First-principle study of the electronic band structure and the effective mass of the ternary alloy $Ga_xIn_{1-x}P$

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Abstract. In this work, the electronic band structure and the effective mass of the ternary alloy $Ga_xIn_{1-x}P$ are studied by the first principle calculations. The software QUANTUM ESPRESSO and the generalized gradient approximation (GGA) for the exchange correlations have been used in the calculations. We calculate the lattice parameter, band gap and effective mass of the ternary alloy $Ga_xIn_{1-x}P$ for the Ga composition x varying from 0.0 to 1.0 by the step of 0.125. The effect of the Ga composition on the lattice parameter and the electronic density of states are discussed. The results show that the lattice parameter varies with the composition almost linearly following the Vegard's law. A direct-to-indirect band-gap crossover is found to occur close to $x = 0.7$. The effective masses are also calculated at $\Gamma(000)$ high symmetry point along the [100] direction. The results show that the band gap and the electron effective mass vary nonlinearly with composition x.

1. Introduction

Extensive experimental investigations of the electronic structure of the group III-V semiconductors and their alloys have been carried out because of their importance in the optoelectronic device technology. Several methods have been developed to calculate the electronic properties of the ternary alloy $Ga_xIn_{1-x}P$. Bouarissa [1] studied the electronic properties of the ternary alloy $Ga_xIn_{1-x}P$ by using the empirical pseudopotential method (EPM) within the virtual crystal approximation (VCA). Onton et al. [2] employed the cathodoluminescence (CL) and photoluminescence (PL) approaches to investigate the conduction-band structure of $Ga_xIn_{1-x}P$. Kumar et al. [3] calculated disorder effects on electronic and optical properties of the ternary alloy $Ga_xIn_{1-x}P$ ($x = 0.25$, $x = 0.5$, and $x = 0.75$) by using the WIEN2k code. The effect of the alloy composition on physical properties is important and should been investigated in detail.

In this paper the electronic band structure and the effective mass of the ternary alloy $Ga_xIn_{1-x}P$ are studied. The calculations are based on first-principle calculations within the framework of the density functional theory.

2. Calculation model and methods

The first principle calculations have been performed by using the software QUANTUM ESPRESSO [4] and the generalized gradient approximation (GGA) for the exchange correlations.

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Based on the conventional cell illustrated in figure 1(a), we build a supercell ($1\times1\times2$) illustrated in figure 1(b) for substitutional doping. Convergence with respect to k points and energy cutoff is carefully checked. The plane-wave cutoff energy is set to 75 Ry, and the numerical integration of the Brillouin zone (BZ) is performed using a k-mesh of dimensions $6 \times 6 \times 6$.

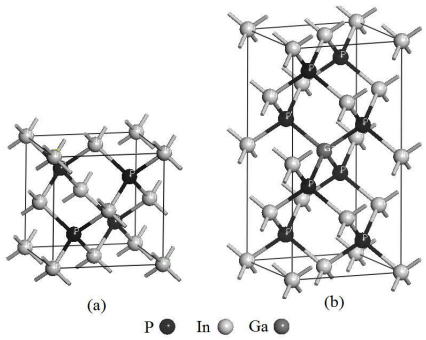

Figure 1. Crystal structures: (a) InP or GaP, (b) $Ga_xIn_{1-x}P$.

3. Result and discussion

3.1. Lattice parameters

In our calculation, the supercell contains sixteen atoms. We perform an iterative process in which the coordinates of the atoms and the cell parameters are adjusted so that the total energy of the structure is minimized. The calculated lattice parameters as functions of the compositions x for the ternary alloy $Ga_xIn_{1-x}P$ are illustrated in the figure 2. From it, we can find that the lattice parameter of the ternary alloy $Ga_xIn_{1-x}P$ decreases with increasing Ga composition x. It is almost linearly following the Vegard's law. The equation of lattice parameter a can be obtained by a linear fitting method as follows:

$$a\,(Ga_xIn_{1-x}P) = 5.87063 - 0.45537x. \tag{1}$$

Our conclusions are very close to other theoretical calculations [2].

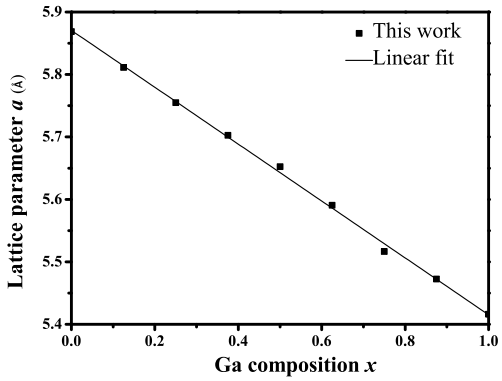

Figure 2. Lattice parameters of the ternary alloy $Ga_xIn_{1-x}P$ for different Ga compositions x.

3.2. Energy band gap

The calculated band gaps are listed in table 1 and compared with other theoretical results [3] as well as the available experimental [5] data.

Table 1. Band gap E_g calculated by GGA for InP, GaP and $Ga_xIn_{1-x}P$ and the corresponding experimental Ref[5] and other theoretical Ref[3] values

x	Γ_v–Γ_c			Γ_v–X_c		
	this work	Ref[5]	Ref[3]	this work	Ref[5]	Ref[3]
InP	0.444	1.34	0.67	1.201	2.19	1.77
$Ga_{0.125}In_{0.875}P$	0.517	–	–	1.83	–	–
$Ga_{0.25}In_{0.75}P$	0.628	–	0.79	1.156	–	1.74
$Ga_{0.375}In_{0.625}P$	0.754	–	–	1.113	–	–
$Ga_{0.5}In_{0.5}P$	0.91	1.846	0.97	1.115	–	1.72
$Ga_{0.625}In_{0.375}P$	1.008	–	–	1.128	–	–
$Ga_{0.75}In_{0.25}P$	1.133	–	1.32	1.115	–	1.68
$Ga_{0.875}In_{0.125}P$	1.288	–	–	1.133	–	–
GaP	1.559	2.78	1.81	1.155	2.26	1.65

We also illustrate the band gap of the ternary alloy $Ga_xIn_{1-x}P$ as functions of Ga composition x in figure 3 (a). It is found that a direct-to-indirect band-gap crossover [3, 6] occur close to $x = 0.7$. The band gaps show nonlinear behavior with the composition x. By fitting the non-linear variation of the calculated band gaps in terms of the composition with polynomial function, the relationship between the band gaps and the composition is obtained as follows:

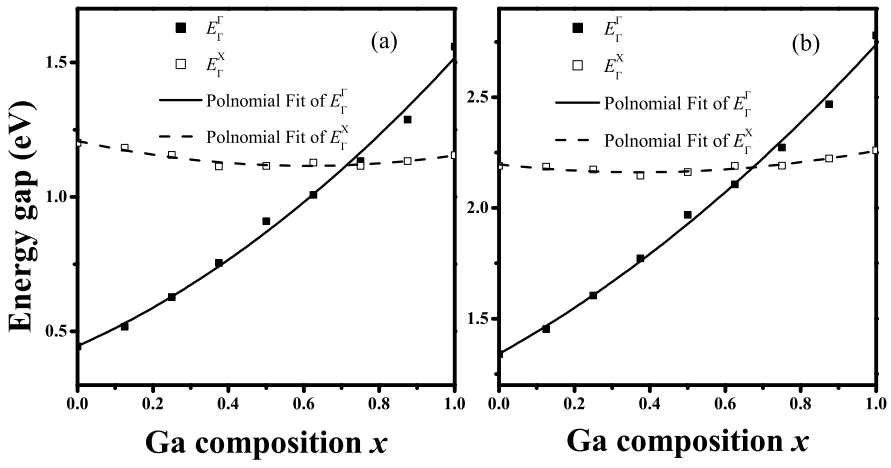

Figure 3. Band gap E_g as a function of the composition x.(a) for calculation.(b)for correction

$$E_\Gamma^\Gamma(x) = 0.44529 + 0.62298x + 0.44862x^2, \quad (2)$$

$$E_\Gamma^X(x) = 1.20758 - 0.30386x + 0.25039x^2. \quad (3)$$

We have computed the Kohn-Sham band structure of the ternary alloy $Ga_xIn_{1-x}P$. As was seen, the calculated results for the band gaps are underestimated in comparison with experimental results. Now let us amend the band gaps by the the following correction formula of ternary alloy:

$$E^{\rm cor}_{g,{\rm Ga}_x{\rm In}_{1-x}P} = E^{\rm cal}_{g,{\rm Ga}_x{\rm In}_{1-x}{\rm P}} + (1-x)\cdot\Delta E_{\rm InP} + x\cdot\Delta E_{\rm GaP}, \tag{4}$$

where

$$\Delta E_{\rm InP} = E^{\rm exp}_{g,{\rm InP}} - E^{\rm cal}_{g,{\rm InP}}, \tag{5}$$

$$\Delta E_{\rm GaP} = E^{\rm exp}_{g,{\rm GaP}} - E^{\rm cal}_{g,{\rm GaP}}. \tag{6}$$

$E^{\rm cal}_{g,{\rm Ga}_x{\rm In}_{1-x}{\rm P}}$ are calculation values and $E^{\rm cor}_{g,{\rm Ga}_x{\rm In}_{1-x}{\rm P}}$ are the correction values. $E^{\rm exp}_{g,{\rm InP}}$ and $E^{\rm exp}_{g,{\rm GaP}}$ are experimental values of InP and GaP. $E^{\rm cal}_{g,{\rm InP}}$ and $E^{\rm cal}_{g,{\rm GaP}}$ are the calculation values of InP and GaP. Finally, the correction band gap of the ternary alloy $Ga_xIn_{1-x}P$ as functions of Ga composition x is showed in figure 3(b). By fitting the non-linear variation of the calculated band gaps in terms of concentration with polynomial function, the relationship between the band gaps and the composition is obtained as follows:

$$E^{\Gamma}_{\Gamma}(x) = 1.34129 + 0.94796x + 0.44864x^2, \tag{7}$$

$$E^{X}_{\Gamma}(x) = 2.19658 - 0.18786x + 0.25039x^2. \tag{8}$$

3.3. Effective mass

The theoretical effective mass is a tensor with nine components defined as:

$$\frac{1}{m^*_{ij}} = \frac{4\pi^2}{h^2}\frac{\partial^2 E(k)}{\partial k_i \partial k_j}, \tag{9}$$

where E is the energy and k_i are the components of the wave vector $\mathbf{k}$ in a periodic potential field of a semiconductor [3]. Here we restrict ourselves to a particular case and regarded the effective mass as a scalar. Then the electrons effective mass can be defined as:

$$\frac{1}{m^*} = \frac{4\pi^2}{h^2}\frac{\partial^2 E\,(k)}{\partial k^2}. \tag{10}$$

We have calculated the effective mass of the electrons at the conduction-band minima at Γ and along the [100] direction and the results for various composition are listed in table 2. Figure 4 shows the effective mass as a function of the composition x. It is clearly seen form table 2 that the electron effective mass increases monotonously with the Ga composition x. The calculated value of m^* for InP and GaP is in good agreement with the experimental data. The nonlinear behavior of electron effective mass with composition x is also found from figure 4.

By piecewise fitting method, we get the following equation of effective mass m^*:

$$m^* = \begin{cases} 0.0740 + 0.0925x & (0 \le x \le 0.625) \\ 2.0493 - 6.0572x + 4.7890x^2 & (0.625 \le x \le 1)\,. \end{cases} \tag{11}$$

An inflection-point is found to occur around at $x = 0.7$, where a change of the direct-to-indirect band-gap arises for the ternary alloy $Ga_xIn_{1-x}P$.

Table 2. Effective mass m^* calculated according by GGA for InP, GaP and $Ga_xIn_{1-x}P$ and the corresponding experimental Ref[7] and other theoretical Ref[3] values

	x	m^*		
		this work	Ref[7]	Ref[3]
InP	0.000	0.073060	0.077	0.0768
$Ga_{0.125}In_{0.875}P$	0.125	0.089079	–	–
$Ga_{0.25}In_{0.75}P$	0.250	0.096235	–	0.099
$Ga_{0.375}In_{0.625}P$	0.375	0.105914	–	–
$Ga_{0.5}In_{0.5}P$	0.500	0.120593	–	0.121
$Ga_{0.625}In_{0.375}P$	0.625	0.133188	–	–
$Ga_{0.75}In_{0.25}P$	0.750	0.203615	–	0.1938
$Ga_{0.875}In_{0.125}P$	0.875	0.412529	–	–
GaP	1.000	0.782270	0.82	0.6

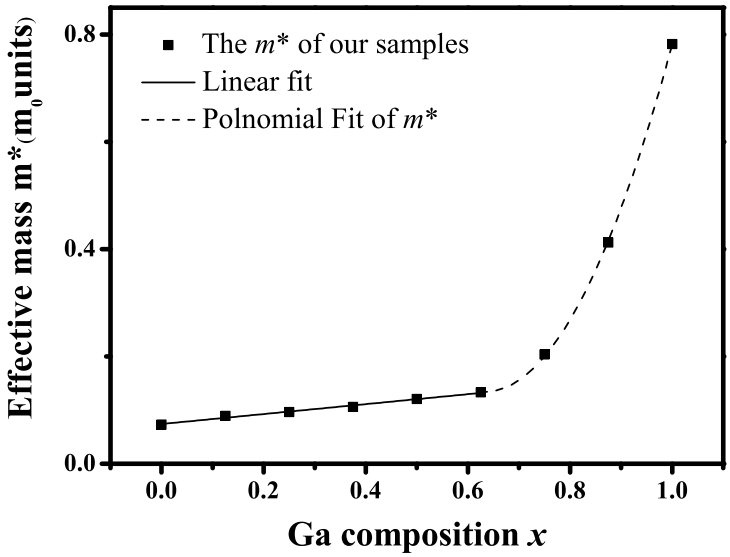

Figure 4. Effective mass as a function of the composition x.

4. Conclusion

In this paper, the band structure and the effective mass of the ternary alloy $Ga_xIn_{1-x}P$ are calculated using the software QUANTUM ESPRESSO and the generalized gradient approximation (GGA). The lattice parameter, band gap, and effective mass of the ternary alloy $Ga_xIn_{1-x}P$ for the Ga composition x varying from 0.0 to 1.0 by the step of 0.125 are presented. The results show that the lattice parameter varies with the composition x almost linearly following the Vegard's law. A direct-to-indirect band-gap crossover is found to occur close to $x = 0.7$. The effective masses are also calculated at $\Gamma(000)$ symmetry point along the [100] direction. The results show that the band gap and the electron effective mass vary nonlinearly with composition x.

Acknowledgments
This work was supported in part by the PhD Progress Foundation of Higher Education Institutions of China (No.20111501110003), the National Natural Science Foundation of China (No.11347208), the key Educational Science Foundation of Inner Mongolia Autonomous Region of China (Grant NJZZ14004) and the enhancing comprehensive strength project of Inner Mongolia University (No.14020202).

References
[1] Bouarissa N 2010 *Materials Chemistry and Physics* **124** 336–341
[2] Onton A, Lorenz M R and Reuter W 1971 *Journal of Applied Physics* **42** 3420–3432
[3] Kumar S, Parashari S S and Auluck S 2009 *phys. stat. sol. (b)* **246** 2294–2300
[4] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti G L, Cococcioni M, Dabo I, Corso A D, Gironcoli S d, Fabris S, Fratesi G, Gebauer R, Gerstmann U, Gougoussis C, Kokalj A, Lazzeri M, Martin-Samos L, Marzari N, Mauri F, Mazzarello R, Paolini S, Pasquarello A, Paulatto L, Sbraccia C, Scandolo S, Sclauzero G, Seitsonen A P, Smogunov A, Umari P and Wentzcovitch R M 2009 *J. Phys.: Condens. Matter* **21** 395502
[5] Levinshtein m, Rumyantsev S and Shur M 1996 *Handbook Series on Semiconductor Parameters* vol 2 (World Scientific)
[6] Adachi S 2009 *Properties of Semiconductor Alloys: Group-IV, III-V and II-VI Semiconductors* 1st ed (Chichester, U.K: Wiley)
[7] Madelung O 2013 *Semiconductors: Group IV Elements and III-V Compounds* softcover reprint of the original 1st ed. 1991 edition ed (Berlin ; New York: Springer)