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Phonon transport properties of two-dimensional electride Ca$_2$N—A first-principles study

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We investigate phonon transport in dicalcium nitride (Ca$_2$N), an electride with two-dimensional confined electron layers, using first-principles density functional theory and the phonon Boltzmann transport equation. The in-plane ($\kappa_{[100]}$) and out-of-plane ($\kappa_{[001]}$) lattice thermal conductivities at 300 K are found to be 11.72 W m$^{-1}$ K$^{-1}$ and 2.50 W m$^{-1}$ K$^{-1}$, respectively. Spectral analysis of lattice thermal conductivity shows that $\sim$85% of $\kappa_{[100]}$ and $\kappa_{[001]}$ is accumulated by phonons with frequencies less than 5.5 THz and 2.5 THz, respectively. Modal decomposition of lattice thermal conductivity further reveals that the optical phonons contribute to $\sim$68% and $\sim$55% of overall $\kappa_{[100]}$ and $\kappa_{[001]}$, respectively. Phonon dispersion suggests that the large optical phonon contribution is a result of low frequency optical phonons with high group velocities and the lack of phonon bandgap between the acoustic and optical phonon branches. We find that the optical phonons with frequencies below $\sim$5.5 THz have similar three-phonon phase space and scattering rates as acoustic phonons. Comparison of the contributions from emission and absorption processes reveals that the three-phonon phase space and scattering rates of phonons—optical or acoustic—with frequencies below 5.5 THz are largely dominated by absorption processes. We conclude that the large contribution to lattice thermal conductivity by optical phonons is due to the presence of multiple low frequency optical phonon modes with high group velocities and similar phase space and scattering rates as the acoustic phonons. This study provides the frequency and temperature dependent lattice thermal conductivity and insights into phonon transport in Ca$_2$N, both of which have important implications for the development of Ca$_2$N based devices. Published by AIP Publishing.

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The electrode dicalcium nitride (Ca$_2$N) has received significant attention for its potential applications in areas such as high-performance electronic devices and chemical synthesis. Ca$_2$N has a layered structure in which two-dimensional (2D) confined electrons behave as anions, a topology unique to 2D electrode materials. The existence of the free-electron-like electron layers of Ca$_2$N results in excellent electronic properties such as a low work function, a long electron mean free path, and a high electron mobility. Additionally, it has been demonstrated theoretically that the Ca$_2$N structure has potential application as an effective electron transport channel due to the reduced nuclear scattering in its intrinsic two-dimensional electron gas in free space (2DEG-FS) state. Ca$_2$N has been identified as a promising electronic device material, and it is important to study the thermal properties which can affect the electronic transport in devices using Ca$_2$N and remain unexplored.

In this letter, we use first-principles density functional theory (DFT) with the Boltzmann transport equation (BTE) to investigate the phonon transport properties and lattice thermal conductivity of Ca$_2$N. DFT calculations are performed using the Vienna ab initio simulation package (VASP). A plane-wave basis set and the projector augmented-wave (PAW) method are used with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional. The Ca$_2$N hexagonal unit cell structure is optimized using a plane-wave basis cutoff energy of 700 eV and a 3$\times$3$\times$1 supercell, respectively. The obtained lattice parameters, $a = 3.609$ Å and $c = 19.246$ Å, are within $\pm 0.56\%$ and $+0.60\%$ of recent experimental results, respectively. The second-order harmonic and third-order anharmonic interatomic force constants (IFCs) are calculated using 5$\times$5$\times$1 and 3$\times$3$\times$3 supercells, respectively, with a 3$\times$3$\times$1 centered grid of k-points. The convergence criteria and plane-wave basis cutoff energy for IFC calculations are maintained at 10$^{-9}$ eV and 700 eV, respectively. To properly account for interactions between atoms in neighboring layers, a large cutoff of 1 nm is used for computing the anharmonic IFCs using a finite displacement method. This is sufficiently large to consider interactions between all atoms in a given pair of neighboring layers within a hexagonal unit cell. The dielectric tensor and Born effective charges are calculated from density functional perturbation theory and included in the phonon calculations to account for the longitudinal and transverse optical phonon (LO-TO) splitting at the $\Gamma$ point. The phonon relaxation times and lattice thermal conductivity are...
calculated using Fermi’s golden rule\textsuperscript{13} with the iterative solution to the BTE.\textsuperscript{14–16} A 19 × 19 × 5 mesh of q-points is used for the thermal conductivity calculations.

The electron band structure of the conventional hexagonal unit cell is shown in Fig. 1(a). The three bands cross the Fermi level with high dispersion along the Γ → M and Γ → K paths inside the Brillouin zone, which correspond to [100] and [110] in the real space hexagonal unit cell structure [Figs. 1(b) and 1(c)]. From T → A (along [001]), none of the bands cross the Fermi level, suggesting that electrons near the Fermi level may be two-dimensionally confined.\textsuperscript{17} Previous studies show that the electrical conduction of Ca\textsubscript{2}N and the bands crossing the Fermi level are related to the 2D confined anionic electron layers [represented by blue in Fig. 1(c)].\textsuperscript{17–19} Our electron band structure is in good agreement with the current literature,\textsuperscript{5,17} which uses computational methods similar to those used in this work. Features of our electronic structure, such as band dispersion widths, the maximum energy of the three bands that cross the Fermi level (≈1.25 eV), and the lack of bands crossing the Fermi level along the [001] direction, are also similar to those observed in earlier studies using different computational methods such as ultrasoft pseudopotentials, the localized spherical wave method, and the linear muffin-tin orbital method.\textsuperscript{19,20} In conventional layered 2D materials, van der Waals (vdW) interactions are often needed to describe interlayer interactions. However, in 2D electrides, the anionic electrons distributed in the cavity space create a strong interlayer electrostatic interaction.\textsuperscript{21} The Coulomb interaction becomes the critical component in stabilizing the electride layers, and the effect of vdW forces is negligible.\textsuperscript{21,22} We confirmed that the interlayer distance of Ca\textsubscript{2}N is accurately described without adding any vdW corrections. Our hexagonal lattice parameters, calculated without vdW corrections, are within −0.56% and +0.60% of recent experimental results\textsuperscript{5} for a and c, respectively, whereas those including vdW corrections are within −0.94% and −1.25%, respectively.

The phonon dispersion and projected density of states (PDOS) are shown in Figs. 1(d) and 1(e), respectively. We observe that heavier elements mostly contribute to the low frequency phonon modes—over 85% of the phonon DOS below 8.0 THz is from Ca atoms. All of the five significant peaks in the DOS (≈5.0 THz, ≈7.3 THz, ≈7.6 THz, ≈9.2 THz, and ≈13.5 THz) occur at frequencies common to multiple low group velocity phonon modes. The first peak (≈5.0 THz) is wide because there are many low group velocity phonon modes spanning the ≈4.5–5.5 THz range, whereas the fourth peak (≈9.2 THz) is narrow because the fewer low group velocity phonon modes contributing to the DOS are mostly degenerate. The thermal conductivity shows high directional anisotropy: our calculated in-plane (κ\textsubscript{[100]}) and out-of-plane (κ\textsubscript{[001]}) lattice thermal conductivities at 300 K are 11.72 W m\textsuperscript{−1} K\textsuperscript{−1} and 2.50 W m\textsuperscript{−1} K\textsuperscript{−1}, respectively. The temperature dependent lattice thermal conductivity also displays a strong directional anisotropy (Fig. 2). The in-plane thermal conductivity is ≈5X larger than the out-of-plane thermal conductivity at temperatures above 200 K and over 6.5X larger at 100 K. Fitting the thermal conductivity data to the function \(k = AT^{-m}\) reveals that m is larger for \(\kappa_{[100]}\) than \(\kappa_{[001]}\); this means that \(\kappa_{[100]}\) is more sensitive to temperature than \(\kappa_{[001]}\) and suggests that Umklapp scattering is more dominant on \(\kappa_{[100]}\) than on \(\kappa_{[001]}\). The anisotropy of thermal conductivity and weaker temperature dependence of \(\kappa_{[001]}\) are typical properties of layered materials.\textsuperscript{23} The thermal conductivity of Ca\textsubscript{2}N is significantly lower than that of one-atom thick layers, such as multi-layered graphene\textsuperscript{24} (\(\kappa_{[100]}\) ≈2275 W m\textsuperscript{−1} K\textsuperscript{−1}) and hexagonal boron nitride\textsuperscript{25} (\(\kappa_{[100]}\) ≈445 W m\textsuperscript{−1} K\textsuperscript{−1}), while it is comparable to some of the multi-atom thick layered structures, such as Mo\textsubscript{2}.\textsuperscript{26,27}

![Fig. 1. (a) The electron band structure of Ca\textsubscript{2}N along high symmetry paths in the first Brillouin zone of the conventional hexagonal unit cell. (b) The Brillouin zone of the conventional hexagonal unit cell.\textsuperscript{33} (c) The hexagonal unit cell structure with calcium atoms given in green, nitrogen atoms given in red, and a representation of the electron layers given in blue. (d) The phonon dispersion along high symmetry points in the first Brillouin zone of the conventional hexagonal unit cell. (e) The phonon projected density of states.](image)

![Fig. 2. Temperature dependent lattice thermal conductivity of Ca\textsubscript{2}N. The squares are the calculated values, and the lines show a fit to the function \(k = AT^{-m}\).](image)
The accumulated thermal conductivity at 300 K shows that whereas from velocity and reach a maximum at a frequency of C 2.5 THz. The large TA1 contribution to \( \kappa_{[100]} \) is explained by the high group velocity from \( \Gamma \rightarrow M \) (along [100]), those of the acoustic phonon modes. Additionally, the low frequency optical phonon modes have large group velocities similar in magnitude to those of the acoustic phonon modes.

To identify and understand the phonon transport mechanism responsible for the large optical mode thermal conductivity, we examine the three-phonon scattering phase space and phonon scattering rates (Fig. 4). The three-phonon scattering phase space indicates the percentage of allowed three-phonon processes and gives insight into the likelihood of phonon scattering. The total three-phonon scattering phase space is calculated as

\[
P_3 = \frac{2}{3n_1V_{\text{BZ}}^2} \left( P_3^{(+) \ 0} + \frac{1}{2} P_3^{(-)} \right),
\]

where \( V_{\text{BZ}} \) is the Brillouin zone volume and \( n_1 \) is the number of phonon branches. \( P_3^{(+) \ 0} \) and \( P_3^{(-)} \) are the separate contributions to total phase space from the absorption and emission processes, respectively, and evaluated as

\[
P_3^{(\pm)} = \sum_j \int dq D_j^{(\pm)}(q),
\]

where

\[
D_j(q) = \sum_{j' k} \int dq' \delta(\omega_j(q) \pm \omega_{j'}(q') - \omega_k(q'')), \quad \omega_j(q) = \omega_k(q'') + G, \quad \text{where } G \text{ is a reciprocal lattice vector that is only non-zero for Umklapp processes.}
\]

The three-phonon scattering rates are calculated as

\[
\Gamma_{\pm, j, j'} = \hbar n_0 \left| \frac{V_{\pm, j, j'}^2}{4N_0} \left( n_0^0 + 1 \right) \left( n_0^0 + 2 \right) n_0^0 \right| \frac{\omega_j \omega_{j'}^{\pm}}{\omega_j \omega_{j'}},
\]

where \( n_0^0 \) is the Bose-Einstein distribution function for phonon angular frequency \( \omega_j \) and \( N_0 \) is the number of unit cells. \( \Gamma_{\pm, j, j'} \) and \( \Gamma_{\pm, j, j'}^0 \) are the separate contributions to the three-phonon scattering rates from the absorption and emission processes, respectively. \( V_{\pm, j, j'}^0 \) is the three-phonon scattering matrix given by

\[
V_{\pm, j, j'}^0 = \sum_{0k} \sum_{k' l} \sum_{k'' l'} \Phi_{2p}(0k, l, l', k'') \times \frac{e^{\pm \theta_{2p}}}{\sqrt{M_2 M_6 M_{6'}}} \bar{E}_{\pm, j} \bar{E}_{j'} \bar{E}_{j''},
\]

where \( l \) and \( k \) specify the \( k^\text{th} \) atom in unit cell \( l \) and \( e^{\pm \theta_{2p}} \) is the \( z^\text{th} \) component of the phonon eigenvector for atom \( k \) of the unit cell in mode \( \lambda \). \( \bar{E} \) is the location of unit cell \( l \) and \( \Phi_{2p}(0k, l, l', k'') \) are the third-order anharmonic IFCs.
The phase space of optical phonons with frequencies below 5.5 THz is on average larger than that of optical phonons with frequencies above 5.5 THz [Fig. 4(a)]. Therefore, optical phonons with frequencies less than 5.5 THz have more available channels for phonon scattering processes than those with frequencies above 5.5 THz. The three-phonon phase space of optical phonons with frequencies below 5.5 THz is very similar to that of the acoustic phonons, and they also have similar phonon scattering rates [Fig. 4(b)]. As a result, it is reasonable to suspect that an acoustic and optical phonon with similar frequencies would have similar contributions to thermal conductivity. In this case, the multiple low frequency optical phonon modes would make a substantial contribution to the total thermal conductivity. Decomposition of the three-phonon scattering phase space and scattering rates into emission and absorption processes reveals that the phase space and scattering rates of phonons with frequencies below 5.5 THz are largely dominated by absorption processes [Figs. 4(c) and 4(d)]. This means that below 5.5 THz, there is a high probability of phonon scattering processes in which a lower energy phonon is converted into a higher energy phonon by absorbing a phonon. The three-phonon scattering phase space also shows five peaks over the complete phonon frequency range. The first two of these peaks (~2.6 THz and ~4.1 THz) appear in the absorption dominated spectrum, whereas the last two (~10.4 THz and ~12.9 THz) appear in the emission dominated spectrum. The middle peak (~8.3 THz) appears where both absorption and emission processes are important. This is also reflected in the phonon scattering rates; the low frequency peaks are correlated with high absorption scattering rates, whereas the high frequency peaks are correlated with high emission scattering rates. At the middle frequency peak, the absorption and emission scattering rates are very similar.

In conclusion, we calculate the lattice thermal conductivity in Ca$_2$N and investigate its phonon transport using first-principles methods and the phonon Boltzmann transport equation. We find that the in-plane and out-of-plane lattice thermal conductivities at 300 K are 11.72 W m$^{-1}$ K$^{-1}$ and 2.50 W m$^{-1}$ K$^{-1}$, respectively. The phonon dispersion reveals that Ca$_2$N has multiple low frequency optical phonon modes with high group velocities and no frequency bandgap between the acoustic and optical phonon branches. Analysis of the frequency dependence of thermal conductivity shows that over 85% of the total $\kappa_{[100]}$ and $\kappa_{[001]}$ is accumulated by phonons with frequencies below 5.5 THz. The individual phonon mode contributions to thermal conductivity reveal that over 68% and 55% of the total $\kappa_{[100]}$ and $\kappa_{[001]}$ is contributed by optical phonons. Furthermore, over 75% of optical $\kappa_{[100]}$ and $\kappa_{[001]}$ is accumulated by optical phonons with frequencies below 5.5 THz. The three-phonon scattering phase space and scattering rates of acoustic phonons and optical phonons with frequencies less than 5.5 THz are very similar in magnitude, and both are dominated by absorption processes. We conclude that the large optical contribution to thermal conductivity in Ca$_2$N is due to multiple low frequency optical phonon modes with very similar phonon transport properties to those of the acoustic phonon modes. These results may have important implications for the development of Ca$_2$N based devices.

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