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Some vibrational and thermodynamic properties of gallium arsenide

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Gallium arsenide (GaAs) is a III-V direct band gap semiconductor with its zinc blende type crystal structure at ambient conditions. It has a wide usage area changing from microwave frequency integrated circuits to optical windows. Due to this technological importance it is possible to find a significant number of experimental and theoretical works related with the various physical properties of gallium arsenide (GaAs) in the existing literature. All these studies performed on GaAs inspired us to perform this work. We report a computational study for some vibrational and thermodynamic GaAs. Unlike earlier theoretical works, a Stillinger-Weber type interatomic potential has been first time applied to derive the vibrational Helmholtz energy (F), entropy (S) and constant volume specific heat capacity (C_v) of GaAs up to 1500K from phonon calculations through quasiharmonic approximation after optimizing the crystal geometry. Presently calculated room temperature values of S with 63.36 J/mol. K and C_v with 46.23 J/mol.K not only show fair agreement with experiments but also in the range of former theoretical data. Likewise, calculated phonon frequencies through Δ path and corresponding density of states of GaAs are reasonable. Overall, our results for considered quantities show a fair consistency with earlier measurements and available theoretical data.

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Introduction

Predicting good elastic and thermodynamic properties of materials is an attractive issue for today's engineering and technology. In particular, these properties at high temperatures and pressures are of importance during the production of desired materials.

On the other hand, the computational modelling of materials has been an efficient and quick tool to address the unclear topics of physical interest [1-2]. These calculations can easily replace pricey and time-consuming experiments impossible in the laboratory [3].

The focus of this research is GaAs material. GaAs is the outstanding member of the III-V semiconductor family. It has many outstanding features especially for recent optoelectronic industry. The most notable uses of GaAs cover photovoltaics, heterostructures, semiconductor lasers, light-emitting diodes and solar cells [1].

From a crystallographic outlook, GaAs crystallizes in the cubic zinc blend phase (B3) at ambient conditions. Under pressure, zinc blend phase can transform to sodium chloride phase (B1) [1].

Significant number of theoretical investigations were done to clarify the phase transition, mechanical as well as elastic properties of GaAs under pressure by applying different interatomic potentials and using various methods. In addition to these detailed theoretical works [4-12], it is also possible to find many experimental researches concerning the thermodynamic properties of GaAs. For example, excellent experimental review of Blakemore includes various thermodynamic properties of GaAs such as C_v , thermal expansion and thermal conduction [13]. Some of the important theoretical works can be chronologically summarized as in the following. Otes et al. applied the species chemical potential bond energy (SCPE) to determine the

thermodynamic properties of GaAs in 1995 [14]. Later, L.L. Yu et al, reported the temperature-pressure variation of C_v and Debye temperature (Θ_D) of GaAs with ultrasoft pseudo potentials through the generalized gradient approximation of Perdew et al (GGA-PBE) in their density functional theory (DFT) calculations [15]. In 2006, Powell et al. applied a Tersoff potential to the phonon mode calculations of GaAs [16]. Afterwards, in 2007, Adhikari and Kumar estimated several structural and thermodynamic properties incorporating the lattice constant, linear thermal expansion coefficient, nearest neighbour distances and C_v at constant volume of GaAs under various temperatures by using Monte Carlo simulations after using Tersoff type potential to their work [17].

In this work, our purpose is to elaborate some thermodynamic properties of GaAs after phonon calculations with the geometry optimization method. In contrast to existing methods and applied potentials, this is the first report about the application of a Stillinger-Weber type potential to determine some phonon and related thermodynamic properties of GaAs. Since temperature plays a key role during the manufacturing of materials, we focused on the temperature dependence of aforementioned thermodynamics properties of GaAs during this study.

We organized the rest of the paper as follows. Section II gives a brief outline for geometry optimization and other computational details. Section III provides the present and former results on the considered parameters of GaAs with a discussion, and Section IV summarizes the main findings of this research in the conclusions.

Computational Details

All herein, calculations were achieved within GULP molecular dynamics (MD) code [18,19]. Since the accuracy and the

reliability of the computer simulations depend on the quality of the applied interatomic potentials [20], an existing Stillinger-Weber type interatomic potential [21] were employed to present computations, which was originally derived for the vibrational properties of GaAs nanostructures. This modified Stillinger-Weber potential used in this study is composed of bond stretching interaction between the nearest and next-nearest neighbour, a three-body term and a long-range Coulomb interaction. Other details of applied Stillinger-Weber type potential and its modified parameterization procedure can be also found in Ref [21]. Phonon and thermodynamic properties of B3 GaAs were addressed after geometry optimization calculations as a function of temperature within the quasiharmonic approximation. At each temperature, geometry optimization is carried out over all structural degrees of freedom using the internal lattice energy (U_{int}) and the vibrational contributions obtained from the phonon density of states as implemented in GULP. Noteworthy to mention here that, geometry optimization is an effective method used in both classical physics based MD and quantum mechanics based DFT techniques to get a stable configuration for a molecule or periodic structure through fast and inexpensive energy computations. An optimization procedure involves the repeated sampling of the potential energy surface until the potential energy reaches a minimum where all forces on all atoms are zero. Further information about the optimization methods and other points of concern are explained in [22]. During present work, the lattice parameter of B3 GaAs was assigned as 5.66 Å, which is slightly higher than the experimental value of 5.65 Å. To do an effective optimization without constraints, we have applied constant

pressure geometry optimization to the B3 crystal structure of GaAs with phonon calculations as implemented in GULP. The geometry of the cells were optimized via the Newton–Raphson routine based on the Hessian matrix calculated from the second derivatives, in which the Hessian matrix was recursively updated during optimization using the BFGS algorithm [23–26].

After optimizing the crystal structure for each run, we have obtained the values of considered thermodynamic quantities directly from GULP phonon calculations. In GULP phonon calculations, it is possible to get the phonon density of states (DOS) as well as phonon dispersions for a given material after specifying a shrinking factor. As well, phonons are described by calculating their values at points in reciprocal space within the first Brillouin zone of the related crystal. To accomplish the Brillouin zone integration and obtain the DOS, we have used a standard and reliable scheme developed by Monkhorst and Pack [27, 28] with 8x8x8 *k*-point mesh. For a comparison with available experimental data, we have varied the temperature of the B3 crystal structure of GaAs between 0K to 1500K in the steps of 100K in which the maximum temperature is kept below the experimental melting point of GaAs, so that the quasiharmonic approximation remains valid [28].

Results and Discussion

Although, phonon dispersion curves and DOS plots were introduced with the presently used modified Stillinger-Weber potential in its original Ref. [21], there is not any quantitative comparison in this work. Therefore, we present phonon dispersion of GaAs for our case in Fig.1 for a numerical evaluation.

Fig.1. Phonon dispersion curve of GaAs along the Δ path.

Since experimental values of phonon modes were well established between the important Γ and X (Δ path) points of the Brillouin zone, we have also focused on this region. The

obtained dispersion in Fig.1 exposes a typical polar material dispersion in which the phonon mode $\omega_{LO(X)} > \omega_{TO(X)}$ at the zone center between Γ and X (Δ path).

Table 1. Comparing phonon frequencies of GaAs along the Δ path.

Phonon frequency	Present	Exp [30]	Powell et.al [16]
$\omega_{LO(\Gamma)}$ (cm ⁻¹)	286	297	314
$\omega_{TO(\Gamma)}$ (cm ⁻¹)	264	273	314
$\omega_{LO(X)}$ (cm ⁻¹)	226	241	277
$\omega_{TO(X)}$ (cm ⁻¹)	257	252	241
$\omega_{LA(X)}$ (cm ⁻¹)	216	227	232
$\omega_{TA(X)}$ (cm ⁻¹)	99	79	153

Besides, Table 1 also compares the present numerical data and experimental values [29] of the analyzed phonon frequencies. It is clear from both Fig.1 and Table 1. that our results for $\omega_{LO(\Gamma)}$, $\omega_{TO(\Gamma)}$, $\omega_{LO(X)}$ and $\omega_{LA(X)}$ are closer to measurements, whereas $\omega_{TA(X)}$ and $\omega_{TO(X)}$ slightly overestimates the experimental data. In other words, deviations from the experiments are -3.7%, -3.2 %, -6.2%, -4.8%, %25.3 and 1.9% for

$\omega_{LO(\Gamma)}$, $\omega_{TO(\Gamma)}$, $\omega_{LO(X)}$, $\omega_{LA(X)}$, $\omega_{TA(X)}$ and $\omega_{TO(X)}$, respectively. As an impressive result, our findings for the considered phonon frequencies of Δ path are very consistent with experimental data and better than those of Powell et al [16]. This satisfactory agreement certainly originates from the employed potential used in this study since it is mainly designed for the vibrational properties of GaAs.

Fig.2. Density of states of GaAs obtained from the present phonon calculations.

Table 2. Some thermodynamic data of GaAs at room temperature.

Parameter	Present	Exp [31]
S (J/mol.K)	63.36	64.18
C_v (J/mol.K)	46.27	46.85

Fig.2 outlines the corresponding DOS curve of present phonon calculations. Obtained DOS spectrum of this work is not only in harmony with the experimental spectrum of Ref [13] but also consistent with other theoretical curves [21]. In DOS spectrum, a first maximum linking with the ω_{TA} modes appear to be near a frequency value of 72.1 cm^{-1} and agree well with the measured data of 64.5 cm^{-1} [13]. Besides, short wavelength ω_{LA} modes contribute smaller peaks between

the frequency values of 224.1 cm^{-1} and 183.5 cm^{-1} and are consistent within the experimental values of 225.8 cm^{-1} and 185.5 cm^{-1} [13]. The massive concentration of optical phonons gives the largest peak near the frequency at 260 cm^{-1} and adequate enough when compared with the measured data of 266 cm^{-1} [13]. So, both phonon dispersion and DOS results of the present study well correspond within the experiments and give credence to this work.

Fig.3. Temperature dependence of vibrational Helmholtz free energy of GaAs.

Table 3. Comparing our results (given in parentheses) with the previous DFT results [15] for the pressure and temperature dependence of specific heat capacity data.

Temperature / Pressure	0 GPa	6GPa	10GPa	16GPa
300K	46.27 (46.91)	45.69 (46.14)	45.38 (45.68)	44.97 (45.04)
600K	48.93 (49.15)	48.77 (48.94)	48.68 (48.84)	48.57 (48.63)
900K	49.46 (49.58)	49.38 (49.48)	49.34 (49.42)	49.29 (49.34)
1200K	49.64 (49.72)	49.60 (49.66)	49.58 (49.63)	49.55 (49.58)

Fig.3 stands for the vibrational Helmholtz free energy of the GaAs between the temperatures 0K and 1500K. Similar to other III-V semiconductors [30], the vibrational Helmholtz free energy of the GaAs decrease

gradually with the increasing temperature. During this study, the room temperature value of the Helmholtz free energy of GaAs was obtained as -505.13 kJ/mol.K.

Fig.4 Comparing temperature dependence of vibrational entropy of GaAs.

Entropy is a key concept in thermodynamics. The entropy S is an important state function that holds for the effects of the irreversibility in thermodynamic systems. The change of entropy has often been defined as a change to a more disorder state at the molecular level [30]. Fig. 4 displays entropy of GaAs along the studied temperature interval. Present data

for the vibrational S indicates a fair accordance with the experimental data [31] as shown in Fig.4. The room temperature vibrational S value of GaAs was obtained as 63.36 J/mol.K after phonon calculations and found to be increase mostly exponentially with the increasing of temperature.

Fig.5 Comparing temperature dependence of constant volume specific heat capacity of GaAs.

Fig.5 depicts the calculated constant volume heat capacity (C_v) as a function of the temperature together with the experimental data adopted from Ref. [30]. Our data well agree with the experimental data for the C_v . Also, as seen in Fig. 5, C_v of GaAs increases exponentially up to $T < 400\text{K}$ and strictly follows the experiments up to 800K . However, after 800K , because of anharmonic effects at high temperatures our calculated C_v result begins to deviate from the experiments and approaches the Dulong-Petit limit (50 J/mol.K) [30] pointing out the thermal energy excites the all phonon modes at high temperatures.

Conclusion

In summary, we have applied a recent and modified Stillinger-Weber type potential for the first time to evaluate the both phonon and related thermodynamic properties of technologically important GaAs. As our results indicate, application of a Stillinger-Weber type potential well reproduces the phonon modes and corresponding density of states as well as other thermodynamic properties. Our new numerical values for considered properties agree well with the experiments and better than those of some former theoretical data. Finally, these novel results in detail may be helpful to the future theoretical works of GaAs.

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