a Function of Lengths

The electronic thermal conductivity of graphene has been studied by simulations. Length dependence of electronic thermal conductivity has been reported in the case of single layer graphene [18].

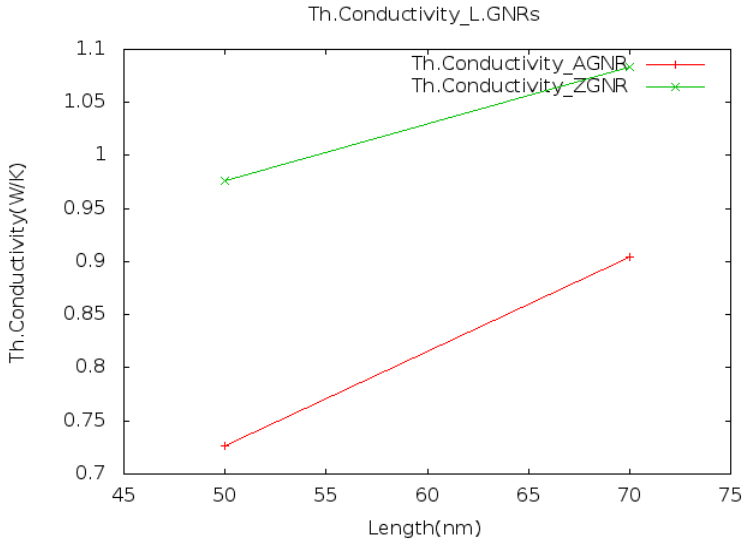

Figure 4. Simulated thermal conductivity κ of graphene versus the length L at room temperature.

Zigzag graphene with width w = 52 å is used [19].

This is the modelled electronic thermal conductivity response of single-layer zigzag graphene with respect to its length at room temperature (Figure 4) [12]. In Figure 5, we show our results of simulated electronic thermal conductivity for armchair and zigzag GNRs as a function of lengths with simulations. Two lengths were simulated – 50 nm and 70 nm. Both structures for these simulations were assumed to have a width of 20 nm. The thermal conductivity is observed to be rising with length for the suspended graphene structures as reported in the literature [20]. This is because, as the sample size is increased, a greater number of low-frequency acoustic phonons become excited to participate in heat transfer, thus making thermal conductivity length dependent. An extremely long wavelength then would mean very low-frequency acoustic phonons capable of ballistic transport.

Thermal Conductivity of Armchair and Zigzag GNRs, as Function of Widths

The single layer graphene is known to show significant effects on their thermal conductivity with variations in widths [17].

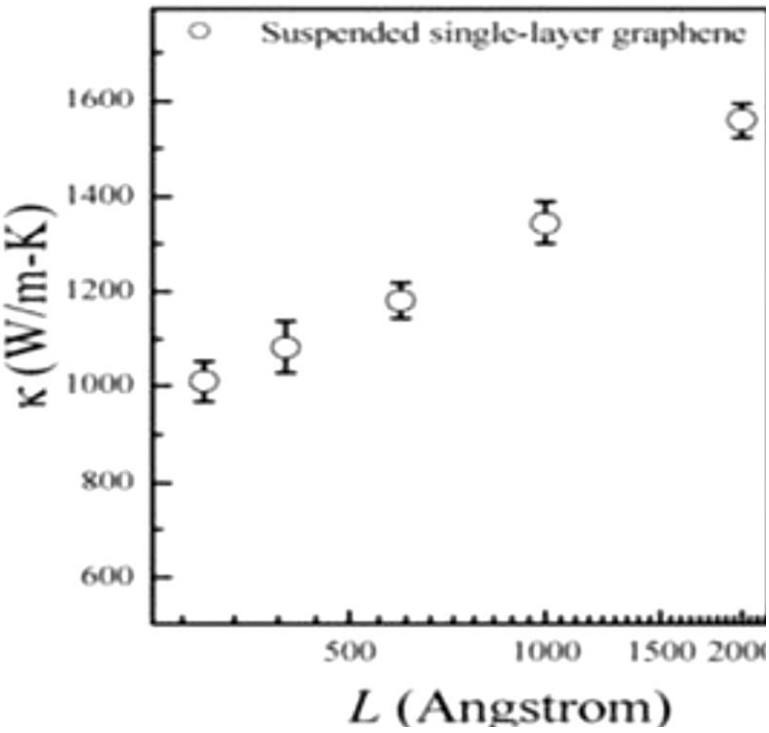

Figure 5. Simulated electronic thermal conductivity for armchair and zigzag GNRs, as a function of lengths with simulations (width: 20 nm), as per our calculations.

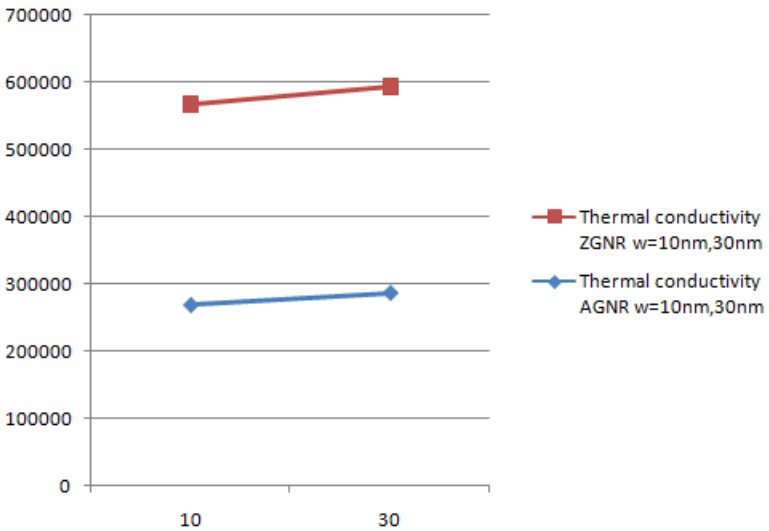

Figure 6. Simulated thermal conductivity for N-AGNR and N-ZGNR at different values of N, for the fixed length of GNRs, L = 11 nm as per literature [11].

Observation of thermal conductivity increasing with increasing widths from 10 to 30 nm for armchair GNR and zigzag GNR results in thermal conductivity as width-dependent, increasing widths of GNRs leading to more phonon modes. For GNRs from up to 3 nm, the trend of thermal conductivity is changing slightly with changing width, is attributed to constant number of edge-localized phonon modes [16, 18]. For small values of GNR width, the number of edge-localized phonon modes remains constant; on the other hand, for larger values of width, the total number of edge-localized phonon modes increases due to the saturation effect leading to increased probability of Umklapp scattering as with increasing width, energy gap between different phonons is reduced, putting a limit to any further increase in thermal states (Figures 6–7).

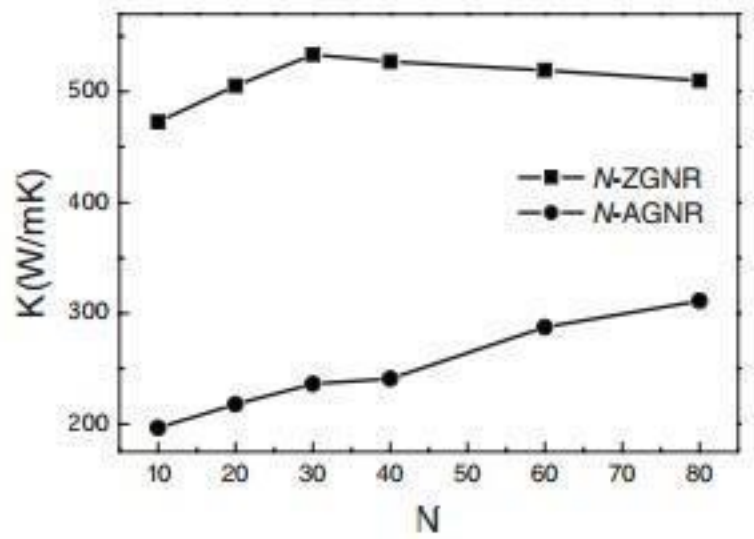

Figure 7. Simulated thermal conductivity of armchair GNR and igzag GNR at two different widths, for fixed length value L = 40 nm, as per our calculations.

Figure-of-Merit (ZT)

The thermoelectric Figure-of-Merit ZT corresponds to performance metrics that need consideration in assessing a material as a thermoelectric material. The electronic band structure, Seebeck coefficient S, electronic thermal conductivity κe, and electrical conductivity are calculated in Quantum Espresso.

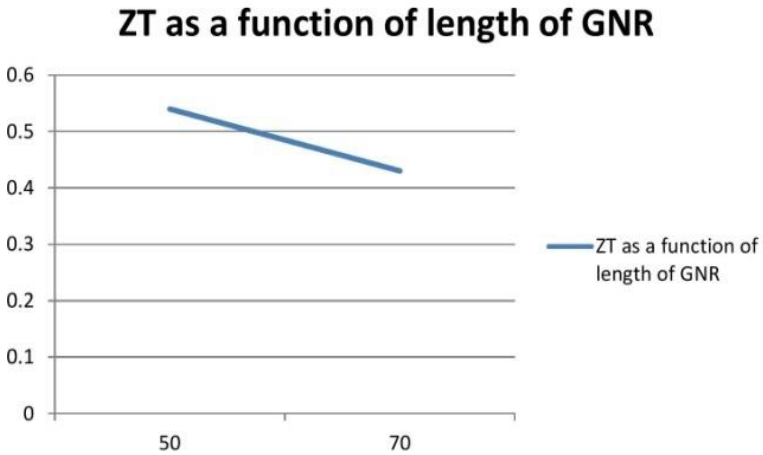

Figure 8. ZT values as a function of AGNR.

First-principal results obtained by Espresso are used by a post-processing tool called "Boltztrap" that determines the semi-classical transport coefficients and Figure-of-Merit (ZT) via Boltzmann transport properties. Figures 8 shows ZT calculated for AGNRs, as a function of length (20 nm), and constant width. ZT shows a decrease when increasing the AGNR length from 50 nm to 70 nm, as the thermal conductivity also increases with respect to length [19].

CONCLUSIONS

The Figure-of-Merit (ZT) is the performance gauge for a material used in thermoelectric applications. The Figure-of-merit ZT is related by ($ZT = S^2\sigma T/\kappa$) which reduces to modifying the expression for power factor with respect to compositions.

The thermal conductivity (κ) shows an increase with length for the graphene structures. Furthermore, thermal conductivity experiences a slight change of fashion at higher width for armchair GNR as well

as zigzag band and this variation in style results in a size dependent behavior concerning thermal conductivity.

These simulations as we can see in the trends, it is found that variations of thermal conductance study for ZGNR with length and width have a higher magnitude than AGNR. The thermal conductivity slope of ZGNRs is not as steep for the width range given above with respect to AGNRs. Small sized AGNR is better towards (ZT) Figure-of-merit, considered as an appropriate measure of the performance of a material for thermoelectric applications at lower thermal conductivities.

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