Ab initio phonon dispersion calculations for $\text{Ti}_x\text{Ga}_n\text{As}_m$ and $\text{Ti}_x\text{Ga}_n\text{P}_m$ compounds

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Abstract

We have calculated and predicted the phonon dispersion and phonon density of states of $\text{Ga}_n\text{As}_m\text{Ti}$ and $\text{Ga}_n\text{P}_m\text{Ti}$ half-metallic semiconductor compounds using an eight-atom simple cubic cell structure. We use the ab initio density functional frozen phonon method in the LDA and GGA approximation. We have first determined the phonon spectra of $\text{GaAs}$ and $\text{GaP}$ and found very good agreement with experimental results. We find that (i) in all $\text{Ga}_n\text{As}_m\text{Ti}$ and $\text{Ga}_n\text{P}_m\text{Ti}$ cases studied, the acoustic modes could be easily identified with the phonon modes of $\text{GaAs}$ and $\text{GaP}$ respectively, and (ii) additional Ti high frequency optical modes appear well separated in all the Brillouin zone for $\text{Ga}_3\text{As}_4\text{Ti}$ and $\text{Ga}_3\text{P}_4\text{Ti}$ semiconductor compounds.

Keywords: Phonon spectra; Intermediate band semiconductor; Low energy photons

1. Introduction

Over the past few decades, a detailed knowledge of the electronic and optical properties of important semiconductor materials such as $\text{GaAs}$ or $\text{GaP}$ has been obtained [1]. The optical properties of several III–V diluted semiconductors with the technological possibility of their used as high efficient photovoltaic materials have been the focus of this theoretical study.

Recently, band structures of ternary semiconductor compounds of the $\text{GaAsX}$ and $\text{GaPX}$ type, X being a transition metal, have been investigated in the cubic zincblende structure using an accurate ab initio code based on the density functional theory [2]. Results obtained for these compounds
present in some of their structures an isolated intermediate half-filled band located in the semiconductor energy band gap, showing both direct and indirect band gaps in their calculated band diagrams [3,4].

The quantum efficiencies of the photovoltaic conversion of these materials are related to efficient light absorption. It is important for the intermediate band to be isolated from the ordinary band to avoid fast de-excitation as a result of the interaction with phonons. We have searched for compounds with an intermediate band and not an isolated level, as in the case of impurities, to avoid the non-radiative recombination process, which drastically reduces the efficiency of the photovoltaic cells [5].

Using the intermediate band to enhance the use of sub-band gap energy photons, optical absorption could be determined by means of quantum mechanic calculations of the transition matrix elements between the corresponding band states. However, due to the major LDA and GGA shortcoming associated with excitation energies, mainly represented by band gap problems in semiconductors, the ab initio calculations of the optical properties for the related host GaAs and GaP semiconductors still show large discrepancies from experiments. In order to be consistent with the experimental values, we have implemented and applied the exact exchange method (EXX) to improve all the results [6]. In particular, the application of the EXX to the TiGa₄As₃ and TiGa₄P₃ systems, still confirms the existence of the half-metallic intermediate band isolated in the semiconductor band gap with two sub-band gaps, one direct and other indirect involving coupling with phonons for optical absorptions [7].

At the moment, only ab initio studies of the optical properties for direct transitions have been carried out on TiGa₄As₃ and TiGa₄P₃ systems [8]. However, because these materials exhibit both direct and indirect transitions in their band structures in the multiple band gaps, and in taking into account all these possible transitions, phonons spectra and electron-phonon coupling must be determined.

In the present work, first-principles theoretical investigations of the phonon spectra and phonon density spectra (DOS) of these novel semiconductor GaₙAsₙTi and GaₙPₙTi compound systems have been studied using the frozen phonon approximation as implemented in the SIESTA program [9]. It has been well established that GGA calculations give total and cohesive energies closer to experimental ones than the LDA in semiconductors, but at the same time lattice parameters are overestimated. For these diluted semiconductors materials we have found the same behaviour compared to that of the host semiconductors [3,4]. We now use both LDA and GGA approaches to determine the phonon properties of these compounds to understand the effect of the lattice parameter increase on the vibrational eigen-modes. To assess the validity of our results, we present first, equivalent ab initio calculations for GaAs and GaP host semiconductors. The calculated LDA phonon dispersion curves for the binary systems are in very good agreement with experimental points measured by inelastic neutron scattering [10,11]. In Section 2, we describe the calculation methods and in Section 3, we present and discuss the results of our calculations.

2. Calculation methods

To determine phonon dispersion curves and phonon density spectra of the crystalline structure, the frozen-phonon method or direct approach [12,13] requires the use of supercells where the ab initio force constant matrix is calculated in real space. The method does not depend on the symmetry of the crystal and the capacity to obtain forces on the ions allows simple calculations of the phonons in specific parts of the Brillouin zone. The supercells must be created in those directions in which we may have periodicity, in our case in all the space and distances have to be sufficiently large so that the neighbour’s interaction tends to zero.

To obtain the vibration eigen-frequencies, the interatomic force constant representing the interaction between atom pairs must be determined first. An atom $j$ in a primitive cell $l$, of bulk $M_j$, is displaced in the balance by $u(l)$ when a vibration is produced in the net. The force in each atom comes given as the second derivative from total energy.
\[ \Phi_{ij}(l', j') = \frac{\partial^2 E}{\partial u_{ij}(l) u_{ij}(l')} \]

Here \( z_p \) are polarization vectors and \( l' \) and \( j' \) are the positions of atoms in the unit cells \( R \) and \( R' \) respectively. The vibration mode is defined as a movement: \( F_{ij} = -M \omega^2 u_{ij}(l, j) \).

Small displacements of each atom of the central cell inside the supercell in different directions take place and then, the forces exercised on the others atoms of the supercell are calculated. The fast Fourier transformed to the dynamical matrix for each \( k \), \( D(k) \) is then obtained

\[ D_{ij}(j'|k) = \sum \frac{1}{\sqrt{M_i M_j}} \Phi_{ij}(0l') \epsilon^k [x_l - x_0] \]

and the secular equation is solved: \( -\omega^2 \Phi = D(k) \Phi \).

The ground state descriptions of the systems are obtained first by using the direct diagonalization method of the fully self-consistent ab initio SIESTA [9] program. The code makes all the calculations projecting electron wave functions and density onto a real space grid. The basis set used to describe valence electrons was a double zeta plus polarization DZP (2s and 6p orbitals for Ga, As, and P and 2s and 10d orbitals for Ti adding 5d orbitals more for Ga, As and P and 3p orbitals more for Ti for the polarization) with different cutoff radius for s, s', p, p' and d orbitals. The calculations were made first for GaAs and GaP binary systems and then for the different Ga\(_n\)As\(_{3-n}\)Ti and Ga\(_n\)P\(_{n}\)Ti alloy systems to determine the ground state lattice parameters and phonon spectra. An 8-atom simple cubic cell, where a single Ti atom replaces one atom of Ga or one atom of As (or P) respectively have been used. The model is illustrated in Fig. 1 and is assumed to have the smallest possible unit cell and retain the highest symmetry. In this work, we use both the local-density approximation (LDA) in the Ceperley–Alder form [14] with the parametrization fitting given by Perdew and Zunger [15] and the generalized gradient approximation (GGA) corrections in the form of Perdew, Burke, and Ernzerhof (PBE) [16] for the exchange-correlation potential. The core electrons were replaced by Troullier–Martins norm-conserving pseudopotentials [17] in the Kleinman–Bylander form [18] and were taken to be the 3p electrons and below for Ti, 2p and below for P, and 3d and below for Ga and As. We tested the convergence with respect to the basis set and \( k \)-point samplings in the calculations for all systems. The equivalent cutoff energy in a real space grid from the transformed charge density was approximately 80 Ry. This relatively large mesh cutoff is needed to describe the localized d states of titanium. We used more than 200k points for the simple cubic unit cell. To determine the equilibrium structure of the systems studied, all the atomic coordinates were relaxed until the largest force components were below 0.001 eV/Å.

### 3. Results of phonon calculations

In absence of neutron scattering data for the Ga\(_n\)As\(_{3-n}\)Ti and Ga\(_n\)P\(_{n}\)Ti alloy systems, we have calculated first the LDA and GGA phonon spectrum of pure binary compounds GaAs and GaP in the two atoms zinc-blende structure with a DZP basis for all atoms, in order to compare as benchmark our results with the available experimental data from inelastic neutron scattering in the crystals. Phonon dispersion spectra results for the LDA calculation for the two systems are shown in Fig. 2 in high symmetry fcc directions together with the experimental points [10,11]. GaP phonon spectra exhibits as expected, a wider phonon gap between
the acoustical and optical modes, because a larger mass difference between the atoms. Our ab initio calculations are in very good agreements with the experiment data and other published theoretical work [19,20]. The largest discrepancy appears for the LO optical phonon at the limit of the \( \Gamma \)-point where the macroscopic electric field of the long range ion–ion interaction modifies the LO modes. No LO–TO phonon splitting is shown in our frozen-phonon calculations. However, the overall shape of all phonon spectra is reproduced very well for the both systems.

Then, we have made the calculations for GaP (GaAs) using both the LDA and GGA exchange and correlation potential, with an eight-atom simple cubic cell structure to compare to the similar phonon structure of the \( \text{Ga}_n\text{As}_m\text{Ti} \) and \( \text{Ga}_n\text{P}_m\text{Ti} \) alloy systems. The optimized lattice parameter constants for GaP (GaAs) for LDA calculation are 5.44 (5.68) Å and for GGA calculations are 5.63 (5.85) Å, compared with the experimental data 5.45 [11] (5.65 [10]) Å respectively. LDA lattice constants calculations agree very well with experimental ones whereas the theoretical GGA lattice constants show a lattice expansion of 3.3 (3.5)% respectively. Fig. 3 shows the GaP two phonon spectra displayed in the fcc structure in several high symmetry directions. The results exhibit smaller frequencies values for the GGA case in all vibrational modes related to the LDA one. This is a consequence of the lattice constants increase in this method that softens the frequencies of the phonons and worsens the results. We have
observed the same behaviour for LDA/GGA phonon dispersion relationship in the GaAs system.

We then determine the lattice dynamics and phonon density of states (DOS) of all Ga$_n$As$_{4-n}$Ti and Ga$_n$P$_{4-n}$Ti alloy periodic systems with the same simple eight-atom cubic cell structure and ab initio calculation conditions as before, in order to analyze the influence of the Ti atom in the high energy vibration lattice dynamics.

In Fig. 4, we compare the computed phonon dispersions spectra of Ga$_3$As$_4$Ti and Ga$_3$P$_4$Ti, in the LDA with the GGA calculations. As expected, we found a wider phonon gap in Ga$_3$P$_4$Ti between the acoustical and optical modes (52.45 cm$^{-1}$ in the LDA case) and higher phonon frequencies than in Ga$_3$As$_4$Ti, for both LDA and GGA cases, because the greater difference in masses as in the corresponding binary system (Fig. 2). Moreover, the appearance of the acoustic modes of the new structures remains almost unchanged. However, in the both ternary systems and for the two different LDA and GGA exchange and correlation potential, in the optical branches new additional isolated high vibrational optical modes appear in the main high symmetry direction in the whole Brillouin zone corresponding to the Ti atoms vibrations. Since there is a greater mass difference between Ti and As than in the Ti and P, these new optical vibrational modes have a wider phonon optical gap ($\Delta = +35.90$ cm$^{-1}$) in the Ga$_3$As$_4$Ti. These results are clearly shown in frequency in the DOS displayed in Fig. 5 for these two systems. Moreover, as is shown in Fig. 5, all calculated GGA phonon modes have lower energies than

![Fig. 4. Phonon dispersion diagram. LDA (solid line), and GGA (dashed line) displayed in the fcc high symmetry directions in the Brillouin zone for the (a) Ga$_3$As$_4$Ti and (b) Ga$_3$P$_4$Ti systems.](image)

![Fig. 5. Phonon density of states. LDA (solid line) and GGA (dashed line) for the (a) Ga$_3$As$_4$Ti and (b) Ga$_3$P$_4$Ti systems.](image)
the corresponding LDA ones, because of the lattice expansion of the GGA values as already explained.

Fig. 6 present GGA calculations of phonon spectra for Ga₄As₃Ti and Ga₄P₃Ti alloy semiconductor systems. The general pattern of these spectra shows lower vibrational energies for all acoustical and optical modes compared with the GGA calculations of the corresponding Ga₃As₄Ti and Ga₃P₄Ti (Fig. 4). However, the new optical modes of highest vibrational energy due to the small Ti mass are broader and less sharp than those of the aforementioned dilution, as displayed in Fig. 7 for the corresponding density of states.

All theoretical lattice constants obtained for these GGA and LDA calculations after the dynamical relaxation of the systems, are detailed in Table 1.

![Fig. 6. GGA phonon dispersion diagram displayed in the fcc high symmetry directions in the Brillouin zone for the (a) Ga₄As₃Ti. (b) Ga₄P₃Ti systems.](image)

![Fig. 7. GGA phonon density of states for the Ga₄X₃Ti systems. X = As (solid line) and X = P (dashed line).](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>a₀(LDA)(Å)</th>
<th>a₀(GGA)(Å)</th>
<th>a₀(exper.)(Å)</th>
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<tr>
<td>Ga₃As₄Ti</td>
<td>5.68</td>
<td>5.85</td>
<td>5.65</td>
</tr>
<tr>
<td>Ga₃P₄Ti</td>
<td>5.44</td>
<td>5.63</td>
<td>5.45</td>
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<tr>
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<td>Ga₄P₃Ti</td>
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<tr>
<td>Ga₃As₄Ti(Ti)</td>
<td>5.70</td>
<td>5.87</td>
<td></td>
</tr>
</tbody>
</table>

We also show the experimental lattice constant for Ga₃As₄Ti and Ga₃P₄Ti.

4. Conclusions

We have calculated accurate ab initio LDA and GGA phonon dispersion relations and density of states for GaₙAsₘ₉Ti and GaₙPₘ₉Ti alloy semiconductor systems, using the frozen phonon method. We have calculated first, with similar accuracy, the phonon spectra of the host Ga₃As₄Ti and Ga₃P₄Ti semiconductors and compared them with experimental data in order to validate our results of the ternary systems. We found that the LDA ab initio calculations are in very good agreement with the experimental data. The corresponding Ti diluted semiconductor compounds present many more dispersion phonon curves in all cases. The acoustic modes of the GaₙAsₘ₉Ti and GaₙPₘ₉Ti compounds could be easily identified with the phonon modes of Ga₃As₄Ti and Ga₃P₄Ti respectively.
However, we found for the optical branches additional high vibration modes in all Brillouin zone for all Ti substituted semiconductor compounds studied. Due to the larger mass difference between the Ti and As, these new optical vibrational modes have higher phonon energies in the Ga$_3$As$_4$Ti case. Moreover, ab initio computations of systematically accurate vibrational frequency of Ti transition metal impurity substitution are very sensitive on the specific bonding geometry and electronic structure mainly for the optical phonon branches.

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