

An ab initio study of ground state, electronic and thermodynamical properties of GaP and Ga₂P

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Abstract In the present paper, we report an ab initio calculation of the ground state, electronic and thermodynamical properties like constant volume lattice specific heat, vibrational energy, internal energy, and entropy for GaP and Ga₂P is presented. These properties are obtained after calculating the phonon spectrum over the entire Brillouin zone. The calculations were performed using the ABINIT program package, which is based on density functional theory (DFT) method and the use of pseudopotentials and plane wave expansion. Difference in the ground state properties such as electronic structure and thermodynamical properties are discussed. The thermodynamical properties follow the expected trend. There is a good agreement between present theoretical and limited available experimental data in the case of ground state such as lattice constant and bulk modulus and electronic properties. With the increase of Ga atoms in the unit cell the semiconducting nature of Ga₂P turns to metallic. There is a noticeable difference in the thermodynamical properties in the case of both gallium compounds.

Keywords Thermal properties · Semiconductor · Density functional theory · Band structure

Introduction

The chemistry and physics of the compounds formed by the elements in groups III and V is extraordinarily rich and

their usefulness in the semiconductor industries has been a motivation for numerous experimental and theoretical studies. An increasing interest to investigation of clusters is determined by the fact that cluster systems represent an intermediate state between atoms and bulk metals. Properties of clusters strongly depend on size, which provides a potential ability of application of clusters in nanotechnologies. Moreover, clusters can be considered as models of surface and thin films, and cluster models are widely used for investigation of adsorption and heterogeneous catalysis [1]. The study of materials and their thermodynamical properties is experiencing recent activity because of its fundamental research interest and technological applications in the field of microelectronics and optoelectronics, as a substrate for high speed electrical and optoelectronic devices, optical switches, and so on [2, 3]. The comprehension of mechanisms of fabrication processes such as chemical etching depends on the thermodynamic and kinetic data of the chemical species, which in turn require elucidation of the low-lying states of these species. Furthermore, theoretical and experimental studies of such clusters provide significant insight into the properties of these species as a function of their sizes, as these species exhibit significant variations in their properties.

In these structures, each atom is tetrahedrally bonded to its first neighbors [2, 3]. The gallium arsenide clusters of the general formula Ga_xAs_y using laser-vaporization of gallium arsenide crystal has been generated recently [4]. The photofragmentation pattern of these clusters also deviated from the corresponding patterns of the group IV clusters as a function of their sizes. In this regard, photoelectron spectroscopy (PES) has proven to be a very useful technique for studying the electronic and vibrational structures of mass-selected clusters [5, 6]. One of the key problems in the investigation of clusters is the

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limited data on their geometry and hence further study of structural, electronic and thermal properties of clusters is very important. Peltier devices [7] and the studies in this area are aimed at clarifying the role of quantum confinement of phonons on the thermoelectric figure of merit of the entire device. Melting and fragmentation of clusters are studied to gain insight in the cluster bonding mode by eliciting the existence of stable units within the cluster structure [8]. For this purpose clusters formed by rare-gases, metallic and covalent elements have been considered and the number of studies on this subject is now very abundant [9]. Recently, Hayashi et al. [10] investigated electronic states of low lying of Ga_2X ($\text{X} = \text{P}, \text{As}$), which are nearly degenerate. They used effective core pseudopotentials of the Ga and As atoms and the associated cc-pVTZ basis sets for geometry optimization and vibrational frequency calculation. Neumark and co-workers [11] reported anion photoelectron spectroscopy of Ga_xP_y clusters having 18 atoms. Here, they showed the adiabatic electron affinities (AEAs) of the neutral clusters and estimated the vertical excitation energies involving the low-lying electronic states of the neutral species. Prior to the work of Neumark and co-workers, Weltner and his associates [12, 13] have obtained the far-infrared spectra of small gallium arsenide molecules obtained by laser vaporization into Ar and Kr gases followed by condensation on a Au surface at 4 K. Andreoni [14] used molecular dynamics to study the structure, stability, and melting of small clusters of GaP.

To our knowledge, there are no reports of ab initio thermodynamical calculations on Ga_2P so far. The first-principle pseudopotential method for total-energy calculations [15] has been shown to be capable of predicting ground state electronic and thermal properties of properties for group-IV elements and their structures. In the present paper, we have come out with a study on the structural, electronic and thermodynamic properties of the GaP and Ga_2P using the ab initio pseudopotential method based on local density approximation of the density functional theory (DFT). The thermodynamical properties have been calculated using density functional perturbation theory (DFPT). Differences in the ground state, electronic and thermodynamic properties of GaP and Ga_2P compounds have been discussed.

Computational details

Cluster expansion, whereby properties are expanded in terms of the distribution of atoms on a topology of sites, is a powerful technique for the optimization or ensemble averaging of properties. Its most common use is in the

parametrization of total energy and derivatives thereof, although there have been extensions to other properties such as ground state properties. The cluster expansion of total energy has been used extensively, often with ab initio calculations, to build effective Hamiltonians for the prediction of thermodynamic and electronic properties. Unlike atomic potential models, which are rapidly evaluated but require extensive chemistry-dependent parametrization and are not universally available, or ab initio calculations, which are almost universally available but are computationally intensive, the cluster-expansion approach is a widely applicable parametrization method which allows rapid evaluations for a large number of different atomic configurations.

To determine the electronic structure and thermal properties in GaP and Ga_2P , we have performed density functional theoretical calculations using ABINIT code (The Abinit Code is a common project of the University Catholique de Louvain, Corning Incorporated, and other contributors <http://www.abinit.org>). The local density approximation (LDA) has been used for the exchange and correlation energy density function. A fully relativistic calculation is performed for core states, whereas the valence states are treated in a scalar relativistic scheme. In order to find an appropriate energy cutoff, the total energy as a function of the energy cutoff has been calculated for 23 different energy cutoff ranging from 10 to 125 Ry. The total energy converges near the energy cutoff of 50 Ry for GaP and Ga_2P . The self consistent calculations are considered to be converged when the total energy of the system is stable within 5–10 Ry. Here, for the self consistency, the initial potential for the next iteration is constructed using a convergence stabilization scheme. The number of sampling k -points used in the Brillouin zone (BZ) summation of the electronic density and total energy is increased until the total energy converges to the desirable tolerance. Thirty six special k -points in the irreducible BZ are sufficient to achieve the convergence for the total energy. To generate the $(4 \times 4 \times 4)$ mesh for GaP and $(8 \times 8 \times 8)$ mesh in Ga_2P the BZ, the scheme of Monkhorst–Pack [16] has been used. The crystal structure and associated equilibrium lattice constants for both compounds have been obtained by minimizing the calculated total energies as function of a lattice constant. Further, to calculate the lattice dynamics of GaP and Ga_2P , we have used density functional perturbation theory (DFPT) [15]. In this method, the dynamical matrix which provides information on lattice dynamics of the system can be obtained from the ground state electron charge of the nuclear geometry. The kinetic energy cut off and numbers of k -points mentioned above are found to yield phonon frequencies converged to within $2\text{--}5 \text{ cm}^{-1}$.

Table 1 Calculated equilibrium lattice constants (Å), bulk modulus (GPa) and first order pressure derivative for GaP and Ga₂P

Compound	Parameters	Present work	Experimental	Other calculations
GaP	<i>a</i>	5.2953	5.451 ^a	5.34 ^b , 5.386 ^c , 5.35 ^f , 5.36 ^f
	<i>B</i>	86.396	88.1 ^d	89.7 ^b , 86.8 ^c , 106 ^f , 96 ^f
	<i>B'</i>	4.337	4.79 ^e	4.0 ^c , 2.95 ^f , 3.44 ^f , 3.10 ^f
Ga ₂ P	<i>a</i>	5.7449		
	<i>B</i>	67.54		
	<i>B'</i>	4.64		

^a [17]^b [20]^c [21]^d [18]^e [19]^f [22]

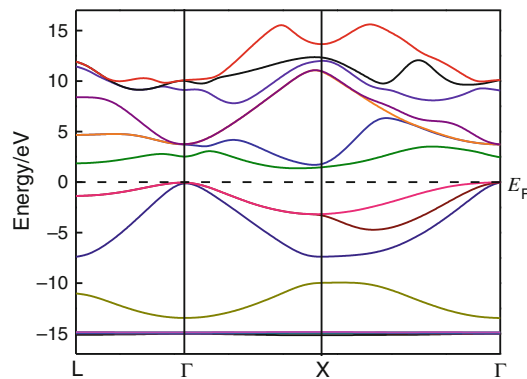
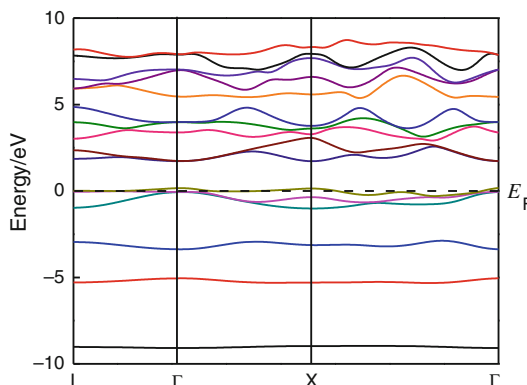
Results and discussion

To calculate any ground state properties, we need to first optimize the crystal structure and obtain the equilibrium ground state lattice constant. The GaP compound considered here has zinc blende structure (space group 216) with Wyckoff positions of atoms Ga (0.00,0.00,0.00) and P (0.25,0.25,0.25), whereas Ga₂P compound considered has perovskite structure with Wyckoff positions of atoms Ga (0.25,0.25,0.25), Ga (0.75,0.75,0.75), and P (0.00,0.00,0.00) (space group 225). The theoretical ground state properties such as lattice parameter, bulk modulus, and pressure derivative of bulk modulus of GaP and Ga₂P are obtained using the method discussed in above section and listed in Table 1, which also includes the available experimental [17–19] and other theoretical data [20–22] for the comparison. The total energy versus volume curve is fitted to the Birch–Murnaghan equation of state [23] to obtain the bulk modulus value as below

$$E(V) = E_0 - \frac{B_0 V_0}{B'_0 - 1} + \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] \quad (1)$$

where B_0 and B'_0 are the bulk modulus and its derivative, respectively, E_0 is the ground state total energy and V_0 is the volume.

To analyze the electronic properties of GaP and Ga₂P, we present electronic bandstructure along the high symmetry directions in first BZ using the calculated equilibrium lattice constant in Figs. 1 and 2 for GaP and Ga₂P, respectively. Further, Fig. 1 depicts a large band opening below Fermi level at Γ -point ($E - E_F$ is set to zero). The

**Fig. 1** Calculated energy band structure of GaP**Fig. 2** Calculated energy band structure of Ga₂P

levels at the symmetry points have been connected by smooth curve and crossings of bands are observed, which is due to relative magnitudes of effective masses. In Fig. 2, the bands at Γ - and X -points touch or approach to the Fermi level ($E - E_F$), shows nearly metallic nature of the Ga₂P compound. This indicates the transformation of semiconducting GaP to metallic with the formation of clusters.

The general features of the bands for the compounds GaP and Ga₂P are different. There are more bands above Fermi level in both compounds. The bands are more dispersive near Fermi level in the case of GaP. The two distinctive flat bands near -15 eV in the case of GaP shift to lower value. The nearly 1.9 eV gap observed in GaP is in fairly good with the experimental report [24] (~ 2.2 eV). Further, above Fermi level in Fig. 2, more bands are observed, which is due to one extra Ga atom, contributing more bands to conduction bands. In the case of GaP (Fig. 1), above Fermi level some bands are crossing each other at Γ -point.

The total electronic density of states (DOS) for the two compounds are displayed in Figs. 3 and 4 for GaP and Ga₂P, respectively. The key features of the DOS for the two compounds are quite similar. It is interesting to note that there is a sharp peak in the DOS close to the Fermi

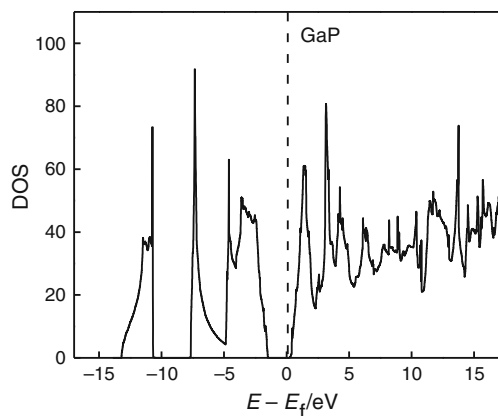


Fig. 3 Calculated density of states for both GaP

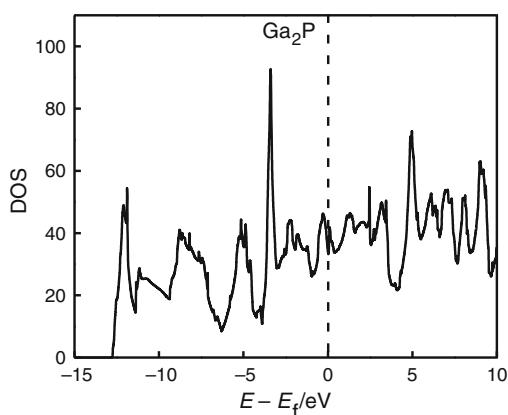


Fig. 4 Calculated density of states for both Ga₂P

level for Ga₂P. This peak is associated with the quasiflat bands close to the Fermi level that is predominantly due to Ga d_{xz} , d_{yz} states; while in the case of GaP, the lower bands of the conduction band partially touching Fermi level indicate the semiconducting nature of GaP. Further, there is another bandgap in DOS in energy range -12.23 eV to -4.9 eV for GaP, which confirms the semiconductor behavior, but this is shifted to higher energy in the case of Ga₂P. This is due to the strong hybridization resulting in covalent bonding and separation of the bonding states. The less intense peaks at Fermi level in Fig. 4 is due to the contribution of Ga 'd' and 'd' states hybridization. No gap in the case of Ga₂P at the Fermi level indicates the metallic nature of Ga₂P.

A complete knowledge of the vibrational spectrum over the entire BZ is required for the calculation of the thermodynamic function like the Helmholtz free energy (ΔF), the internal energy (ΔE), the entropy (S), and the constant volume specific heat (C_v), at temperature (T). They are calculated using the following formulas within the harmonic approximation [25].

$$\Delta F = 3nNk_B T \int_0^{\omega_{\max}} \ln \left\{ 2 \sin h \frac{\hbar \omega}{2k_B T} \right\} g(\omega) d\omega \quad (2)$$

$$\Delta E = 3nN \frac{\hbar}{2} \int_0^{\omega_{\max}} \omega \cot h \left(\frac{\hbar \omega}{2k_B T} \right) g(\omega) d\omega \quad (3)$$

$$S = 3nNk_B \int_0^{\omega_{\max}} \left[\frac{\hbar \omega}{2k_B T} \cot h \frac{\hbar \omega}{2k_B T} - \ln \left\{ 2 \sin h \frac{\hbar \omega}{2k_B T} \right\} \right] \times g(\omega) d\omega \quad (4)$$

$$C_v = 3nNk_B \int_0^{\omega_{\max}} \left(\frac{\hbar \omega}{2k_B T} \right)^2 \csc h^2 \left(\frac{\hbar \omega}{2k_B T} \right) g(\omega) d\omega \quad (5)$$

where k_B is the Boltzmann constant, n is the number of atoms per unit cell, N is the number of unit cells, ω_{\max} is the largest phonon frequency, ω is the phonon frequency, and $g(\omega)$ is the normalized phonon density of states with integration $g(\omega)d\omega$. Figures 5, 6, 7, and 8 display the

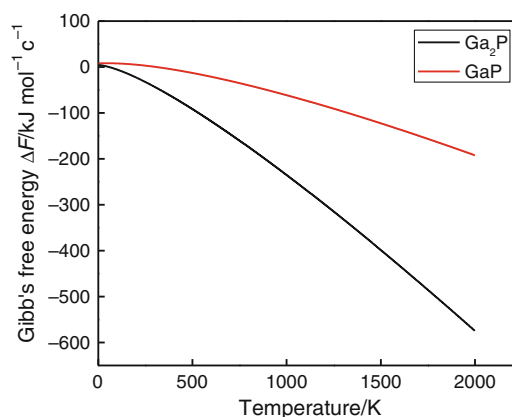


Fig. 5 Calculated Gibbs's free energy as a function of temperature for both GaP and Ga₂P

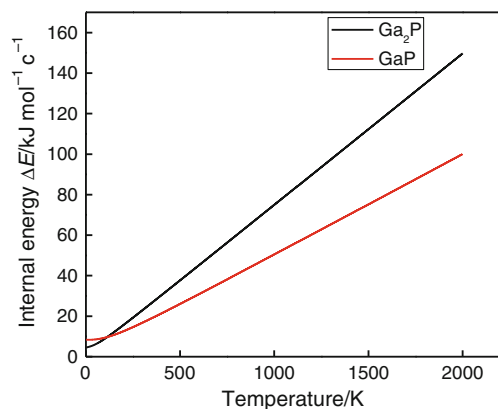


Fig. 6 Calculated internal energy as a function of temperature for both GaP and Ga₂P

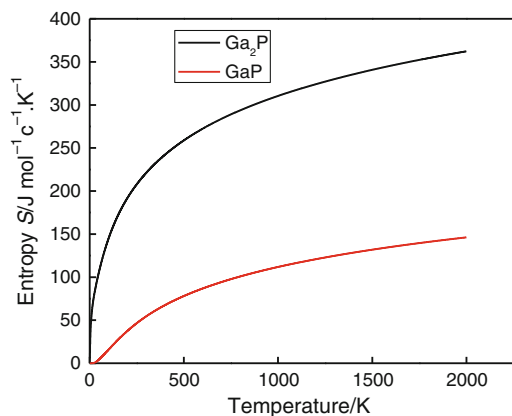


Fig. 7 Calculated entropy as a function of temperature for both GaP and Ga₂P

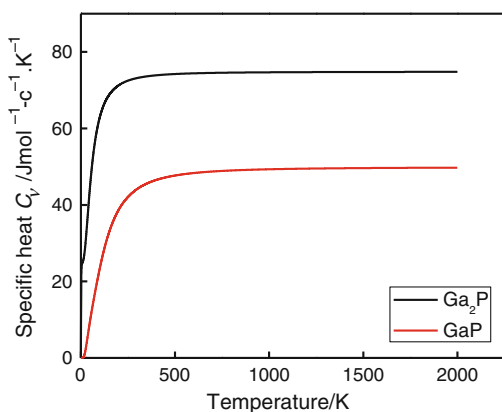


Fig. 8 Calculated specific heat as a function of temperature for both GaP and Ga₂P

calculated ΔF , ΔE , S , and C_v , respectively, for the GaP and Ga₂P, the shape of which is similar, while the range is different.

At the low-frequency limit, the factor multiplying the densities of states shows logarithmic divergence in Eqs. 2 and 5, and quadratic divergence in generalized density of states, which contains the Debye–Waller factor. However, since the density of states and generalized density of states both behave as the square of frequency at the low-frequency limit, the actual integrand behave regularly, approaching to zero.

The zero-temperature values of Helmholtz and internal energies, ΔF_0 and ΔE_0 , respectively, do not vanish, due to the zero point motion in both compounds. However, the value of ΔF_0 and ΔE_0 is higher for GaP than Ga₂P. This may be due the small additional energy due to effective mass of gallium and its relative mass. The ΔE is larger at higher temperatures for Ga₂P (Fig. 6). The calculated entropy and the constant volume specific heat for GaP and Ga₂P are plotted in Figs. 7 and 8, respectively. The entropy of Ga₂P at $T = 0$, $\Delta S_0 = \Delta E_0 \sim 348$ J/mol-c.K is twice than that of

GaP, while ΔF is lower in the case of Ga₂P. This corresponds to the more rigid structure. It is also noted that the entropy $\Delta S = 0$ reaches at nearly 0 K in case of Ga₂P (Fig. 7), but it shows somewhat different behavior for GaP (see Fig. 7), which may be due to some disorderness present in the structure and correspond to non-rigid structure.

From Fig. 8 it is clear that the constant volume specific heat for both compounds has a similar trend, but with different values in almost all temperature range. It is shown that when $T < 300$ K the heat capacity C_v is dependent on temperature T due to the anharmonic approximation of the Debye model. The specific heat is larger for Ga₂P than GaP. At room temperature the specific heat C_v is 74.3 J/mol-c.K for Ga₂P which is almost double than that for GaP. The reason may be thermal expansion due to the anharmonic interaction is larger in Ga₂P than in the GaP. There is slight anomaly at very low temperature in the case of Ga₂P where it seems that the temperature dependence of specific heat shows a slight deviation from Debye T^3 law. In summary, it is expected that the Ga₂P can be better used in the thermal devices.

Conclusions

In conclusion, we have presented the ground state, electronic and thermal properties of GaP and Ga₂P using the local density approximation of the DFT and ab initio pseudo potentials first principles method. Our calculated results for the lattice constants and bulk modulus agree reasonably well with the earlier theoretical and available experimental results. Lattice dynamics of these two III–V group compounds has been studied by employing a linear response approach based on density functional perturbation theory to calculate the thermodynamical properties. The thermal properties of these compounds are reported for the first time. There is a remarkable difference in the case of Ga₂P in comparison to GaP. The specific heat at constant volume is almost double for Ga₂P than for GaP, which may be useful for the thermo-elastic devices.

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