

# First-principles study on the formation energies of $\text{Ga}_{1-x}\text{Cr}_x\text{As}$

N Martínez<sup>1,2</sup> and J A Rodríguez Martínez<sup>1</sup>

<sup>1</sup> Universidad Nacional de Colombia, Bogotá, Colombia.

<sup>2</sup> Universidad de los Llanos, Villavicencio, Colombia.

E-mail: nmartinez@unillanos.edu.co

**Abstract.** The electronic structure and formation energy of the  $\text{Ga}_{1-x}\text{Cr}_x\text{As}$  compound has been studied by principles of methods based on the Density Functional Theory. The formation energy of the compound is calculated, as well as the vacancies and substitutions. The equations of Kohn-Sham are solved employing the plane wave method and the ultra-soft atomic pseudopotentials approximation. The generalized gradient approximation was employed for the exchange and correlation energy in the Perdew-Burke-Ernzerhof (PBE) parametrization as it is implemented in the computational code Quantum Espresso. It was found that the most favourable configuration is the GaAs lattice by doing the substitution of one Ga atom by one Cr in the analyzed lattices.

## 1. Introduction

The analyzed structures in this study of the formation energy compound  $\text{Ga}_{1-x}\text{Cr}_x\text{As}$  are: cubic cell of pure GaAs, 1x1x2 and 2x2x2 supercells, with vacancies and substitutions as detailed below.

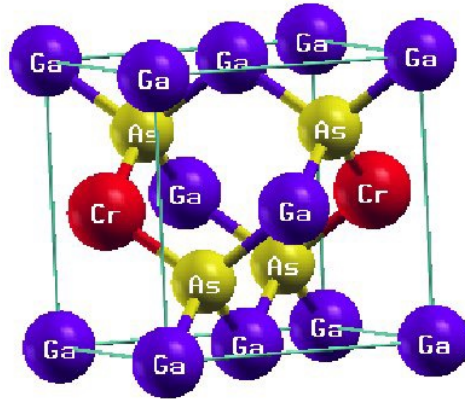
The  $\text{Ga}_{1-x}\text{Cr}_x\text{As}$  ( $x=0.25$ ) structure is presented in the Figure 1, the substitution was done in the position (0.0, 0.5, 0.5). As each atom is bound to other 4 atoms of opposite kind, forming a regular tetrahedron, the surrounding of each one is similar. For instance, it can be done in any position of a Ga atom and the results will not present relevant variations because of the lattice symmetry. When a Ga atom is substituted by one Cr in the right position, the structure is considered cubic.

For each As atom the surrounding is similar, since it is bound to 4 Ga atoms, forming a regular tetrahedron. A similar situation happens for each Ga atom that bonds with four As atoms. The As atom that is located at position (0.25, 0.25, 0.25) is bound to the Ga atom that is located at (0.0, 0.5, 0.5). At the Ga atom site, the substitution by the Cr atom was made; and there, the Ga vacancy was made too. As a result, the As vacancy was generated at (0.25, 0.25, 0.25). This process was necessary to do the comparisons and analysis of the structural, electronic and magnetic alterations of the compounds.

In order to analyse the possible alterations that the formation energy of the  $\text{Ga}_{1-x}\text{Cr}_x\text{As}$  suffers, the concentration of the Cr atom was varied from 0.25 to 0.125, creating a 1x1x2 structure. The concentration value of the Cr atom agrees with what is reported by L. M. Sandratskii *et al* [1] and Masafumi Shirai [2]. The substitutions of the Ga atom were made by the Cr in different positions, finding that the most stable is at (0.50, 0.50, 0.00). In the same way, it was demonstrated that in terms of formation energy, it will not change significantly in the diverse positions considered for the Cr atom. In the structure without vacancies and no substitutions, the As atom is at position (0.75, 0.75, 0.125). It is bound to four Ga atoms; one of them is located at (0.50, 0.50, 0.00). It was made a substitution by Cr, in the mentioned site of the Ga. In addition, the Ga vacancy was made in that site



also. Due to the reasons mentioned before, the As vacancy was generated in the site indicated at the beginning of this paragraph.



**Figure 1.** The crystal structure of Ga(Cr)As.

The  $2 \times 2 \times 2$  supercell has a lattice constant  $a = 11.32 \text{ \AA}$ . The Zincblende structure was taken to calculate it, and it was repeated in each axis twice. When the formation energy of the compounds is analysed, as presented in the results chapter, it is found that changing the atomic position for the substitution; does not exhibit big alterations. It is due to the reason that the surrounding of each As atom is similar, as well as the surrounding of each Ga atom. In addition, a  $2 \times 2 \times 2$  supercell was employed for the compound  $\text{Ga}_{1-x}\text{Cr}_x\text{As}$  with a Cr concentration of 0.03125. The concentration value of the dopant agrees with what is reported by V.I. Baykov, *et al* [3], and L. M. Sandratskii *et al* [1]. A substitution of one Ga atom by one Cr was made in this  $2 \times 2 \times 2$  supercell, at position (0.00, 0.75, 0.25), because of the reasons explained in the previous paragraph.

In order to do the comparisons and analysis of the structural, electronic and magnetic alterations of the compounds, it was necessary to do a substitution of the Ga atom at position (0.00, 0.75, 0.25) by a Cr atom. That Gallium atom is bound to other four As atoms, one of them is located at position (0.125, 0.125, 0.125). In that site, an As vacancy was made, and a Ga vacancy was also made in its corresponding site.

## 2. Parameters optimization

The calculations were done under the formalism of the Density Functional Theory, employing the plane wave methods and the ultrasoft atomic pseudopotentials, as it is implemented in the computational code Quantum Espresso [4]. The plane wave basis was expanded to an energy cut-off of 30Ry. The G vectors that allow the expansion are vectors of reciprocal lattice. Initially, an infinite number of vectors are required to represent the wave functions with an infinite precision. However, the expansion of the plane waves may be truncated to a finite number of terms, to limit the wave functions with a lower kinetic energy than an energy cut-off  $E_{\text{cutoff}}$  [5].

The Generalized Gradient Approximation (GGA) was used to get the exchange and correlation effects, in the parametrization of Perdew, Burke and Ernzerhof (PBE) [6]. The GaAs was studied in the Zincblende crystallization phase, with a constant optimized lattice of  $5.66 \text{ \AA}$ , employing a k Monkhorst-Pack point mesh [7] of  $6 \times 6 \times 6$ , in the first Brillouin zone.

In order to choose the entrance parameters of the calculations, the Energy cut-off was optimized and the K points mesh, according to the equilibrium volume and the lattice constant. The value of the minimum energy is calculated by using the Murnaghan state equation, equation [8].

## 3. Results and discussion

In Table 1, it is presented a comparison of the value of the lattice constant and the calculated volume module, for GaAs in the zincblende structure with other data reported in the literature. Error rates relate to each one in relation to the parameters chosen.

**Table 1.** Lattice constant, bulk modulus, calculation method, the error rate for the GaAs.

$a_o$ (Å)	$B_o$ (GPa)	Method	% $a_o$ (Å)	% $B_o$ (GPa)
5.608 [9]	75.2 [9]	FP-LDA	0.94%	-18.94%
5.748 [9]	60.8 [9]	FP-GGA	-1.51%	0.24%
5.654 [10]	77.0 [11]	Experiment	0.12%	-20.84%
5.653 [12]	76.0 [12]	Experiment	0.14%	-19.80%
5.66*	60.95*	Pseudopotentials		

\*Present work

The values reported in reference [9] are theoretical, calculated by the method FP-LDA, and GGA Full-potential linear augmented plane wave (FP-LAPW) with local density approximation - LDA-, and generalized gradient approximation (GGA), respectively. The calculations were done by the WIEN2K code; the data reported by R.W.G. Wyckoff [10], K. H. Hellwege, [11] and B. Fillipi, *et al* [12] is experimental. The difference among the calculated values is due to the methods used to calculate that parameter.

In order to calculate the most stable structure, the formation energy was calculated using the following expression [13]:

$$E_f = E_b^{\text{doped}} + \mu_y - E_b^o + \mu_x \quad (1)$$

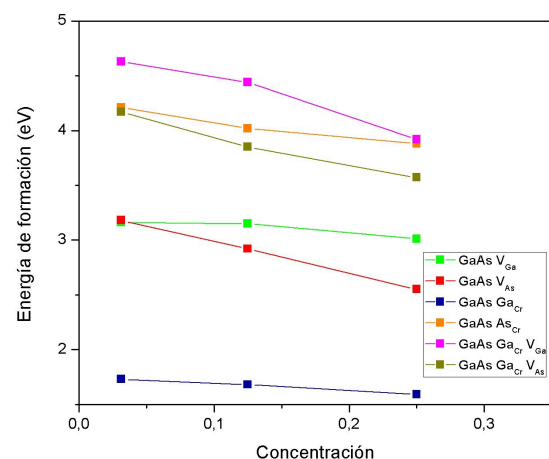
Where  $E_b^{\text{doped}}$  and  $E_b^o$  are the total energies of the supercell with and without defects respectively, and  $\mu_y$ ,  $\mu_x$  are chemic potential of the atom that was substituted and of the impurity that in this case is from the Cr. The formation energy is presented in Table 2.

Regarding the GaAs formation energy, it is found that the calculated value agrees with the results reported in the review of literature [14].

According to the data in the Table 2, and represented in Figure 2, the structures with less formation energy are: GaAs substituting a Gallium atom in the lattice by one Chromium, GaAs with a As vacancy, and GaAs with a Ga vacancy as it can be observed.

**Table 2.** Energy of formation for the compounds studied for GaAs in zincblende structure, and the 1x1x1 and 2x2x2 supercell.

Structure	1x1x1 $E_f$ (eV)	1x1x2 $E_f$ (eV)	2x2x2 $E_f$ (eV)
GaAs	-0.7	-0.7	-0.7
GaAs $V_{Ga}$	3.01	3.15	3.16
GaAs $V_{As}$	2.55	2.92	3.18
GaAs $Ga_{Cr}$	1.59	1.66	1.73
GaAs $As_{Cr}$	3.88	4.02	4.21
GaAs $Ga_{Cr} V_{Ga}$	3.92	4.44	4.63
GaAs $Ga_{Cr} V_{As}$	3.57	3.85	4.17

**Figure 2.** Energy of formation as a function of the concentration of the impurity.

#### 4. Conclusions

According to the results, when the formation energy was analysed for the GaAs structures in the 1x1x1 unit cell, 1x1x2, and 2x2x2 supercells, in their pure structure, with vacancies and substitutions, it was found that the lattice constant calculated by pseudopotentials is in agreement with the data reported experimentally. The most favourable energy-efficient configuration or the most favourable

energetically is the GaAs, when it is made a substitution of one Ga atom by one Cr in the lattice, for the lattices 1x1x1, 1x1x2, and 2x2x2. The least favourable structure energetically is the GaAs making simultaneously a substitution of a Ga atom by a Cr one and a As vacancy. A projection of this study is to consider bigger supercells, it is to work with fewer concentrations of the dopants, since when the size of the supercell increases, the formation energy starts to diminish.

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