Phonon transport in Na$_2$He at high pressure from a first-principles study

San-Dong Guo and Ai-Xia Zhang

$^1$School of Physics, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China

Phonon transport of recently-fabricated Na$_2$He at high pressure is investigated from a combination of first-principles calculations and the linearized phonon Boltzmann equation within the single-mode relaxation time approximation (RTA). The calculated room-temperature lattice thermal conductivity is 149.19 Wm$^{-1}$K$^{-1}$, which is very close to one of Si. It is found that low-frequency optical modes comprise 16% of the lattice thermal conductivity, while high-frequency optical modes have negligible contribution. The high lattice thermal conductivity is due to large group velocities, small Grüneisen parameters, and long phonon lifetimes. The size effects on lattice thermal conductivity are considered by cumulative thermal conductivity with respect to phonon mean free path (MFP). To significantly reduce the lattice thermal conductivity, the characteristic length smaller than 100 nm is required, and can reach a decrease of 36%. These results may be useful to understand thermal transport processes that occur inside giant planets.

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Email: guosd@cumt.edu.cn

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I. INTRODUCTION

Helium is chemically inert, and it is difficult to form thermodynamically stable compounds. Recently, a stable high-pressure phase Na$_2$He with a fluorite-type structure is discovered in experiment, which is stable from 113 GPa up to at least 1000 GPa$^1$. By the first-principles calculations, it is predicted that Na$_2$He displays insulating properties, and the energy band gap increases with increasing pressure. It is interesting and necessary to investigate other physical properties of Na$_2$He, such as heat transport. In semiconductors, the lattice part usually carries the majority of heat around room temperature and higher, while electronic part has negligible contributions to the thermal conductivity. The lattice thermal conductivity is mainly an anharmonic phenomenon. Recently, the first-principles calculations can predict anharmonic force constants quantitatively, and then provide accurate information about the intrinsic phonon-phonon scattering based on the solution of the phonon Boltzmann transport equation$^2$–$^{11}$. Further, the lattice thermal conductivity can be well reproduced, being in agreement with experimental results using no adjustable parameters.

Here, we investigate phonon transport of Na$_2$He with the single-mode RTA of the linearized phonon Boltzmann equation. The lattice thermal conductivity with respect to temperature is calculated, and the room-temperature value is 149.19 Wm$^{-1}$K$^{-1}$, which is very close to 155 Wm$^{-1}$K$^{-1}$ of Si$^{12}$. The small Grüneisen parameters of Na$_2$He indicates a weak anharmonicity, leading to the high thermal conductivity. The large group velocities and long phonon lifetimes can also explain high thermal conductivity. Moreover, we find that the low-frequency optical modes contribute observably to the total thermal conductivity, while high-frequency optical phonons can be neglected. To measure phonon MFP, the thermal conductivity spectroscopy technique has been developed$^{13}$, which can measure MFP distributions over a wide range of length scales. Therefore, the cumulative lattice thermal conductivity with respect to phonon MFP is calculated, which can be used to study size effects in heat conduction.

The rest of the paper is organized as follows. In the next section, we shall give our computational details. In the third section, we shall present phonon transport of Na$_2$He. Finally, we shall give our discussions and conclusions in the fourth section.

II. COMPUTATIONAL DETAIL

The lattice thermal conductivity of Na$_2$He is performed with the single mode RTA and linearized phonon Boltzmann equation, which can be achieved by using Phono3py+VASP codes$^5,15$–$^{17}$. For the first-principles calculations, the framework of the all-electron projector augmented wave (PAW) method within the density functional theory$^{14}$ is employed, as implemented in the package VASP$^{15}$–$^{17}$. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is adopted as the exchange-correlation functional$^{18}$. A plane-wave ba-
sis set is used with kinetic energy cutoff of 1000 eV. The second order harmonic and third order anharmonic interatomic force constants (IFC) are calculated by using a $3 \times 3 \times 3$ supercell and a $2 \times 2 \times 2$ supercell, respectively. Using the harmonic IFCs, the group velocity and specific heat can be attained by phonon dispersion relation, and phonon dispersion determines the allowed three-phonon scattering processes. The third-order anharmonic IFCs can determine the phonon lifetimes, which can be attained by calculating the three-phonon scattering rate. To compute lattice thermal conductivities, the reciprocal spaces of the primitive cells are sampled using the 20 $\times$ 20 meshes.

III. MAIN CALCULATED RESULTS AND ANALYSIS

The Na$_2$He has a fluorite-type structure with space group $Fm\overline{3}m$ at 300 GPa$^1$. The Na and He atoms occupy the Wyckoff position 8c (0.25,0.25,0.25) and 4a (0,0,0), respectively. The schematic crystal structure is shown in Figure 1. The experimental lattice parameter $a=3.95$ Å is employed to investigate it’s phonon transport. Based on harmonic IFCs, the phonon dispersions are calculated along high-symmetry paths, which is shown in Figure 2, together with partial density of states (DOS). The unit cell of Na$_2$He contains three atoms, resulting in 3 acoustic and 6 optical phonon branches in the phonon spectra. According to Figure 2, a gap of 6.09 THz can be observed, which separates three high-frequency optical modes from the low-frequency modes. The high-frequency optical modes are mainly from He vibrations, while the acoustic and low-frequency optical modes of phonon dispersions mainly is due to the vibrations of the Na atoms. The low-frequency optical modes have larger dispersion than high-frequency ones, indicating that low-frequency ones have relatively large group velocities.

Figure 3 shows the lattice thermal conductivity of Na$_2$He as a function of temperature, the accumulated lattice thermal conductivity (300 K) along with the derivatives, and phonon modes contributions toward total lattice thermal conductivity (300 K). The room-temperature lattice thermal conductivity is 149.19 Wm$^{-1}$K$^{-1}$, and the lattice thermal conductivity nearly meets the $1/T$ relation at high temperature (above room-temperature). As shown in Figure 3(Middle), the acoustic phonon branches below the 13.34 THz dominate lattice thermal conductivity, and the peak of the derivatives drops rapidly at 13.34 THz. The remaining contribution is almost from low-frequency optical modes, while the high-frequency optical modes show a negligible contribution to lattice thermal conductivity, also found in other semiconductors$^{12}$. Further, the relative contributions of every acoustic and optical phonon mode to the total lattice thermal conductivity are examined. The two trans-

FIG. 2. Phonon band structures and partial DOS of Na$_2$He.

FIG. 3. (Color online) Top: the lattice thermal conductivity of Na$_2$He as a function of temperature; Middle: the accumulated lattice thermal conductivity (300 K), and the derivatives; Bottom: phonon modes contributions toward total lattice thermal conductivity (300 K).
verse acoustic (TA) branches have almost the same contributions of about 20%, while the longitudinal acoustic (LA) branch has the largest contributions, as high as 44%, which is twice the contribution of TA branch. The low-frequency optical branches provide a contribution of about 16%, while high-frequency ones only 0.12%.

The phonon mode group velocities and mode Grüneisen parameters ($\gamma$) of Na$_2$He in the first Brillouin zone are plotted in Figure 4. It is found that the group velocity of LA branch is larger than ones of TA branches at low-frequency region, and the largest group velocity for LA and TA branches near $\Gamma$ point is 13.74 kms$^{-1}$ and 5.79 kms$^{-1}$, respectively. It is also clearly seen that the third optical branch shows relatively large group velocities due to larger dispersion. Mode Grüneisen parameters are calculated from third order anharmonic IFCs, and they all are positive throughout the Brillouin zone. The mode Grüneisen parameters can reflect the strength of anharmonic interactions, and larger $\gamma$ induces lower lattice thermal conductivity due to strong anharmonicity. The high value region of mode Grüneisen parameters focuses primarily between 8 THz and 16 THz, and the maxima is 1.72. The mode Grüneisen parameters of Na$_2$He are smaller than ones of Bi$_2$CuOsSe$_3$ and PbTe with low high lattice thermal conductivities as representative thermoelectric materials. The average mode Grüneisen parameters is 1.02, which means weak anharmonicity, leading to high lattice thermal conductivity.

The three-phonon scattering rate can be attained by third-order anharmonic IFCs, and phonon lifetimes can be calculated. Phonon lifetimes of Na$_2$He at room temperature are shown in Figure 5, which are reciprocal of the phonon linewidth. The lattice thermal conductivity and phonon lifetimes are merely proportional to each other in the single-mode relaxation time method. The lifetimes of most acoustic modes are between 40 ps and 90 ps, and the ones of low-frequency optical modes decrease with increasing frequency. The first optical branch of they has long lifetimes, being well-matched with ones of acoustic modes. They lie in 2 ps to 22 ps for high-frequency optical modes. The distribution of phonon lifetimes can mainly explain the relative contributions of every acoustic and optical phonon mode to the total lattice thermal conductivity.

The cumulative lattice thermal conductivity along with the derivatives with respect to phonon MFP is shown in Figure 6 at room temperature, which provides information about the contributions of phonons with different MFP to the total thermal conductivity. The phonon MFP is also useful to understand and engineer size effects on lattice thermal conductivity. The total accumulation increases with MFP increasing, and the accumulation gradually approaches plateau after MFP reaches 440 nm. Phonons with MFP smaller than 100 nm contribute around 64% to the lattice thermal conductivity.

IV. DISCUSSIONS AND CONCLUSION

It is interesting to compare phonon transport of Na$_2$He with other semiconductor materials, such as Si and PbTe. The frequency range of acoustic modes between Na$_2$He and Si is almost the same, and their phonon lifetimes have the same order of magnitude. Therefore, the room-temperature lattice thermal conductivity of Na$_2$He (149.19 Wm$^{-1}$K$^{-1}$) is very close to 155 Wm$^{-1}$K$^{-1}$ of Si. The acoustic frequency range of Na$_2$He is very wider than one of PbTe, which leads to larger group velocities. The phonon lifetimes of PbTe are very shorter than

FIG. 4. (Color online) The phonon mode group velocities (Top) and mode Grüneisen parameters (Bottom) of Na$_2$He in the first Brillouin zone.

FIG. 5. Phonon lifetimes of Na$_2$He at room temperature.
ones of Na$_2$He. So, the lattice thermal conductivity (1.9 W m$^{-1}$K$^{-1}$) of PbTe at 300 K is very lower than one of Na$_2$He. The similarity between Na$_2$He and PbTe is that the contributions of optical phonons to lattice thermal conductivity remain very large, 16% for Na$_2$He and 22% for PbTe at room temperature. However, for Si, the optical branches comprise only 5% of the lattice thermal conductivity$^{21-23}$. The difference among them is size effects on lattice thermal conductivity, which can be described by cumulative lattice thermal conductivity as a function of MFP. MFPs smaller than 10 nm contribute to around 90% of the lattice thermal conductivity for PbTe$^7$. Phonons with MFP smaller than 100 nm comprise around 64% of the lattice thermal conductivity for Na$_2$He. MFPs smaller than 1000 nm contribute to almost half of the total thermal conductivity for Si$^6$.

In summary, the intrinsic lattice thermal conductivity of Na$_2$He is calculated based mainly on the reliable first-principle calculations and Boltzmann transport theory. The room-temperature lattice thermal conductivity is found to be 149.19 W m$^{-1}$K$^{-1}$. The acoustic and low-frequency optical branches provide nearly 100% contribution to total lattice thermal conductivity. The high lattice thermal conductivity is due to weak anharmonicity and high group velocities. In addition, the size effects on thermal conductivity are also studied by cumulative lattice thermal conductivity with respect to MFP. The present work can encourage further efforts to investigate other chemical and physical properties of Na$_2$He.

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