

Lattice parameters and band structure of ternary mixed crystals $\text{Al}_x\text{Ga}_{1-x}\text{As}$ from first-principle calculations

Y. Mao, X. X. Liang, G. J. Zhao and T. L. Song

Department of Physics, School of Physical Science and Technology, Inner Mongolia University, Hohhot, 010021, P. R. China

E-mail: xxliang@imu.edu.cn

Abstract. Lattice parameters and band structure of the ternary mixed crystal $\text{Al}_x\text{Ga}_{1-x}\text{As}$ of zinc blende structure are calculated by first-principle calculations within the framework of the density functional theory. The results for the equilibrium lattice parameters and band gaps of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for the Al-composition varying from 0.0 to 1.0 by step of 0.125 are presented and discussed. The results show that the lattice constants vary with the composition almost linearly following the Vegard's law. The electron band gap at Γ point exhibits non-linear behavior versus the composition. The Al-3s, 3p states shift to high energy region in the conduction band with increasing the Al concentration. It leads to an increase of the band gap and the blue shift phenomenon.

1. Introduction

Group III-V compounds are a type of most important semiconductor materials due to their applications in electronic and optoelectronic devices [1-3]. As typical III-V semiconductors, GaAs, AlAs and their alloy, which plays a vital role in high speed optoelectronic devices and nanostructure [4], have been attracting great research interest.

Several methods have been developed to calculate the electronic properties of GaAs, AlAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$. An effective method, for example, is the so called empirical pseudo-potential method (EPM) [5-7] based on the virtual crystal approximation (VCA) [8]. Kurt and Alex studied the empirical atomic pseudo-potentials for AlAs/GaAs superlattices, alloys and nanostructures [9]. Boykin and Kharche et al calculated the band structures of the semiconductor alloy $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by the tight-binding supercell method [10]. Wang and Zahid et al employed the coherent potential approximation (CPA)-modified Becke-Johnson (MBJ) approach to quantitatively calculate the band offsets of GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heterojunctions [11]. However, only a few theoretical calculations of the TMC $\text{Al}_x\text{Ga}_{1-x}\text{As}$ energy band structures have been carried out for a couple of composition values because of computational complexities. In order to understand the composition dependence of the electronic properties completely and accurately, the first-principle studies for the whole composition range are invoked.

The aim of this work is to obtain a full understanding for the structural and electronic properties of the TMC $\text{Al}_x\text{Ga}_{1-x}\text{As}$. We have performed the first-principle calculations for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ within the framework of the density functional theory (DFT). The composition dependences of the optimal lattice constants and the corresponding electronic band structures for the TMC $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($0 \leq x \leq 1$) are



obtained and discussed.

2. Computational methods

The calculations are performed within the framework of the density-functional theory (DFT) by using **the** plane-wave pseudopotential approach in the CASTEP package [12]. The exchange-correlation energy of the electrons are described by an improved generalized gradient approximations (GGA) given by Wu and Cohen (WC) [13]. The plane-wave energy cut-off is determined as 330eV in our calculations. The numerical integration of the Brillouin zone (BZ) was performed using a k-mesh of dimensions $6 \times 6 \times 3$ k-points mesh in the Monkhorst–Pack scheme [14]. The convergence threshold of 2×10^{-5} eV/atom is used for total energy, 0.05 eV/Å for maximum force, 0.1 GPa for pressure and 0.002 Å for displacement. We consider **the** zinc-blend structure with space group $Td^2-F\bar{4}3m$ for GaAs (AlAs) crystal [Figure 1(a)] and adopt a 16-atom simple cubic supercell by modeling. The corresponding TMCs are modeled by a $1 \times 1 \times 2$ supercell structure [Figure 1(b)]. The crystal structure is optimized by minimizing the total energy with the quasi-Newton algorithm (BFGS).

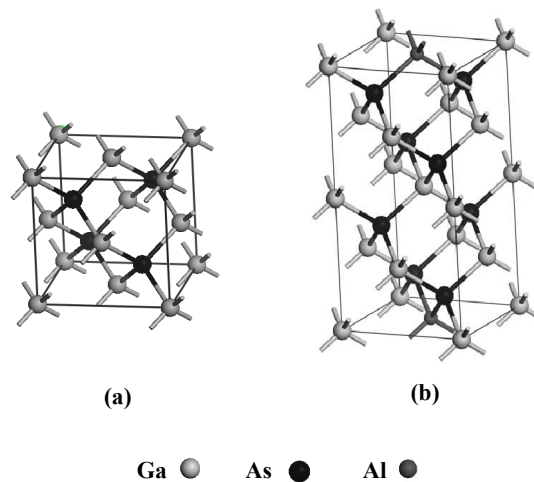


Figure 1. Crystal structures of (a) GaAs (AlAs) and (b) $Al_xGa_{1-x}As$.

The aluminum $3s^23p^1$, gallium $3d^{10}4s^24p^1$ and arsenic $4s^24p^3$ orbitals have been treated as **the** valence states during the whole calculation.

3. Results and discussions

3.1. Lattice parameters

The structural optimization has been performed starting from an experimental value with respect to the cell parameters and also the atomic positions for $Al_xGa_{1-x}As$ with various compositions. Table 1 presents our calculated values compared with available experimental and theoretical values. It is seen that our results are in agreement with **the** previous theories and experimental data.

Table 1. Lattice constants according to WC-GGA for GaAs, AlAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ compared to experimental values and other theoretical studies.

Compound	$a(\text{\AA})$		
	This work	Theoretical studies	Experimental
GaAs	5.685	5.666 ^a , 5.75 ^a	5.653
$\text{Al}_{0.125}\text{Ga}_{0.875}\text{As}$	5.690	-	-
$\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$	5.694	-	-
$\text{Al}_{0.375}\text{Ga}_{0.625}\text{As}$	5.698	-	-
$\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$	5.703	5.6482 ^b (T=0)	-
$\text{Al}_{0.625}\text{Ga}_{0.375}\text{As}$	5.707	-	-
$\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$	5.710	-	-
$\text{Al}_{0.875}\text{Ga}_{0.125}\text{As}$	5.711	-	-
AlAs	5.717	5.678 ^c , 5.736 ^c	5.661

^aRef.[16]. ^bRef.[17]. ^cRef.[18].

The calculated equilibrium lattice constant a of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of the concentration x is shown in Figure 2(a). The variation of the lattice constant of TMCs with the composition is usually described phenomenologically by the so-called Vegard's law [15]. Fitting the calculated results gives following linear equation conformable with the Vegard's law:

$$a(\text{Al}_x\text{Ga}_{1-x}\text{As}) = 5.686 + 0.031x = 5.717x + 5.686(1-x). \quad (1)$$

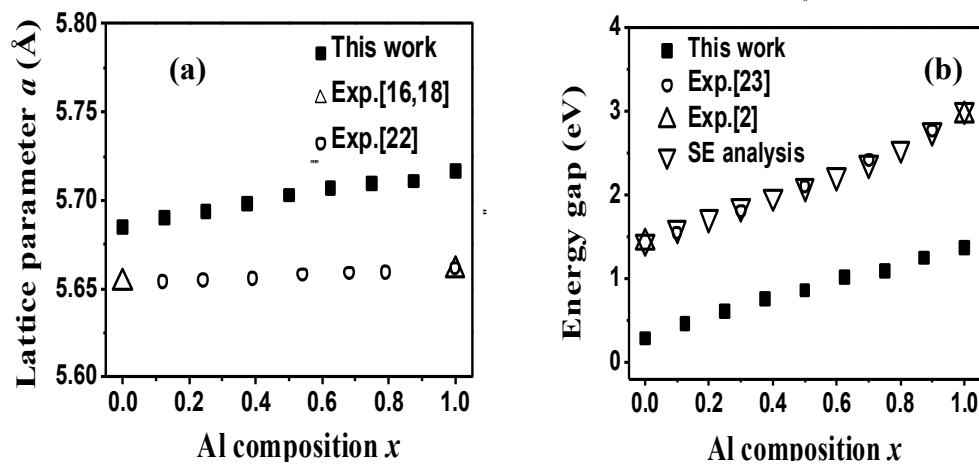


Figure 2. (a) Lattice constants and (b) band gaps as functions of x for $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

3.2. Electronic band structure and density of states

We have carried out the computations for the band structures and density of states (DOS) of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for the composition in the range of $0 \leq x \leq 1$. Here we illustrate the Al composition dependence of the band gap and DOSs in Figures 2(b) and 3, without showing the band structures for lack of space. It is found that the electron band gap at Γ point exhibits strong composition dependence and increases non-linearly with the Al composition.

By fitting the non-linear variation of the calculated band gaps in terms of concentration with polynomial function, the relationship between the band gap and the composition is obtained as follows:

$$E_g^\Gamma(x) = 0.282 + 1.490x - 0.871x^2 + 0.465x^3$$

$$= 0.282 + 1.084x + x(1-x)(0.406 - 0.465x). \quad (2)$$

The band gap versus the composition has a bowing range with $b = (-0.406 + 0.465x)$ eV.

The computational values of the band gap are listed in Table 2 and compared with other theoretical and available experimental data. It is clearly seen that the band gaps are underestimated in comparison with experimental results. This is mainly due to the fact that the simple form of GGA does not take into account the quasi-particle self-energy correctly [20], and DFT is not suitable for describing excited-state properties (energy gap belongs to excited-state). However, it is widely accepted that GGA electronic band structures are qualitatively in good agreement with experiments as regards the ordering of the energy levels and the shape of the bands. This obstacle can be overcome by taking into account the scissor correction scheme [21].

Table 2. Band gap E_g calculated according to the WC-GGA schemes for GaAs, AlAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and the corresponding experimental and other theoretical values.

Material	E_g (eV)		
	This work	Theoretical studies	Experimental
GaAs	0.283	0.336 ^a	1.52
$\text{Al}_{0.125}\text{Ga}_{0.875}\text{As}$	0.454	-	-
$\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$	0.606	-	-
$\text{Al}_{0.375}\text{Ga}_{0.625}\text{As}$	0.748	-	-
$\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$	0.857	2.0775 ^b	2.0924
$\text{Al}_{0.625}\text{Ga}_{0.375}\text{As}$	1.007	-	-
$\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$	1.082	-	-
$\text{Al}_{0.875}\text{Ga}_{0.125}\text{As}$	1.243	-	-
AlAs	1.363	1.65 ^c	2.22

^a Ref.[16]. ^b Ref.[17]. ^c Ref.[19].

Figure 3 shows the partial and total DOS for the $\text{Al}_{0.125}\text{Ga}_{0.875}\text{As}$ and $\text{Al}_{0.625}\text{Ga}_{0.375}\text{As}$, as an example. It is found that the lowest valence bands in the range of -15.3 eV to -13.8 eV are provided by Ga-3d states and it has stronger locality. The valence bands in the range of -13.5 eV to -9.3 eV are dominated by As-4s states, while the upper part in the range of -7.4 eV to -0.2 eV results from the contributions of As-4p, Al-3s and Al-3p states. The conduction band is of predominantly from the hybridization Al-3p states.

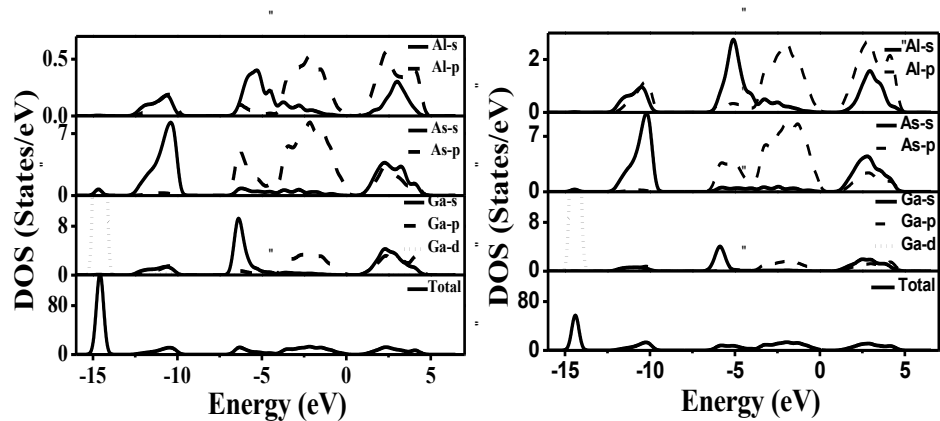


Figure 3. Total and partial density of states for $\text{Al}_{0.125}\text{Ga}_{0.875}\text{As}$ and $\text{Al}_{0.625}\text{Ga}_{0.375}\text{As}$.

To understand clearly the doping effect, we have also illustrated the DOS for the different concentration of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ in Figure 4. It indicates that the band contributions of Ga-*s*, *p*, *d* orbitals are gradually weakened but Al-*s*, *p* contributions strengthen. We can also see that the Al-3*s*, 3*p*, Ga-4*s*, 4*p* states shift to high energy region in the conduction band when Al concentration increases and the Al-3*p* state is more dominant in the region. This leads to an increase in the band gap and the blue shift phenomenon, i.e. the famous anti-Stokes shift, occurs.

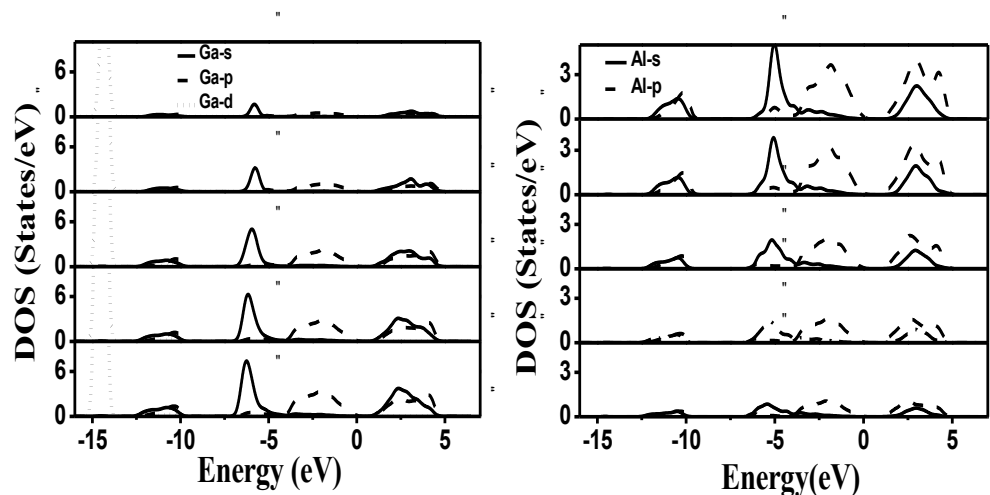


Figure 4. Partial density of states of Al-3*s*, 3*p* and Ga-3*d*, 4*s*, 4*p* bands of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with $x = 0.25, 0.375, 0.5, 0.75, 0.875$, respectively.

4. Conclusions

We have used first-principle calculations to study the composition dependences of the lattice constants and electronic band structure of the ternary mixed crystals $\text{Al}_x\text{Ga}_{1-x}\text{As}$, applying DFT within the

WC-GGA to treat the exchange correlation energy. The results show that the characteristics of equilibrium lattice parameters and band gap are sensitive to **the** composition. The composition dependence of the calculated lattice constant is found to be almost linear and obey the Vegard's law. The electron band gap at Γ point exhibits non-linear increase with **the** composition. The results for the DOS show that the blue shift occurs owing to Al-3s, 3p, Ga-4s, 4p states shifting to high energy region in the conduction band when Al concentration increases.

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