



First Principles Study of Thermo-Mechanical Properties of Gallium Phosphide

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Abstract

Using first principles approach, we calculated the structural, elastic, thermal and thermodynamic properties of semiconducting Gallium Phosphide (GaP). Quantum Espresso (QE) code with plane-wave pseudopotential approach to Density Functional Theory (DFT) and the more recently developed Generalized Gradient Approximation (GGA) scheme for solids (PBE sol) was utilized. The calculated lattice constant, elastic constants, bulk modulus, and Young's modulus are in excellent agreement with the known experimental values. The electron density of states revealed the hybridization between Ga (2p) and P (2p) and their covalent bonding. We also calculated the phonon dispersion relationship of GaP using the Density Functional Perturbation Theory (DFPT) as implemented in QE and the obtained phonon dispersion compares well with the available experimental results. Further, we calculated the lattice-assisted properties such as volume thermal expansion and heat capacity within Quasi-Harmonic Approximation (QHA) and the predicted properties are consistent with the experimental data. Finally, we presented the phonon contribution of thermal conductivity as a function of temperature up to 1400 K using the Slack model and Boltzmann Transport Equation (BTE).

Keywords

GaP, First principles, Electronic structure, Thermal conductivity, BTE, Slack model

Introduction

GaP is a semiconducting material that finds application in high power electronic devices such as Light Emitting Diodes (LEDs). With the advancement in semiconducting technologies, and the growing need for smaller and faster devices the manipulation of the material properties has become indispensable. For smaller and faster devices the unrestrained increase in temperature is apparently a constricting strand for the device behavior and dependability. Hence, an efficient heat withdrawal is essential for the performance and reliability of GaP-based electronic devices [1].

Moreover, the thermophysical properties are fundamental characteristics to be considered in selecting the cooling schedule of a GaP-based device. Therefore to improve the reliability and efficiency of GaP devices, it is important to evaluate the thermal properties of GaP up to relatively high temperatures. Some previous works had determined properties such as indirect band gap [2], thermal expansion [3] and thermal conductivity [4] at lower temperatures. Theoretically, some previous works have used first principles approach to determine thermal transport properties of GaP and other semiconducting materials. Nina Shulumba, et al. [5] determined the effect of harmonicity on the thermal conductivity of Al-

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Table 1: Structural and mechanical properties of cubic GaP at 0 K and 300 K evaluated by QHA in comparison with other DFT calculations [6,25] and experiments [18,19]. The lattice parameter (a_0) is in Å, the mechanical properties (elastic constants (C_{11} , C_{12} , and C_{44}), Bulk modulus (B), Shear modulus (G) and Young modulus (Y)) are in GPa, and the Poisson ratio (η) has no unit.

Properties	PBESOL (0 K)	PBESOL (300 K)	Ref [6] (0 K)	Ref [25] (0 K)	Exp. [18]	Exp. [19]
Lattice parameter (Å)	5.449	5.454	5.502	-	5.451	5.451
C_{11} (GPa)	130.3	129.2	123	137.5	-	-
C_{12} (GPa)	56.6	55.9	50.9	59.4	-	-
C_{44} (GPa)	88.9	87.8	70.9	72.2	-	-
Bulk modulus (B) (GPa)	81.2	80.3	75.1	-	88.7	-
Shear modulus (G) (GPa)	68.1	67.4	54.2	-	-	-
Young modulus (Y) (GPa)	149.2	147.7	-	-	-	-
Poisson ratio (η)	0.1939	0.1937	-	-	-	-

uminiun Nitride (AlN) at relatively high temperature using the GGA Perdew-Burke-Ernzerhof (PBE) functional. Liu li, et al. [6] have investigated the phase transition, elastic and thermodynamic properties of GaP by the DFT using the Perdew-Wang (PW91) version of the GGA exchange-correlation functional. Rashid Ahmed, et al. [7] studied the structural and electronic properties of group III phosphides, including GaP, using the full potential linearized augmented plane wave method within the Local Density Approximation (LDA). Previously, Lindsay, et al. [8] used the BTE to predict the Lattice Thermal Conductivity (k_L) of GaP and other semiconductors at low temperature (< 400 K) using the LDA norm-conserving pseudo potentials. However, the data on transport properties of GaP at high temperature are limited. Therefore, in this work, we used the first principles calculation to evaluate the thermal properties of GaP at relatively high temperature.

Methodology

We performed the first principles calculation by using Quantum ESPRESSO (QE) [9] and also utilized an interface QE_NIPY-advanced developed by our group [10] to run the code and analyze outputs. To determine the equilibrium structural properties, we performed structural optimization by varying cell parameters and atomic positions such that the difference of total Energy (E) converged to less than one meV. To evaluate the Bulk modulus (B_0), we fitted the total Energy (E) versus Volume (V) using the third order Birch-Murnaghan equation of state [11]. We calculated the Phonon Density of States (PDOS) that includes all the phonons over the entire Brillouin zone needed to estimate the phonon-assisted properties by using Density Functional Perturbation Theory (DFPT). All the lattice assisted properties such as fixed volume Heat Capacity (C_v), and Volume Thermal Expansion (α_v) were calculated within QHA [12]. The phonon contribution to k_L is predicted using the Slack model [13]. The detailed description of the methodology and the equations used to calculate all the properties mentioned above can be found in our previous work [14,15] and is not repeated here for brevity. Moreover,

we have found in our previous work [15] that the new PBE sol potential for solids predict material properties in better agreement with the experiments and therefore we have used the same potential for this work. We also compare the k_L by Slack method with the solutions of BTE. To solve BTE we used the recently developed software package (Sheng BTE) by Wu Li, et al. [16].

Computational Details

All our calculation uses the norm-conserving PBE sol (new exchange-correlation functional for solids) [17] functional. We obtained the total energy convergence using a Monkhorst-Pack sampling of $10 \times 10 \times 10$ and 100 Ry plane wave's cut-off energy. On a mesh of $5 \times 5 \times 5$ q-points, we calculated the dynamical matrices for phonon density of states, in the irreducible Brillouin zone.

We considered a super cell of $4 \times 4 \times 4$ to calculate the third order Inter atomic Force Constants (IFCs) using sheng BTE. The calculated third order IFCs was used for solving BTE. The force cutoff distance was set such that the interaction range is up to the three nearest neighbors. A mesh of $5 \times 5 \times 5$ q-points was used to calculate the second order IFCs by QE and needed by BTE to compute the k_L of GaP.

Results and Discussions

Structural and mechanical properties

Listed in Table 1 are the calculated ground state structural and mechanical properties of cubic GaP in comparison with experimental values obtained from refs. [18,19] at room temperature. Table 1 also provides the calculated structural and mechanical properties of GaP at 300 K within QHA. At room temperature (300 K), the calculated lattice constant shows excellent agreement with experiments [18,19]. The cubic structure GaP has three independent elastic constants: C_{11} , C_{12} , and C_{44} and to obtain the single crystal stiffness constants we used the stress-strain method [20,21] implemented in the QE_nipy-advanced interface [10]. From the calculated stiffness constants, using the Voigt-Reuss-Hill averaging scheme [22-24], we determined the Bulk Modulus (B),

Shear Modulus (G), Young's Modulus (Y), and the Poisson's Ratio (η). All the predicted mechanical properties (as shown in Table 1) agree well with the experimental values. We also note that the new PBE sol functional predicted the structural and mechanical properties more accurately than the previous DFT calculations [6,25] using the PW GGA exchange-correlation function. For example, the bulk modulus we predicted, using Voigt-Reuss-Hill averaging scheme, which is 80.3 GPa is more accurate than the previous prediction of 75 GPa when compared to the experimental value of 88.7 GPa [18]. In this work, we used the revised Perdew-Burke-Ernzerh of (PBEsol) Generalized Gradient Approximation (GGA) functional because it improves the equilibrium properties of densely packed solids and their surfaces. More detailed descriptions regarding the underlying physics of the PBE sol functional is provided in ref. [26]. Since the agreement of calculated and experimental properties is essential, we, therefore, study the electronic density of

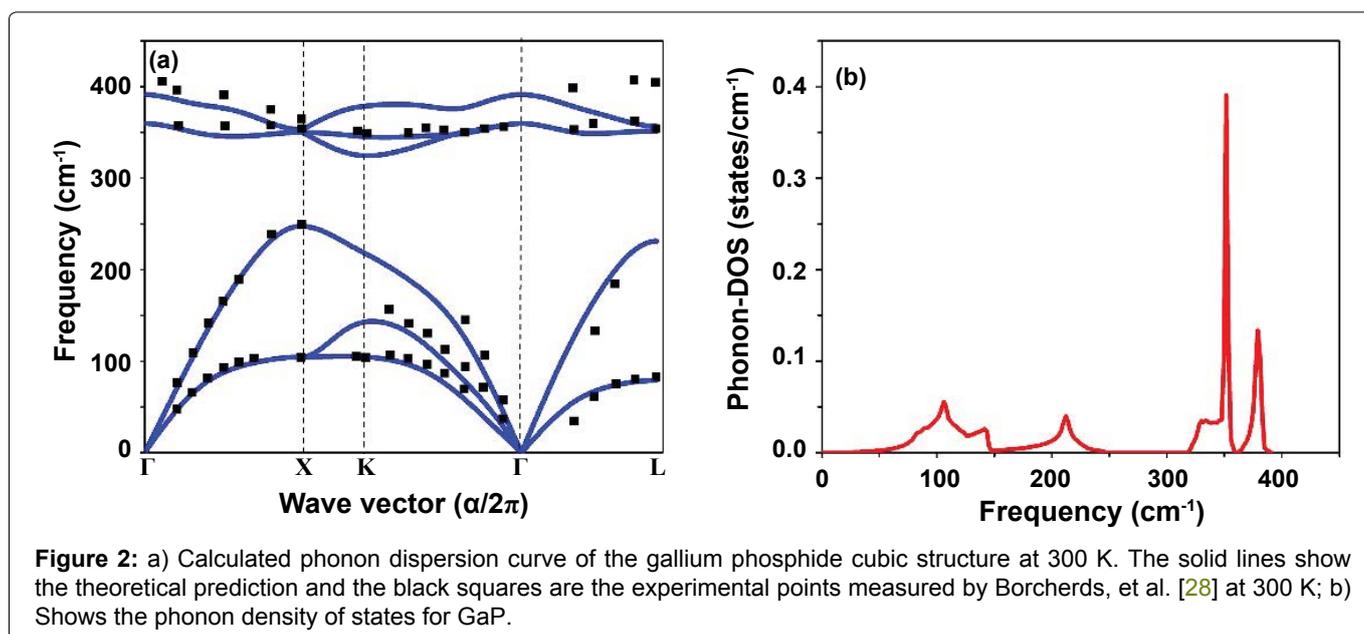
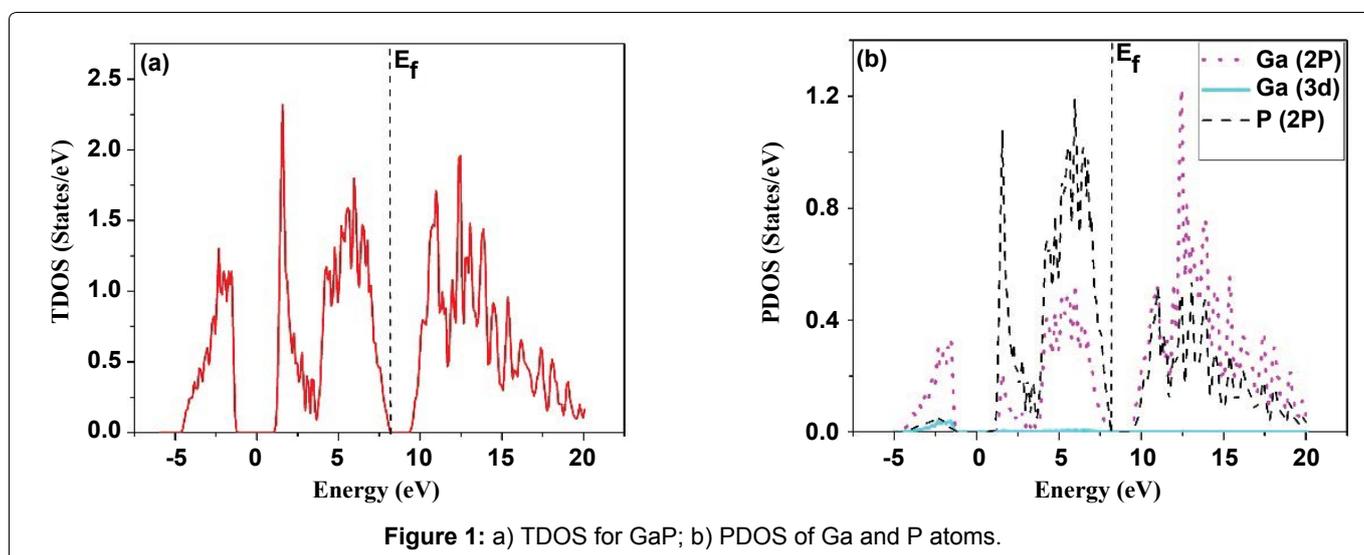
state, phonon dispersion, and thermodynamic properties of GaP using the same PBE sol functional.

Electronic structure

Figure 1a and Figure 1b shows the Total Density of States (TDOS) and Partial Density of States (PDOS) of GaP respectively. Figure 1a clearly indicates that GaP is a semiconductor. Although, the calculated band gap (1.7 eV) is better than the previous DFT calculation (1.44 eV) using Local Density Approximation (LDA) potential [7], but when compared to the experimental value of 2.35 eV [27] our prediction is under estimated. The PDOS (shown in Figure 1b) indicates a hybridization of Ga (2p) and P (2p) which accounts for the covalent bonding of GaP. The Fermi energy of GaP is evaluated to be 8.25 eV.

Phonon dispersion and thermodynamic properties

The phonon vibrational spectra are the fingerprint of materials. The frequency of vibration is the measure



of the stiffness of a bond and also a function of atomic mass. Therefore, knowledge of phonon dispersion in the entire Brillouin zone is necessary to understand the thermodynamic properties, thermal expansion, and thermal conductivity. In Figure 2a we present the phonon dispersion of GaP at its equilibrium volume along the high symmetric Γ -X-K- Γ -L directions. GaP has two (n) atoms in its primitive unit cell and therefore six phonon modes are produced in the dispersion relations. There are three dimensions ($d = 3$), and thus three acoustic modes and $d(n-1)$ equals three optical modes. The calculated acoustic and optical modes are in excellent agreement with the experiment done by Borcherds, et al. [28] at room (300 K) temperature.

The density of states plots in Figure 2b clearly indicates that in the region around 315-390 cm^{-1} the phonon states are densely populated. The sharp peak in phonon density of states of GaP is due to the flat transverse optical branch. The gap between the acoustic and optical branch is the region where frequencies are not allowed to be propagated, and this occurred because of the difference in masses of two atoms. In the case of GaP, this phonon gap occurs at ~ 250 -315 cm^{-1} . The accurate prediction of phonon density of states for a variable lattice constant allows us to predict the thermodynamic properties as a function of temperatures such as the coefficient of linear thermal expansion (α) and heat capacity at fixed volume (C_v) correctly.

Thermal properties: The DFPT combined with QHA, at relatively low temperatures, is a powerful method to predict the lattice assisted properties. The vibrational Helmholtz free energy is calculated by evaluating the phonon density of states at different volume [12], integrating the energy of phonons over the density of states and weighting it by the temperature-dependent Boltzmann factor [29,30]. The thermal expansion over a wide temperature range is an important design parameter for high-temperature applications especially in choosing the post growth cooling schedule in GaP-based components.

Figure 3a shows the change in volume of GaP as a function of temperature in comparison with the experimental data by Deus, et al. [31]. Comparison of the results indicates that at a temperature lower than 250 K the calculated volume expansion is in excellent agreement with experiment. However, at 900 K temperature, the value is slightly overestimated by 2.2%. Figure 3b shows the heat capacity at constant volume (C_v) as a function of temperature, and the calculated values are in good comparison with available data by Lui Li, et al. [6].

Lattice thermal conductivity

Thermal conductivity, in applications involving thermal management, is an important material property to

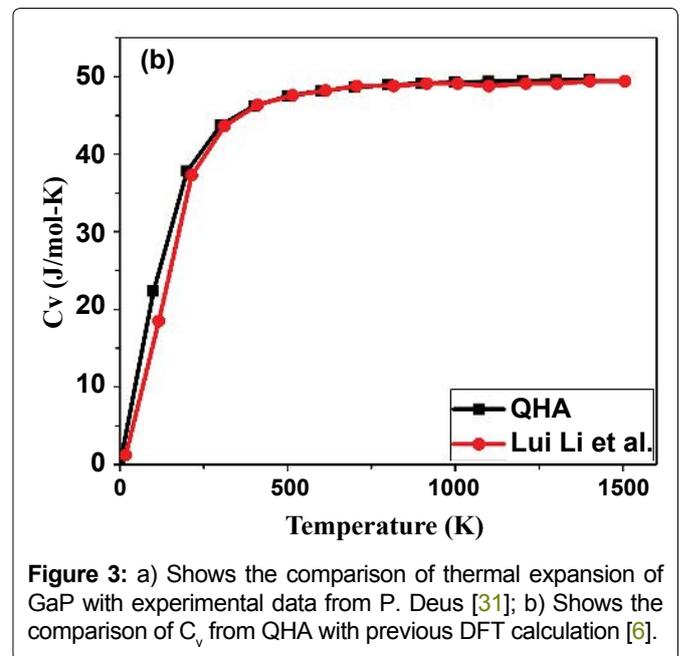


Figure 3: a) Shows the comparison of thermal expansion of GaP with experimental data from P. Deus [31]; b) Shows the comparison of C_v from QHA with previous DFT calculation [6].

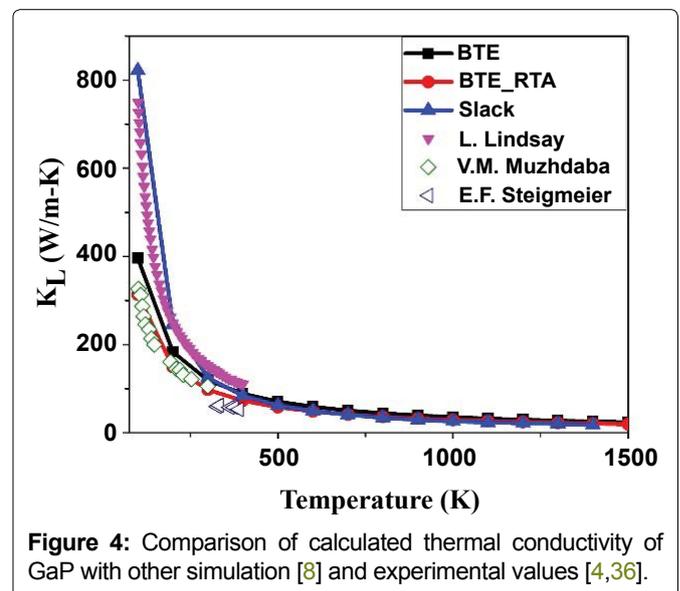


Figure 4: Comparison of calculated thermal conductivity of GaP with other simulation [8] and experimental values [4,36].

be considered. In nonmagnetic materials, the transfer of heat is governed by phonons, electrons, and radiation energy at very high temperatures. In the usually studied temperature range, the main contribution to thermal conductivity in semiconductors is made by lattice vibrations (phonons) while contributions from electrons and radiation are negligible. Therefore, in this work, we calculate only the lattice contribution to thermal conductivity (k_L) of GaP. Various models have been considered to evaluate thermal conductivity depending on the mechanisms of phonon scattering. Different methods [13] can be used to calculate the value of k_L for materials, and such method includes Relaxation Time Approximation (RTA) [32], Callaway model [33], Slack model [13] and Boltzmann Transport Equation (BTE) [16]. In this work, we calculate the lattice thermal conductivity (k_L) of GaP using both Slack model and Boltzmann Transport Equa-

tion (BTE) using both RTA and iterative method solution with the inclusion up to three phonons scattering [16]. We compare our results using these methods with available experimental data.

Figure 4 shows that the k_L predicted by the Slack model at lower temperatures is overestimated compared with the experimental measurement by Muzhdaba, et al. [4]. However, close to the Debye temperature (467 K) the calculated k_L shows excellent agreement with the experimental data [4]. The high value of k_L at low temperatures is because the Slack method does not consider quasi-momentum conserving (normal process), which becomes important at low temperatures but represents well high-temperature behavior due to dominated Umklapp scattering. Although, as it is well known that N process alone does not lead to final conductivity. However, it is important to be included especially at lower temperature as it leads to the redistribution of the phonon momentum [34]. The Slack model predictions are better at a relatively high temperature near to the Debye temperature where the non-quasi-momentum conserving Umklapp process is dominant.

We get a good prediction for overall temperature range using BTE because it considers the boundary scattering, normal process, and the Umklapp process. Figure 4 also compares the calculation in the RTA as well as the full BTE solution. The comparison shows that the BTE exact solution is 18% higher than the RTA solution. It has been reported that any difference greater than 10% indicates that N scattering process is dominant [35]. Also, we calculated the percentage isotope effect for isotope composition of GaP to be less than 6% using the contribution to phonon scattering from isotopic disorder as implemented in Sheng BTE [16]. At low temperature, the k_L predicted by BTE compares well with the experiment done by Muzhdaba, et al. [4]. Moreover, our prediction of k_L from BTE are in better agreement with both experimental data from Muzhdaba, et al. [4] and Steigmeier, et al. [36] than the work done by Lindsay, et al. [8]. We have also extended the prediction of k_L to relatively higher temperatures than in previous calculations. Analytically, k_L is expressed well as a function of $[a+bT]^{-1}$, even at higher temperatures where Umklapp scattering is dominant, with constant a and b . For GaP, we obtained ($R^2 = 0.9488$) the analytical expression of $k_L = [4.45 \times 10^{-11}(\text{mK/W}) + 3.07 \times 10^{-05}(\text{m/W}) T(\text{K})]^{-1}$ from the simulated values of k_L using Slack method.

Conclusion

In conclusion, we have predicted the structural, electronic, mechanical and thermal properties of the GaP cubic phase using new PBE sol functional. The evaluated properties in comparison with experiments are significantly more accurate than the previous DFT calculations.

We have predicted that GaP is a semiconductor with a slightly under predicted band gap of 1.7 eV as expected within DFT approximation. The calculated phonon dispersion relation of GaP also the thermal conductivity of GaP cubic phase, using two complementing methods: The Slack model and BTE. For the first time, we have predicted the thermal conductivity of GaP at relatively high temperatures and our predictions are more accurate than the previously reported data and therefore they are in better agreement with experiment. The knowledge of thermal expansion, heat capacity and thermal conductivity in the broad range of temperatures would help in designing devices that can work in extreme conditions. Also, our finding of thermo-mechanical properties of GaP at high temperatures can be used as a complementary data in the design of devices involving thermal management.

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