Profiling novel high-conductivity 2D semiconductors

Thibault Sohier\textsuperscript{1,2} \textsuperscript{a}, Marco Gibertini\textsuperscript{2,3,4} \textsuperscript{b} and Nicola Marzari\textsuperscript{1} \textsuperscript{a}

\textsuperscript{1}\textsuperscript{a} Dipartimento di Fisica Informatica e Matematica, Università di Modena e Reggio Emilia, Via Campi 213/a, I-41125 Modena, Italy

\textsuperscript{2}\textsuperscript{b} Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

\textsuperscript{3}nanomat/QMAT/CESAM and European Theoretical Spectroscopy Facility, University of Liege (ULiege), Liege, Belgium

\textsuperscript{4}Department of Quantum Matter Physics, University of Geneva, CH-1211 Geneva, Switzerland

\textbf{E-mail:} thibault.sohier@uliege.be

\textbf{Keywords:} electronic transport, electron-phonon coupling, first-principles, materials discovery

Abstract

When complex mechanisms are involved, pinpointing high-performance materials within large databases is a major challenge in materials discovery. We focus here on phonon-limited conductivities, and study 2D semiconductors doped by field effects. Using state-of-the-art density-functional perturbation theory and Boltzmann transport equation, we discuss 11 monolayers with outstanding transport properties. These materials are selected from a computational database of exfoliable materials providing monolayers that are dynamically stable and that do not have more than six atoms per unit cell. We first analyze electron-phonon scattering in two well-known systems: electron-doped InSe and hole-doped phosphorene. Both are single-valley systems with weak electron-phonon interactions, but they represent two distinct pathways to fast transport: a steep and deep isotropic valley for the former and strongly anisotropic electron-phonon physics for the latter. We identify similar features in the database and compute the conductivities of the relevant monolayers. This process yields several high-conductivity materials, some of them only very recently emerging in the literature (GaSe, Bi\textsubscript{2}Se\textsubscript{3}, Sb\textsubscript{2}Se\textsubscript{3}), others never discussed in this context (AlLiTe\textsubscript{2}, BiCTe, CIGaTe, AuI). Comparing these 11 monolayers in detail, we discuss how the strength and angular dependency of the electron-phonon scattering drives key differences in the transport performance of materials despite similar valley structure. We also discuss the high conductivity of hole-doped WSe\textsubscript{2}, and how this case study shows the limitations of a selection process that would be based on band properties alone.

1. Introduction

Two-dimensional (2D) semiconductors with excellent intrinsic transport properties would be beneficial to many applications [1–3], e.g. transistors or optoelectronic devices. Some well-known 2D materials like transition-metal dichalcogenides (TMDs), phosphorene or silicene have been extensively studied both experimentally (MoS\textsubscript{2} [4, 5], Si [6–8]) and theoretically (MoS\textsubscript{2} [9–13], P\textsubscript{2} [13–16]). Other candidates [17] have been proposed using approximate deformation potential models and the Takagi [18] formula, but it has been shown that such approaches suffer from limited reliability [19]. The full potential of 2D materials for future device applications could be much broader than the dozen materials currently under extensive experimental investigation, since many more monolayers have been predicted to be either exfoliable from experimentally known layered materials [20–23] or synthetizable [24, 25]. Such computational collections of prospective 2D materials would likely contain some promising candidates for electronic transport in various contexts.

Finding the ideal material for a given device would require the cross-examination and co-optimization of many different properties [26]. Here, rather than focusing on one particular application, we are interested in the physical features leading to good transport performance. We describe the tools and knowledge needed to explore large databases with an informed, purposeful approach, and eventually identify the candidates with the highest conductivity.

We focus here on room-temperature phonon-limited electronic transport and search across 2D semiconductors. First-principles methods [27] have proven quite useful and successful in predicting
physics and properties in this regime [28] and for 2D materials [29, 30], provided one is aware of its limits [19]. Although dedicated codes exist [31, 32], performing state-of-the-art first-principles transport simulations on large sets of materials remains nevertheless a challenge, and few works tackle more than one material at a time. Yet, an overall panorama on the property landscape would be very valuable to materials design. For example, in a previous work involving five materials [13], we have shown the importance of intervalley scattering, while the authors of reference [33] have studied four hexagonal elemental materials to show the benefits of a sharp and deep single valley.

In this work, we explore our portfolio of dynamically stable 2D materials [23] found to be exfoliable from experimentally known 3D compounds and available on the Materials Cloud [34, 35]. We limit ourselves to at most six atoms per unit cell, although the same approach can be applied to materials with larger unit-cells, at higher computational cost. We select the most promising systems from a band structure analysis, and then study their transport properties using an accurate and automated framework that we recently developed [13], finding several excellent 2D semiconductors. Compared to other methods [28, 36], the approach of reference [13] has two main advantages in the context of this work: (i) it includes several tools to analyze band structure properties like valley structure or Fermi velocity and (ii) the calculation of conductivity is automated within the AiiDA framework [37, 38], which is key to study many materials in a high-throughput fashion. These tools are available [39] to the community on the Archive section of the Materials Cloud [35], in support of the FAIR principles of open science and open data.

We consider a fixed carrier density of $n/p = 10^{13}$ cm$^{-2}$ (electrons or holes) induced by field effect (and not from substitutional doping). Electron-phonon interactions (EPIs) are computed in an electrostatic framework explicitly including such doping [40], as well as screening from the induced free electrons or holes. In this framework, it is preferable to work in the high carrier density regime to limit the computational cost associated with the sampling of small Fermi surfaces. This is in contrast to other first-principles studies, usually simulating EPIs in neutral materials, which would be valid only in the limit of vanishing carrier density. The mobility of materials in the high and low carrier density regimes might differ significantly, so the capability to study explicitly the high-doping regime is a valuable complement to existing methods. It is very relevant for monolayers operating in the degenerate limit, when the chemical potential is close to or inside the conduction or valence band. Carrier densities of $10^{13}$ cm$^{-2}$ are routinely reached experimentally in monolayer 2D semiconductors by field-effect doping, especially using ionic-liquid gating [41–43]. In addition, the predictive accuracy of our method provides meaningful comparisons to experiments. Indeed, the high-doping regime is often used experimentally to characterize the intrinsic properties of novel materials, because it allows to screen charged impurities. Doping regimes and the associated variation of mobility are further discussed in Appendix A.

In this study we find excellent phonon-limited transport properties for electron-doped Bi$_2$Se$_3$, Bi$_2$Se$_3$, BiCTe, Sb$_2$Se$_2$, InSe, GaSe, AlLiTe$_2$ and hole-doped phosphorene (P$_4$), AuI, ClGaTe, and WSe$_2$, all showing mobilities in the range from few hundreds to few thousands cm$^2$ V$^{-1}$ s$^{-1}$. Three of these 2D materials are very well-known and studied (P$_4$ [13–16], WSe$_2$ [13], InSe [44]). The Sb$_2$X$_3$ and Bi$_2$X$_3$ (X = Se, Te, S) compounds are better known for the topological properties of their 3D parents [45, 46]. Monolayers have been recently studied in the context of phonon-limited transport [17, 47, 48], but only within the approximate Takagi formalism [18]. The transport performance of monolayer Sb$_2$Se$_2$ has been confirmed experimentally [49]. GaSe (along with InSe) was studied [50] ab initio with a representation of electron-phonon scattering that goes beyond deformation potential theory while this work was carried out. AlLiTe$_2$, BiCTe, ClGaTe, and AuI are, to our knowledge, still new in the context of 2D charge transport. Beyond the relatively large number of materials identified and the novelty of some of them, this work most importantly provides visual and intuitive understanding of electron-phonon scattering as well as a systematic and data-supported analysis of the features leading to good transport performance. We confirm and extend previous remarks on the importance of band properties such as number of valleys, effective masses or anisotropy; and show that these can be used for larger scale databases studies to shortlist prospective conductors. On the other hand, we also show how differences in the strength and angular dependency of electron-phonon scattering still induce significant variations in the conductivity of materials with similar band properties.

2. Computational and theoretical framework

2.1. Computational details

First-principles calculations of structures, bands, phonons and EPIs are performed with the Quantum ESPRESSO [51, 52] (QE) software, by combining density-functional theory (DFT) and density-functional perturbation theory (DFPT) within the generalized gradient approximation as formulated by Perdew, et al [53] (PBE). 2D periodic-boundary conditions are applied and the electrostatics of a symmetric double-gate field-effect setup are simulated using the approach described in reference [40].
Open-boundary conditions are important to properly describe polar-optical phonons \([54]\) and screening \([55]\). The field-effect setup is used to induce an electron or hole density with a default value of \(n/p = 10^{13} \text{ cm}^{-2}\). Those additional free carriers are explicitly included in the \textit{ab-initio} simulations and screen some of the EPIs, as in a metal. Details about the simulation of this relatively high-doping regime and a qualitative discussion of the effects of screening as a function of doping are included in Appendix A. Calculations are managed using the AiiDA materials informatics infrastructure \([37, 38]\). The AiiDA database containing the provenance for the transport calculations and the tools necessary to reproduce this work are provided in the Archive section of the Materials Cloud \([35, 39]\). The standard numerical setup for all ground state and phonon calculations has \(32 \times 32\) Monkhorst-Pack k-point grids to sample the full Brillouin zone, \(0.02\ \text{Ry}\) cold smearing \([56]\) with SSSP pseudopotentials \([57]\) (efficiency version 0.7) and energy cutoffs recommended therein. PAW pseudopotentials were substituted because they are incompatible with the use of symmetry in the electron-phonon routines of QE. Other minor variations from the standard setup can be found in the AiiDA database provided. The use of cold smearing allows k-point convergence while keeping a lower effective temperature in the calculations, making the free-carrier screening closer to what it would be in real conditions. Spin-orbit interactions are included only for hole-doped WSe\(_2\), where they play a significant role. For other materials, while spin-orbit interactions may have an effect on the band structure in general (e.g. on the band gap for BiSeTe\(_2\) \([17]\)), they will not have large consequences on the conductivity or mobility as long as there is no significant energy splitting of valleys with opposite spins (small variations may come from changes in the effective masses). The analysis starts from a database of band structures computed (non-self-consistently) in the neutral material on very fine electronic momenta grids (about 90 by 90) to analyze the valley structure. These bands are then recomputed with field-effect doping for the selected materials. Phonon momenta are chosen to include only relevant transitions, and the Boltzmann transport equation (BTE) is solved as described in reference \([13]\). We improved the stability for the solution of the BTE by using the velocity of each initial state as a fictitious electric field direction (equation (11) of reference \([13]\)).

Note that the calculations performed here on 11 materials are already computationally demanding at the PBE level. Studying the effects of a higher level of many-body theory such as GW would be quite challenging, and we leave it for future works. Nevertheless, we expect that the related changes in the band structure would have limited impacts on the conductivity. Variations in the gaps are likely, but those do not affect the conductivity at a given carrier density, only the experimental conditions needed to reach that carrier density. Variations of effective masses could impact conductivities, but should be limited to \(~10\%–20\%\). Finally, changes in the relative positions of the valleys might impact the single-valley nature of the transport. As explained later, this is an important feature of the 2D semiconductors in this work, so the selection criteria used to identify high-conductivity candidates include a minimum of 100 meV between the Fermi level and the next valleys at the PBE level. Overall, many-body corrections are not expected to change the main results of this work, i.e. the outstanding transport properties of the selected materials and their relative ranking.

### 2.2. Boltzmann transport equation

The solution of the BTE is briefly outlined here for convenience; more details about the general formalism can be found in reference \([28]\), and the specificities of our approach are detailed in reference \([13]\). The mobility is defined as \(\mu = \sigma/en \ or \ \sigma/ep\) where \(e\) is the Coulomb charge, while \(n\) and \(p\) are electron or hole densities. The (longitudinal) conductivity \(\sigma\), entering the expression for mobility, is computed as follows:

\[
\sigma = \frac{1}{\rho} = 2e^2 \int \frac{d\mathbf{k}}{(2\pi)^3} (\mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E) \tau(\mathbf{k}) \left[ -\frac{\partial \delta(\varepsilon_{\mathbf{k}})}{\partial \varepsilon} \right] \tag{1}
\]

where \(\mathbf{k}, \varepsilon_{\mathbf{k}}, \mathbf{v}(\mathbf{k})\) represent electronic momenta (and band index implicitly), energies, and velocities, respectively. The unit vector \(\mathbf{u}_E\) points in the electric field’s direction and \(f^0\) is the Fermi–Dirac distribution (the dependency on temperature and chemical potential are made implicit to simplify the notation). Here \(\tau\) is an energy- and momentum-dependent variable that has the dimensions of time and solves the linearized BTE:

\[
(1 - f^0(\varepsilon_{\mathbf{k}})) \mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E = \sum_{\mathbf{k}'} P_{\mathbf{k}k'} (1 - f^0(\varepsilon_{\mathbf{k}'\cdot})) \times \left\{ \mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E \tau(\mathbf{k}) - \mathbf{v}(\mathbf{k}') \cdot \mathbf{u}_E \tau(\mathbf{k}') \right\} \tag{2}
\]

\(P_{\mathbf{k}k'}\) being the probability for an electron in state \(\mathbf{k}\) to be scattered into state \(\mathbf{k}'\). In the following we consider only phonon-induced scattering, so that:

\[
P_{\mathbf{k}k+q} = \sum_{\nu} \frac{2\pi}{\hbar} \frac{1}{N} \left( \sum_{\mathbf{q}} |g_{\mathbf{k}+\mathbf{q},\nu}|^2 \left\{ n_{\mathbf{q},\nu} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q},\nu}) \right. \\
\left. + (n_{\mathbf{q},\nu} + 1) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q},\nu}) \right\} \right). \tag{3}
\]

where \(\mathbf{q}, \nu, \hbar\omega_{\mathbf{q},\nu}, n_{\mathbf{q},\nu}\) are phonon momenta, mode index, energy and occupations, and \(g_{\mathbf{k}+\mathbf{q},\nu}\) are the electron-phonon coupling matrix elements.
3. High-conductivity 2D semiconductors

We study in careful detail 11 monolayers obtained from our database of 256 easily exfoliable materials with at most 6 atoms per unit cell [23], as available on the Materials Cloud [34, 35] and in the supplementary material of reference [23]. The corresponding conductivity and mobility, as a function of the PBE gap, are shown in figure 1. At this doping level a conductivity of a few e^2/h is already considered good [4, 8] for a semiconductor, while the best graphene devices yield values around 500 e^2/h [58, 59]. The materials presented in this work are in the intermediary orders of magnitude, with conductivities of 10–100 e^2/h, and mobilities in the same range as bulk silicon (400 cm^2/Vs for holes, 1400 cm^2/Vs for electrons).

In the following, we detail the exploration process that led to those materials. First, two well-known high-conductivity 2D semiconductors are analyzed to identify representative band features. We then search for those features within the Materials Cloud database [23, 34] and compute the transport properties of the most promising candidates. The selection process relies solely on band properties (gap, valley positions, velocities). All 256 easily exfoliable, dynamically stable and small unit-cell (up to six atoms) materials given in the appendix of reference [23] and on the Materials Cloud [34] are considered, irrespective of their belonging to a specific family. Electron-phonon scattering is analyzed in each monolayer. The suffix ‘-e’ or ‘-h’ is attached to the materials’ formula to indicate if either electron doping or hole doping is considered.

3.1. Prototypical high-conductivity materials: InSe and P4

We start by analyzing key features of two well-known semiconductors with excellent transport performance, InSe on the electron side (InSe-e, \( \sigma = 20 e^2/h \)) and phosphorene on the hole side (P4-h, \( \sigma = 57 e^2/h \)). In the following we will use repeatedly two different plots to visualize, understand and compare the details of the transport properties of 2D materials, reported first in figure 2 for InSe and P4. On the left, a ‘velocity plot’ shows the band structure in a format that is relevant for transport. For each electronic state k (each black dot) on the fine k-point grid used for solving the BTE and within a certain energy range from the band edge (set as the origin of the y-axis), the energy \( \epsilon_k \) is plotted against the norm of the velocity \( |v| = \frac{1}{\hbar} \nabla \epsilon_k \), given in atomic Rydberg units (ARU). The spread indicates the anisotropy of the valley. The red scale of the background is proportional to the derivative of the Fermi–Dirac occupation at 300 K, thus highlighting the states participating to transport with a non-vanishing contribution to equation (1). The Fermi level is computed at room temperature (i.e. such that \( \int_0^{\infty} \sigma(\epsilon, T) d\epsilon / (2\pi^2) = 10^{13} \) cm^2 for electrons, and similarly for holes). On the right side, a ‘scattering plot’ shows where and how easily a certain initial state can be scattered. The initial state at \( k_{in} \), indicated by a black square, is chosen to be at the Fermi level (and in the transport direction, when relevant). The gray shading shows the morphology of the valley(s) considered for transport. The red color scale represents an effective coupling constant \( g_{eff} \) which accounts for all phonon modes, their occupation at 300 K, and energy conservation, since this quantity can be meaningfully compared between materials. In practice, \( g_{eff} \) is defined as the square root of the sum of the interpolated \( |\langle \delta_{\epsilon, \nu, q, \Omega} \rangle| \) over all \( \nu \) and \( q \) that fulfill energy conservation during phonon absorption (or emission) when the final state at \( k_{in} + q \) falls into a certain zone (the valley being tessellated into triangles). The value given at the top of each scattering plot is the lifetime of the initial state computed within the momentum relaxation time approximation:

\[
\frac{1}{\tau(k)} = \sum_{k'} P_{kk'} \frac{1 - f^0(\epsilon_{k'})}{1 - f^0(\epsilon_k)} \times \left\{ 1 - \frac{v(k') \cdot v(k)}{v(k)^2} \right\}
\]

(4)

Everything is computed at 300 K, with the corresponding chemical potential in \( f^0 \).

We now discuss qualitatively the features allowing electron-doped InSe and hole-doped phosphorene to maximize the conductivity in equation (1): this is a sum over electronic states weighted by the derivative of the Fermi–Dirac occupation. The weight effectively selects states around the chemical potential within an energy range that scales with temperature, as represented in the left panels of figure 2. The rest of the

Atomic Rydberg units are the most convenient units for velocity in materials. Typical Fermi velocities in the database—including graphene—are on the order of \( 1 \) ARU, which corresponds to around \( 10^5 \) m s^-1.
3.2. More like InSe: Steep and deep single valleys

As shown in figure 2, InSe has a sharp and deep single electron valley, with carrier velocities close to 6 ARU at the Fermi level when \( n = 10^{13} \text{ cm}^{-2} \) (roughly six times larger than the Fermi velocity in graphene, \( \sim 1 \) ARU). Steep isotropic valleys are obviously characterized by low DOS, which means that the Fermi level quickly shifts away from the band edge with increasing carrier density. This allows to reach higher carrier velocities, but it often means that the Fermi level reaches other valleys in the band structure. In that case, the aforementioned benefits of the single valley structure are lost. If the Fermi level is close to the edges of the next valleys, intervalley scattering is activated and the new states populated are not helping to conduct due to their low velocity. Note that, in a similar spirit, the suppression of intervalley scattering via valley-engineering (e.g. through strain) has been proposed \[61\] to enhance the transport properties of multi-valley materials such as arsenene. Thus, a steep valley is not sufficient to have good transport performance: it must also be deep. More precisely, higher-energy valleys need to be far enough for the material to operate effectively as a single valley material for a doping of \( 10^{13} \text{ cm}^{-2} \).

We look for such valleys among the materials in our study set. We use band structures computed on very fine grids in the neutral materials and select materials with positive phonons, a limited gap \( E_g < 2.5 \text{ eV} \), a single valley (within 100 meV of the Fermi level), and a maximum Fermi velocity \( |v_{\text{max}}| > 6 \text{ ARU}. \) These criteria directly lead to the identification of BiClT\(_2\)-e, AlLiT\(_2\)-e, GaSe-e, Bi\(_2\)SeT\(_2\)-e, Bi\(_2\)STe\(_2\)-e, Bi\(_2\)Se\(_1\)-e, and Sb\(_2\)SeT\(_2\)-e as promising candidates. Note that layers similar to the ones listed here (e.g. GaS, GaTe), will likely display similar band properties and might have band features placing them just below the chosen thresholds. Their transport properties could still be quite good. Electron-phonon scattering is studied for the selected monolayers (except Bi\(_2\)STe\(_2\)-e, a bit redundant with respect to the other two members of the Bi\(_2\)X\(_3\) family). The results are shown in figure 3 for Bi\(_2\)SeT\(_2\)-e and AlLiT\(_2\)-e, and in the appendix for the rest. The general similarity of the plots indicates at a glance why these materials have similar transport properties. The carrier velocities at the Fermi level, the strength of EPI, and the scattering times are of similar orders of magnitude. A closer look reveals the reasons underlying their precise ranking. BiSeT\(_2\)-e, BiSe\(_1\)-e, and Sb\(_2\)SeT\(_2\)-e are very similar in terms of chemistry, band structure, and phonons. BiSeT\(_2\)-e (see figure 3) displays the highest conductivity \( \langle \sigma = 42 \text{ e}^2/\text{h} \rangle \), combining some of the weakest EPI with the largest velocities. It is followed by Sb\(_2\)SeT\(_2\)-e \( \langle \sigma = 30 \text{ e}^2/\text{h} \rangle \) with similar EPI but slightly smaller velocities. Bi\(_2\)Se\(_3\)-e \( \langle \sigma = 14 \text{ e}^2/\text{h} \rangle \) also has a very sharp valley, but the EPI is 2–3 times stronger. As could be expected, electron-phonon scattering in GaSe-e \( \langle \sigma = 25 \text{ e}^2/\text{h} \rangle \) is similar.
Figure 2. Transport properties of InSe and phosphorene (P4), two well-known good conductors. On the left, the ‘velocity plot’ shows, for each electronic state \( k \) in the valley, the energy \( \varepsilon_k \) from the band edge plotted against the norm of the velocity \( |\mathbf{v}| = \frac{\hbar}{2} \nabla_k \varepsilon_k \) in ARU. The color scale of the background is proportional to the derivative of the Fermi–Dirac distribution, which appears in equation (1). On the right, the ‘scattering plot’ shows where an initial state (black square) can be scattered within the valley (gray shade). The color scale represents the effective coupling constant \( g_{\text{eff}} \), which accounts for all phonon modes, their occupation at 300 K, and energy conservation. At the top, \( \tau \) is the scattering time of the initial state computed within the momentum relaxation time approximation, equation (4).

To InSe-e (\( \sigma = 20 \, e^2/h \)), with scattering times differing by only ~10%. GaSe-e owes its higher conductivity mostly to a sharper valley and higher velocities. Finally, AlLiTe2-e (\( \sigma = 18 \, e^2/h \), see figure 3) and BiCITe-e (\( \sigma = 16 \, e^2/h \)) have slightly larger velocities but stronger EPIs than InSe-e, making them slightly less conductive. Note that all these systems with sharp valleys are electron-doped, which may be rationalized by considering that conduction bands are more often made of delocalized non-bonding states which tend to be more dispersive. Despite the valleys being very similar (isotropic with \( |v_{\text{max}}| \approx 6 \sim 7 \, \text{ARU} \)), the conductivity varies from 14 to 42 \( e^2/h \). This points to the importance of accounting for the details of EPIs to rank materials accurately.

We also note that the selection process does not guarantee to find all the best conductors, as demonstrated by the example of WSe2-h: TMDs were not selected because they are not single-valley (also their Fermi velocities would be too small). However, thanks to strong spin-orbit interactions, the hole side of TMDs can be considered to be in the steep and deep single valley category. Indeed, as is well known, the hole valleys associated to opposite spin textures split very strongly in energy, of the order of 100 meV, making the lower valleys irrelevant for transport. One effectively obtains two valleys at K and K’ with opposite spin textures. WSe2-h, at least within our computational framework, also has the advantage that the edge of the valence band at \( \Gamma \) is quite low, eliminating a potential intervalley scattering channel. Furthermore, as shown in figure 4, the intervalley scattering, associated with spin-flip EPIs, is weak (<10 meV) compared to intravalley, spin-conserving EPIs (~50 meV). This implies that the two valleys are effectively decoupled as far as phonon-limited transport is concerned and transport is similar to the single valley case, except opposite spins travel in separate channels located at different points in the Brillouin zone. Comparing with the isotropic single-valley materials discussed above, WSe2-h has velocities half as small but EPIs at least three times weaker, leading to the largest conductivity (\( \sigma = 81 \, e^2/h \)). This high value is due to the (effective) absence of the \( \Gamma \) valley. Indeed, opposite spins are degenerate at \( \Gamma \), and if the \( \Gamma \) valley were accessible for scattering, intervalley scattering from both K and K’ would be quite strong. In addition, as shown in reference [61], multi-valley occupations enhances the intravalley coupling to the homopolar optical phonon mode by making free-carrier screening inefficient. At any rate, the extraordinarily weak EPI in WSe2-h is tied to subtle spin-orbit and
screening effects that are difficult to predict and highlights the limitations of simple selection processes based solely on the band structure.

3.3. More like phosphorene: anisotropic single valleys

In contrast with the fairly isotropic band structures of InSe, the case of phosphorene showed that anisotropy can also lead to good performance. So, we look for similar materials in our database, having stable phonons, single valleys and small band gap at the PBE level ($E_g < 2.5$ eV). This time we filter materials keeping those that combine high velocity ratios ($\frac{v_{\text{max}}}{v_{\text{min}}} > 1.7$) and a decent maximum velocity ($v_{\text{max}} > 2.0$ ARU) at the Fermi level. These criteria directly lead to the identification of Aul-h, and ClGaTe-h as well as the electron-side of P$_4$-e as promising candidates. The electron side of phosphorene is a similar, less pronounced version of the hole side, and was already studied in our previous work [13]. Thus, we focus here on ClGaTe-h ($\sigma = 13$ e$^2$/h) and Aul-h ($\sigma = 14$ e$^2$/h).

The results of the electron-phonon calculations are plotted in figure 5. The spread of the velocity
Figure 5. Transport properties of ClGaTe and AuI showing the velocity (left) and scattering (right) plots as described in figure 2. Anisotropic valleys imply there is one optimal transport direction, corresponding to higher velocities. Initial states (marked with a black square) are chosen to be in that direction.

Traces indicates high anisotropy, the velocity varying by a factor 2 at a given energy. The high-velocity direction preferable for transport is $x$ for ClGaTe and $x + y$ for AuI. The anisotropy allows one to benefit from many high velocity states, thanks to a flatter band in the direction perpendicular to transport. However, if the band is too flat and the DOS too high, the Fermi level stays close to the band edges and the velocities are too low. Here, velocities of the order of 3–4 ARU ensure good transport properties. While ClGaTe-h and AuI-h share the anisotropic character of phosphorene, their conductivity remains lower, which in part reflects the fact that the good transport properties of anisotropic materials rely on a more fragile balance of features.

A closer look at the scattering plots in figure 5, contrasted with phosphorene in figure 2 further reveals the reasons behind phosphorene’s superior conductivity. In addition to generally weaker EPIs (which is partly due to the monoatomic nature of P$_4$, eliminating all Born effective charge and piezoelectric couplings), one can observe in P$_4$ a predominance of ‘side-scattering’: states in the direction of transport are mostly scattered to states on the sides of the valley with velocities perpendicular to the direction of transport. As can be seen from equation (4), this leads to a longer scattering times, since the term involving a scalar product of the velocities vanishes. The contribution of the DOS from the integral of the conductivity usually cancels out with the integral over available scattering states. This is not the case here because we benefit from the larger weight of high velocity states in the conductivity integral while having less dense, low-velocity states in the scattering integral. Thus, ‘side scattering’ definitely brings the performance of P$_4$-h from great to exceptional. ClGaTe-h is similar to P$_4$ in terms of velocities, but the EPI is stronger and, importantly, mostly backscattering. The scattering time is consequently ten times larger. AuI-h has lower velocities and higher EPI.

While targeting the band features of phosphorene has allowed us to find other excellent candidates, we see that the essence of its exceptional performance comes from something much harder to identify at the level of a database: the anisotropy of its EPIs. Thus, phosphorene is at the same time both a prototype and an example of the limitations of selection processes based on band structures.

4. Conclusions

State-of-the-art DFPT and the BTE are used to study the outstanding transport properties of several 2D semiconductors. Focusing on conductivity at a fixed density of $n/p = 10^{13}$ cm$^{-2}$, the present results offer a complementary perspective with respect to most first-principles calculations valid in the zero carrier density limit. We provide a detailed analysis
of electron-phonon scattering in two well-known high-conductivity systems: electron-doped InSe and hole-doped phosphorene. While they share some features—like weak EPI and a single-valley electronic structure—they exemplify two different strategies to maximize the conductivity. InSe's high-velocity, isotropic valley can be exploited thanks to the fact that the next valleys are much higher in energy. Phosphorene, instead, owes its excellent transport performance to the anisotropy of both its band structure and electron-phonon scattering. Analyzing the band properties of around ~150 small stable semiconductors with six atoms or less in the unit-cell, from the Materials Cloud, we identify systems with band features similar to either InSe or phosphorene. We find large phonon-limited conductivities for electron-doped Bi$_2$Se$_3$, Bi$_2$Te$_3$, BiI$_3$, Sb$_2$Te$_3$, AlI$_3$, and GaSe, as well as hole-doped AuI, ClGaTe, and WSe$_2$. These results confirm that the band structure landscape plays an important role in determining transport and shows that seeking peculiar features in the electronic structure does lead to high-performance materials. Nevertheless, we also show how the details of the strength and angular dependency of electron-phonon scattering play a critical role in ranking those materials with respect to each other.

Acknowledgments

The authors are grateful to Davide Campi for sharing the initial band structures. This work has been in part supported by NCCR MARVEL. Simulation time was awarded by PRACE on Marconi at Cineca, Italy (project id. 2016163963). Computational resources have been provided by the Consortium des équipements de Calcul Intensif (C2CI), funded by the Fonds de la Recherche Scientifique de Belgique (F.R.S-FNRS) under Grant No. 2.5020.11 and by the Walloon Region. TS acknowledges support from the University of Liege under Special Funds for Research, IPD-STEMA Programme. MG acknowledges support by the Italian Ministry for University and Research through the Levi-Montalcini program and by the Swiss National Science Foundation (SNSF) through the Ambizione program (grant PZ00P2_174056).

Appendix A. Comments on doping-dependent transport performance

The mobility is a typical figure of merit for transport performance: It depends on doping (i.e. the carrier density induced by field effects), and the relevant doping range might vary with the application. Most first-principles computations of mobility are done in the zero carrier density limit $\mu_0 = \lim_{n/p \to 0} \mu$. Here, instead, we focus on 2D semiconductors with high conductivity $\sigma$ at a fixed carrier density of $n/p = 10^{13}$ cm$^{-2}$. Of course, by optimizing $\sigma$ we also maximize the mobility $\mu = \frac{\sigma}{en/p}$ at this particular density, denoted with $\mu_{13}$. It should be highlighted that, in general, $\mu_0 \neq \mu_{13}$, and the variation of the mobility in between these two doping regimes is not obvious to predict.

The low (but finite) doping regime is very challenging to simulate realistically. The chemical potential is below the band edge and depends strongly on temperature. One would ideally run one simulation per temperature, with an electronic smearing corresponding to this temperature and an accordingly dense grid of k-points. Unfortunately, even room temperature corresponds to a very low electronic smearing compared to standard DFT and DFPT calculations, resulting in very dense grids of k-points and prohibitively expensive calculations (especially when studying many materials as in this work). This issue is usually circumvented by simulating the neutral system and computing only $\mu_0$. Sometimes, the most obvious consequence of doping, i.e. screening form free carriers, is added as an analytical post-processing correction [62, 63], but which scattering sources should be screened by free carriers, and how, has been debated [64–66]. Moreover, field effects and screening can have non-trivial consequences, as demonstrated in TMDs [61] or in graphene [40]. In this work we choose to fully account for doping in the calculations, but at relatively high carrier density. This allows us to perform more realistic calculations, easier to converge, with a chemical potential within the band and a well-defined Fermi surface. We use a smearing that is large compared to room temperature in order to have accurate results with affordable k-point grids, but the ‘cold’ nature of the smearing [56] allows to gets closer to room temperature conditions. The effects of smearing can be significant at low doping, when the chemical potential is in the gap; at the high doping levels considered here, however, we expect the calculations to be representative of room-temperature conditions. Note that an alternative consistent approach to smear a finite temperature Fermi–Dirac distribution has been put forward [67], but it is not implemented in our computational framework.

To predict the behavior of the mobility as doping decreases, one needs to account for the variation of EPIs. If the strength of EPIs are constant, simple models using quadratic bands and elastic scattering show that the mobility is roughly constant [62] up to fairly large dopings and then decreases. Considering inelastic scattering increases mobility at small doping because there are no more available states for phonon emission close to the band edge. In any case, maximizing $\mu_{13}$ implies maximizing $\mu_0$. However, for the materials considered here, EPIs are likely to be at least partially doping-dependent via free-carrier screening. Indeed, those are all single-valley materials, implying that scattering is dominated by momenta smaller than the size of the Fermi surface,
where free carriers screening is efficient. If all EPI were sensitive to free-carrier screening, we would see an opposite trend, with mobility increasing as a function of doping [62], as free carriers screen the scattering sources. \( \mu_0 \) might be then significantly lower than the \( \mu_{13} \) computed here. In practice, the magnitude of this trend will depend on which EPIs are sensitive to screening and how strong the bare EPIs are.

The electron-doped materials studied here (InSe, GaSe, Bi\(_2\)Se\(_3\), Sb\(_2\)Se\(_2\)) have strong Born effective charges and Fröhlich couplings, which is screening-sensitive and sharply increases at
small momenta. For InSe, we compute $\mu_{13}=490 \text{ cm}^2/\text{Vs}$, compared to $\mu_0=100 \text{ cm}^2/\text{Vs}$ computed in references [44, 68] including polar effects and $\mu_0 = 488 \text{ cm}^2/\text{Vs}$ when the Fröhlich coupling is suppressed [68] (as due to screening). Similar trends are expected for the other electron-doped materials in this work. Whether $\mu_0$ or $\mu_{13}$ is more relevant to a certain operating doping range depends on the critical carrier density at which free-carrier screening becomes efficient. In 2D and assuming a constant DOS per area $D_1$, one can derive $n = k_B T D_1 \ln \left[ 1 + e^{-\varepsilon_C / k_B T} \right]$ where $k_B T$ is the thermal energy, $\varepsilon_F$ the chemical potential (the Fermi–Dirac distribution) and $\varepsilon_C$: the bottom of the conduction band. If we estimate the onset of free-carrier screening as $\mu_F - \varepsilon_C > -k_B T$ (when the occupations are not dominated by the tail of the Fermi–Dirac distribution), we obtain $n > 5 \times 10^{11} \text{ cm}^{-2}$ for all the electron-doped materials studied here.

The hole-doped materials studied here have weaker Born effective charges, but that is not to say that the remaining EPIs are not sensitive to screening: nevertheless, smaller variations of the mobility are to be expected.

Appendix B. Additional electron-phonon scattering data

Figure B1 shows the transport properties of GaSe-e, Bi$_2$Se$_2$-e, Sb$_2$SeTe$_2$-e, and BiCITe-e.

Figure B2 shows the velocity plot for Bi$_2$STe$_2$-e, for which phonon-limited transport was not computed, but is expected to be similar to Bi$_2$SeTe$_2$-e.

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