Exceptional drag enhancement of electron-phonon transport properties in 3C-SiC from fully coupled ab-initio analysis

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Here we present for the first time a purely ab-initio calculation of fully coupled electron and phonon transport and show that mutual drag causes the thermopower to be dominated by transport of phonons, rather than electrons, at room temperature in the case of n-doped 3C-SiC. The thermopower is insensitive to impurity scattering. Phonon drag also strongly boosts the intrinsic electron mobility, thermal conductivity and the Lorenz number. This work establishes the roles of microscopic scattering mechanisms in the emergence of strong drag effects in transport of the interacting electron-phonon gas.

In a typical electron (phonon) Boltzmann transport problem, the phonon (electron) system acts as a momentum bath as the latter is assumed to return to equilibrium infinitely fast. This famous “Bloch’s Assumption” [1] was first challenged by Peierls [2]. Since then, pioneering work by Gurevich [3] theorized the effect of non-equilibrium phonons and electrons - the mutual drag - on the transport of an interacting electron-phonon gas. Experimental evidence of the phonon drag effect on the thermopower of germanium and silicon was found in the 1950s [4-6]. In 1954 Conyers Herring carried out a calculation combining simple analytical models and a partial coupling of the electron and the phonon Boltzmann transport equations (BTEs) [7]. To date Herring’s analysis of the problem has remained the basis for understanding the drag physics in the context of thermoelectricity. A self-consistent description of the mutual electron and phonon drag effects, however, requires a closed-loop flow of momentum between the two coupled systems of carriers.

To date various approaches have been taken to calculate the electron-phonon mutual drag effect. Some approaches are based on semi-empirical models of interaction and idealized electron and phonon band structures. Approaches in this class include Herring’s original work [7] on bulk materials and Cantrell and Butcher’s work on 2D electron gases [8-10]. In another approach [11], Mahan, Broido, and Lindsay combined semi-empirical electron-phonon interaction and ab-initio fitted phonon-phonon interaction with Rode’s iterative BTE [12] within a partially coupled framework. Very recently, fully ab-initio methods combining density functional theory (DFT) and the partially coupled BTE were employed by Zhou et al [13], Fiorentini and Bonini [14], and Macheda and Bonini [15]. Lastly, semi-empirical models were combined with the DFT+BTE framework to obtain a solution to the fully coupled electron-phonon BTEs in Ref. [16].

Here we present for the first time a purely ab-initio scheme for obtaining the solution of the fully coupled BTEs of the interacting electron-phonon gas. We apply this method to the n-doped cubic phase of silicon carbide (3C-SiC), which is a large band gap material widely used in thermoelectrics and power electronics. We calculate the effect of drag on the various transport coefficients with and without the presence of charged impurity scattering and interpret the results in terms of the various electron-phonon scattering processes. We find surprisingly strong drag-driven increase of the electron mobility in the absence of impurities and of the thermopower and the Lorenz factor with and without impurity scattering at room temperature and over a wide range of the carrier concentrations. Our results build on the recent formulation of the coupled electron-phonon BTEs and prediction of strong phonon drag gain of electron mobility in GaAs using semi-empirical models for electron-phonon scattering [16]. In this work the electron-phonon matrix elements are calculated completely from first principles. This allows us to capture the full wave-vector dependence of the electron-phonon coupling, which is absent in simpler analytical models.

We outline the details of this formalism in Sec. I of the Supplementary Information (SI). In SI Sec. II we discuss the computational details, code validation including comparison to simple analytical models, and numerical convergence.

The electronic scattering rates in the relaxation time approximation (RTA) do not consider drag, but are already useful for the physical interpretation of the roles of the various scattering mechanisms in transport. The charged impurity scattering rates are calculated using the Brooks-Herring formula [17] assuming singly charged defects. Fig. 1 shows the RTA rates for the n-doped 3C-SiC at 300K. The zero of the energy axis is at the conduction band minimum energy, $E_{CBM}$. In the low doping case, when the electron chemical potential is in the band gap, the low energy electrons predominantly scatter against low energy acoustic phonons via the quasielastic piezoelectric and acoustic deformation potential type interactions. Around 80 meV, the acoustic scattering rate increases sharply. This originates from the optical deformation potential type scattering of the longitudinal acoustic phonons.
The phonon-isotope scattering rates are calculated using the Tamura formula. The phonon-phonon scattering rates increase with work. We do not include grain boundary scattering in this model. Figure 1 shows the breakdown of the electronic RTA scattering rates for carrier concentrations $10^{16}$ cm$^{-3}$ (solid symbols) and $10^{20}$ cm$^{-3}$ (hollow symbols) at 300 K. For the latter, the chemical potential is shown by the blue vertical line.

(1) Phonon energy. The phonon energy is given in the SI Sec. V to further demonstrate this point. At $10^{20}$ cm$^{-3}$ doping concentration, the electron drag induced gain of the phonon $\kappa$ is only around 8%, if charged impurity scattering of electrons is not included.

The phonon-electron scattering rates for low energy acoustic phonons drop sharply with increasing energy, which is typical of piezoelectric and acoustic deformation type scattering. There is strong scattering at 80 meV, corresponding to optical deformation type scattering with the X-point LA phonon, which gives dominant contribution to intervalley scattering as mentioned earlier. The phonon-electron scattering rate for the 120 meV LO phonons are also strong owing to the polar nature of their coupling to electrons. The momentum received from the electrons can be distributed and dissipated into the phonon system via anharmonic phonon-phonon interaction and fed back into the electron system via phonon-electron interaction. In general, the flow of momentum back into the electron system results in an enhancement of the electronic transport coefficients (mobility, thermal conductivity, and thermopower) due to phonon drag. On the other hand, a low overall rate of momentum dissipation within the phonon system manifests itself as electron drag induced enhancement of the phonon transport coefficients (thermal conductivity and thermopower), given that the phonon system has received excess momentum from the electron system. Note that the low energy acoustic phonons have low anharmonic scattering rates and have fewer momentum destroying Umklapp anharmonic scattering. As such, they can sustain the momentum received from the electronic system for a long time in contrast to shorter lived optical phonons.

While the analysis presented above based on the RTA scattering rates provides a relatively simple qualitative picture, the iteration process of the coupled BTEs nontrivially mixes the momentum in the interacting system of electrons and phonons. Nonetheless, RTA rates allow us to interpret the drag phenomena predicted by the self-consisted coupled solutions.

Figure 2 shows the phonon RTA scattering rates breakdown into the phonon-electron, phonon-isotope, and phonon-phonon channels. The phonon-isotope scattering rates are calculated using the Tamura formula. We do not include grain boundary scattering in this work. The phonon-phonon scattering rates increase with phonon energy. The phonon-isotope scattering rates are weak for low energy phonons, but are comparable to the phonon-phonon rates for near zone boundary acoustic phonons and the optic phonons. The phonon-electron scattering rates for low energy acoustic phonons drop sharply with increasing energy, which is typical of piezoelectric and acoustic deformation type scattering. There is strong scattering at 80 meV, corresponding to optical deformation type scattering with the X-point LA phonon, which gives dominant contribution to intervalley scattering as mentioned earlier. The phonon-electron scattering rate for the 120 meV LO phonons are also strong owing to the polar nature of their coupling to electrons. The momentum received from the electrons can be distributed and dissipated into the phonon system via anharmonic phonon-phonon interaction and fed back into the electron system via phonon-electron interaction. In general, the flow of momentum back into the electron system results in an enhancement of the electronic transport coefficients (mobility, thermal conductivity, and thermopower) due to phonon drag. On the other hand, a low overall rate of momentum dissipation within the phonon system manifests itself as electron drag induced enhancement of the phonon transport coefficients (thermal conductivity and thermopower), given that the phonon system has received excess momentum from the electron system. Note that the low energy acoustic phonons have low anharmonic scattering rates and have fewer momentum destroying Umklapp anharmonic scattering. As such, they can sustain the momentum received from the electronic system for a long time in contrast to shorter lived optical phonons.

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Figure 3 shows the thermal conductivity, $\kappa$, as a function of the carrier concentration. The phonon contribution completely dominates the electronic contribution to $\kappa$ over the entire range of carrier concentrations. In the low doping limit, the computed phonon $\kappa$ (433 Wm$^{-1}$K$^{-1}$) is similar to the calculated values in literature - about 10% lower than those reported in Refs. [21], [22] and [23]. The literature calculations are formally equivalent to the decoupled, iterative phonon BTE calculation in our formulation. Effect of drag on the phonon $\kappa$, while increasing with carrier concentration, is overall small. This is a consequence of the fact that the drag active zone center and zone boundary acoustic and high energy optical phonons contribute weakly to the phonon $\kappa$. The spectral phonon $\kappa$ is given in the SI Sec. V to further demonstrate this point. At $10^{20}$ cm$^{-3}$ doping concentration, the electron drag induced gain of the phonon $\kappa$ is only around 8%, if charged impurity scattering of electrons is not included.
If charged impurity scattering is included, this drag gain is uniformly negligible, since the amount of momentum feedback from the electronic system diminishes with increasing carrier concentration due to the increasing dissipation of electronic momentum by charged impurities. The calculated weak electron drag effect on the phonon $\kappa$ is in agreement with the findings in Ref. [16] for GaAs and validates the fact that numerous phonon $\kappa$ calculations on different materials that have ignored the electron drag effect have, nevertheless, found good agreement with experiments. The electronic contribution to $\kappa$, while negligible compared to the phonon counterpart, features strong phonon drag effect at high carrier concentrations when charged impurity scattering is ignored for the same reasons given above. At $10^{20}$ cm$^{-3}$ doping concentration, the phonon drag gain of the electronic $\kappa$ is 37% in the presence of charged impurity electron scattering, and 171% in the absence of impurities.

Fig. 4 shows the electron mobility versus carrier concentration. The charged impurity scattering channel begins to limit the mobility above $10^{16}$ cm$^{-3}$ carrier concentration. The highest measured mobility at room temperature is 980 cm$^2$V$^{-1}$s$^{-1}$ for a carrier concentration of $4 \times 10^{16}$ cm$^{-3}$ [24], which is in excellent agreement with our calculated values of 1116 and 888 cm$^2$V$^{-1}$s$^{-1}$ at $10^{16}$ and $10^{17}$ cm$^{-3}$, respectively, when charge impurity scattering is included in the calculation. For the same reasons as for electronic thermal conductivity, the phonon drag enhancement of the mobility increases with increasing carrier concentration. In the absence of impurity scattering of electrons, the phonon drag gain of the mobility is substantial - 16% (191%) at $10^{18}$ ($10^{20}$) cm$^{-3}$ carrier concentration. If techniques such as modulated doping can be realized on bulk samples, then our prediction of the strong phonon drag gain of mobility can be experimentally tested.

Fig. 5 shows the Lorenz number as a function of doping concentration. For metals, the Wiedemann-Franz (WF) law value of the Lorenz number is $2.44 \times 10^{-8}$ WΩK$^{-2}$, and for semiconductors is expected to vary between 1.5 and $2.5 \times 10^{-8}$ WΩK$^{-2}$ [25]. The Lorenz number is a crucial ingredient for decoupling the lattice thermal conductivity $\kappa_{ph}$ and the electronic contribution $\kappa_{el}$ from measurements of the total $\kappa$ [26]. While the deviations of $L$ from the metallic limit are expected in materials that exhibit significant inelastic scattering, our new finding is that it is the drag effect that leads to exceptionally high $L$ values in 3C-SiC over a wide range of carrier concentrations. This strong violation of the WF law is a consequence of the fact that the electron $\kappa$ has a stronger drag enhancement compared to the mobility over a large
We show in the SI that, within numerical errors, within the Seebeck picture since phonons do not carry heat. Such a clean separation is not possible to the thermopower since both phonons and electrons explicitly couple to the applied electric field. As such, no non-zero phonon contribution is purely an electron drag effect. Surprisingly, we find that in the low doping range.

We now examine the absolute value of the thermopower, $|Q|$, in the Peltier picture in Fig. 6. The Peltier picture provides a clear separation of the phonon and electron contributions, $|Q_{ph}|$ and $|Q_{el}|$, respectively, to the thermopower since both phonons and electrons can carry heat. Such a clean separation is not possible within the Seebeck picture since phonons do not carry charge. We show in the SI that, within numerical errors, the Peltier and the Seebeck pictures give the same thermopower, in accordance with the Kelvin-Onsager relation $27$. $|Q_{ph}|$ is non-zero only when the phonon-electron interaction is present, since the phonon system does not explicitly couple to the applied electric field. As such, any non-zero phonon contribution is purely an electron drag effect. Surprisingly, we find that in the low doping limit $|Q_{ph}|$ in the fully coupled BTE solution is noticeably higher than $|Q_{el}|$, whereas in the high doping limit, they are nearly equal. This exceptionally strong drag effect is largely a consequence of the predominance of the scattering of electrons by small energy acoustic phonons, as well as the relatively small anharmonic scattering rates of these phonons, as discussed above in the context of thermal conductivity. As the carrier concentration decreases, $|Q_{ph}|$ is expected to approach a constant $7$. First, we consider the drag effect without the impurity channel for electron scattering. From Fig. 1 we see that the acoustic phonon scattering of electrons is weakly dependent on the carrier concentration. For these phonons the carrier concentration dependence comes only from the reduction of the scattering phase space of electrons at the chemical potential by the $X$-point LA phonons, while low energy acoustic phonon scattering is unaffected by the location of the chemical potential. At low carrier concentrations, when the chemical potential is in the band gap, the rate at which low energy acoustic phonons receive momentum from electrons remains nearly the same as a function of carrier concentration. Since the phonon-phonon scattering rates are independent of the carrier concentration in our rigid band model, and since the phonon-electron scattering rates scale linearly with the concentration in the low doping limit (see Fig. 9 in the SI), the total amount of momentum received from the electron system that is sustained in the phonon system thus approaches a constant with decreasing carrier concentration. With increasing carrier concentration, the phonon-electron scattering rates begin to dominate the phonon-phonon scattering rates and progressively more of the excess momentum is returned to the electronic system. As a consequence, $|Q_{ph}|$ decreases with increasing carrier concentration. This has been described as the “saturation effect” $7$. On the other hand, the drag enhancement of $|Q_{el}|$ is negligible. The reason for this lies in the fact that $|Q_{el}|$ is proportional to the ratio of the carrier heat and charge current densities, both of which are boosted by the phonon drag with increasing carrier concentration, leading to significant cancellation. Very similar arguments explain the strong drag effect on $|Q|$ in the Seebeck picture. We discuss this in the SI Sec. IV.

Lastly, we discuss the striking insensitivity of the thermopower to the presence of impurity scattering. In the Seebeck picture, the rate of momentum received by the phonons from the temperature gradient field and, thus, the momentum transfer to the electronic system remains the same as before. With increasing doping concentrations, the rate of draining of momentum from the electronic system in the impurity channel increases. As such the same steady state voltage will develop in the end. In other words, the total momentum received per electron from the phonon system remains the same regardless of the presence of impurities. Similar arguments hold in the Peltier picture in terms of the constancy of the momen-
tum retaining capacity of the phonons in the presence of an impurity scattering channel in the electronic system. $|Q_{el}|$ is unaffected by impurity scattering for similar reasons which has previously been demonstrated by ab initio calculations in Ref. [14]. For the drag component of the thermopower the same has been shown in Ref. [13]. We have numerically verified this phenomenon by artificially increasing the electron-charged impurity scattering rates by a factor of 100 at both the $10^{15}$ and $10^{20} \text{ cm}^{-3}$ doping concentrations and found that the same $|Q_{ph}|$ and $|Q_{el}|$ as before are reproduced. In the SI we performed a similar analysis to show that $|Q_{ph}|$ and $|Q_{el}|$ are also largely unaffected by phonon-isotope scattering, corroborating the results in Ref. [13].

In summary, in this work we obtained the full solution of the coupled electron and phonon BTEs, treating electron-phonon coupling entirely from first principles, and also considering the effects of impurity scattering. We found that the phonon thermal conductivity is weakly affected by the electron drag effect, whereas the electron mobility is significantly enhanced by the phonon drag effect in the absence of charged impurity scattering. The presence of impurity scattering suppresses this strong drag effect and in order to observe (and, possibly, exploit in a technological setting) the drag gain of the mobility, charge carriers have to be introduced into the material without introducing charged dopants. We also found that over a large doping range, the direct phonon contribution to, or, equivalently, the phonon drag enhancement of the thermopower is exceptionally large. These are consequences of the strong piezoelectric and acoustic deformation potential type scattering of small energy acoustic phonons and optical deformation type scattering of the zone boundary LA phonons, and the large LO phonon energy in this material. This scenario guarantees that the electrons will strongly interact with the low energy acoustic phonons over a large range of doping levels. Based on this analysis, we predict that the hexagonal polytypes - 2H-, 4H-, and 6H-SiC will also exhibit similarly strong drag phenomena. Lastly, we showed that the thermopower is insensitive to the impurity scattering channels in both the electron and the phonon systems. We also find that electron-phonon drag causes a significant increase in the Lorenz number, outside the range previously expected in semiconductors.

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