Supplemental information: Physically founded phonon dispersions of few-layer materials, and the case of borophene

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DETAILS ON THE AB-INITIO CALCULATIONS FOR PMMN BORON

The phonon contribution to the $\alpha\beta$ component of the thermal conductivity tensor can be computed as[1]

$$\kappa_{\ell}^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0 (f_0 + 1) (\hbar \omega_\lambda)^2 v_\lambda^\alpha F_\lambda^\beta. \quad (1)$$

Here, $\lambda$ runs over phonon branches and over points in the Brillouin zone, $\Omega$ is the volume of the unit cell, $N$ is the number of wave vectors included in the summation, $\omega_\lambda$ and $v_\lambda$ are each mode’s angular frequency and group velocity, and $f_0$ is the Bose-Einstein distribution. $F_\lambda$ is a measure of the difference between the equilibrium and steady-state distributions induced by a temperature gradient $\nabla T$ in the linear regime:

$$f_\lambda = f_0 (T) - F_\lambda \cdot \nabla T \frac{df_0}{dT}. \quad (2)$$

Hence, to compute $\kappa_{\ell}$ for a given crystalline solid, both its phonon dispersion relations and $F_\lambda$ must be known. We obtained those two elements completely from first principles using the parameter-free approach implemented in ShengBTE and described in detail elsewhere.[2] Here we summarize the essential aspects of the method.

We started by performing an unconstrained structural relaxation of the Pmmn boron structure using VASP[3] with projector-augmented-wave (PAW) pseudopotentials[4] and Perdew-Burke-Ernzerhof (PBE) exchange and correlation functionals.[5] As starting coordinates we took those reported by Zhou et al.[6] and we ran the relaxation iteratively until the total change in energy between iterations was less than $10^{-7}$ eV. We employed a plane-wave energy cutoff of 414 eV and a $5 \times 7 \times 1$ $\Gamma$-centered Monkhorst-Pack[7] grid. Our unit cell had a length of 20 Å along the $OZ$ axis, which provided a thick enough vacuum layer to prevent interactions between periodic copies of the boron slab. Our fully relaxed orthorhombic unit cell has side lengths $a = 4.52$ Å and $b = 3.25$ Å, almost identical to Zhou et al.’s result.[6] We obtained $(0.500, 0.753, 0.555)$ and $(0.184, 0.500, 0.520)$ as the reduced coordinates for the two non-equivalent atomic positions in the structure which, after accounting for the different height of our simulation box, are also in fair agreement with Zhou et al. With these coordinates, the difference between the maximum and minimum atomic positions along the $OZ$ axis is 2.21 Å. The slab is formed by four atomic layers along this axis, with an average distance between them of 0.74 Å. Hence we take $2.21 + 0.74 = 2.95$ Å as the total thickness of the slab for thermal conductivity calculations.

We then computed the phonon spectrum of Pmmn boron by means of a real-space supercell method. We used Phonopy[8] to generate a minimal set of displaced $5 \times 7 \times 1$ supercells, for each of which we ran a $\Gamma$-point-only VASP calculation with a stringent convergence threshold of $10^{-8}$ eV for the self-consistent electronic iterations. We employed Phonopy again to extract the second-order interatomic-force-constant (IFC) matrix from the forces on atoms in those displaced supercells, build the dynamical matrix at each point in reciprocal space and obtain the phonon frequencies and group velocities. We included a long-range electrostatic correction[9] based on dielectric parameters obtained from density functional perturbation theory using VASP, even though its effect was found to be negligible.

The last step before performing the integral in Eq. (1) was to obtain $F_\lambda$ from an iterative solution to the full linearized Boltzmann transport equation (BTE) for phonons,[10–14]

$$F_\lambda = \tau_\lambda^0 (v_\lambda + \Delta_\lambda), \quad (3)$$
where $\tau_0^\lambda$ is the relaxation time of mode $\lambda$ computed from perturbation theory. Its full expression, as well as that of $\Delta_\lambda$, are given in Ref. 2. The scattering sources we took into account were isotopic disorder and three-phonon processes. While the effect of the former can be computed from knowledge of the projected phonon densities of states,[15] dealing with the latter relies on obtaining a set of third-order IFCs. In analogy with the second-order ones, we obtained them by means of a real-space approach, harnessing the system symmetries to reduce the number of supercell calculations needed.[2] We used the same supercell size and DFT parameter set as for the second-order calculations, while enforcing a 3 Å (sixth-nearest neighbor) cutoff for the interactions. We solved the BTE on a $50 \times 70 \times 1 \Gamma$-centered mesh; such $q$-point density was needed to afford a fully converged value of the conductivity.

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