First Principle Calculations of Effect of Hydrostatic Pressure on Ga$_{0.75}$Cr$_{0.25}$P

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Abstract: In this paper, the investigation of effect of hydrostatic pressure on the structural, electronic and magnetic properties of Ga$_{0.75}$Cr$_{0.25}$P ternary alloy in Zinc Blende (B3) phase at 0 GPa to 26 GPa pressure range has been done using first principle calculations as implemented in Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code. The theoretical investigation of electronic and magnetic properties of this compound represents that the compound is half-metallic ferromagnet and show 100% spin polarization at different values of pressure. It is found that band gap increases with increase in pressure as spin polarized band structures experience changes with applied pressure. The calculated results show that lattice constant and volume of compound decrease along with increase in induced local magnetic moments values on non-magnetic gallium and phosphorus atoms with applied pressure.

Keywords: Pressure effect; GaP; Dilute Magnetic Semiconductor; DFT

1. Introduction

Nowadays, Spintronics is multidisciplinary field that involves manipulation of electronic spin in addition to electron charge in information technology and provides opportunities for generation of new advanced devices by combining both spin-dependent effects and standard microelectronics [1-3]. The doping of transition metal atoms in nonmagnetic semiconductor material results into formation of Dilute Magnetic Semiconductors (DMS) that can be promising candidates for spintronics industry. GaP belongs to III-V semiconductor category and is soft semiconductor in nature. The substitution of Ga with transition metal ion is relatively easy than other hard members of this group due to its soft nature [4]. Also, III-V semiconductors are interesting compounds because they have important optical and spin dependent electron transport properties, show flexibility of both n and p type doping and are compatible with other parts of electronic devices [5]. The numbers of researchers are studying various properties of transition metal doped GaP using different methods both experimentally and theoretically. Iftibhar Ahmad et al investigated 100% spin polarization of Ga$_{1-x}$Mn$_x$P and Ga$_{1-x}$Mn$_x$As ($x$=0.125) using FP-LAPW method [6]. Hardev S. Saini et al studied Ga$_{1-x}$Cr$_x$P at $x$=0.25, 0.125, 0.06, 0.03 and predicted that HM gap increases with reduction in dopant concentration [7]. Owens et al. synthesized ternary alloy of Cu doped GaP and found out room temperature ferromagnetism upto 0.03% dopant concentration [8]. M. E. Overberg et al synthesized and studied the GaMnP using both ion implantation method and molecular beam epitaxy [9]. Gokş et al prepared and investigated the different properties of Cr doped GaP and GaAs crystals [10]. Zhi et al studied V, Cr and Mn doped...
GaAs and GaP compounds at 25% doping concentration and observe room temperature ferromagnetism behavior of these compounds [11]. Schulthes et al investigated electronic and magnetic properties of Mn doped GaAs, GaP and GaN [12]. Huang et al used FPLAPW method to found out half metallic nature of Ga$_{1-x}$Cr$_x$P at x=0.125, 0.25 and 0.50 [13]. Djedid et al. theoretically investigated the structural, electronic, elastic and magnetic properties of Ga$_{1-x}$MnP and In$_{1-x}$MnP at x=0.25 [14]. Ribeiro-Silva et al investigated the effect of temperature on structural phase transitions of GaP [15]. M. Zafar et al theoretically studied the structural, electronic, optical and elastic properties of Al$_x$Ga$_{1-x}$P [16]. Bruno C. da Silva et al studied GaP nanowires by growing GaP structures with large volumes in the hexagonal phase [17]. R. Belacel et al investigated different properties of alloys and super lattices of TIP and GaP in the zinc-blende form [18].

The pressure has significant effect on different properties of semiconductor materials because inter-atomic distance undergoes significant change with applied pressure [19-22]. The hydrostatic pressure results into change in atomic positions of material that may causes phase transition, also. The volume of compound changes with change in pressure that further effects inter-atomic binding of atoms and results into significant change in properties of compounds. In this paper, pressure from 0 GPa to 26 GPa range is applied on Ga$_{0.75}$Cr$_{0.25}$P and theoretically investigated the effect of hydrostatic pressure structural, electronic and magnetic properties of Ga$_{0.75}$Cr$_{0.25}$P.

2. Computational Details

In this paper, the structural, electronic and magnetic properties of Ga$_{0.75}$Cr$_{0.25}$P in the Zinc Blende phase at different pressure have been investigated using Density Functional Theory as implemented in SIESTA code [23]. The Local Density Approximation LDA+U (U=3) parameterized by CA was used as exchange correlation potential [24]. The super cell of eight atoms having 1×1×1 dimension is used to generate crystal structure of Ga$_{0.75}$Cr$_{0.25}$P by substituting the gallium atom at (0,0,0) position with Cr. The norm-conserving pseudo-potentials in the manner of Troullier and Martins have been generated [25] and semi-core Cr-3d states are used as valence electrons in our calculations. The double zeta polarization and energy shift of 100 meV is used to obtain well conserved results and 4×4×4 k-point sampling of Monkhorst Pack Pack Scheme was used for calculations of different properties of compound [26].

3. Results and Discussion

3.1. Structural and Electronic Properties

First of all, crystal structure of pure GaP semiconductor is generated and investigated the lattice constant (LC), bulk modulus ($B_0$) and band gap ($E_g$) values. The calculated results of pure GaP are in good agreement with literature data [27-30] as represented in Table 1. Then, the crystal structure of Ga$_{0.75}$Cr$_{0.25}$P alloy was optimized by using different values of lattice constant within range of its experimental data. The Murnaghan’s equation of state [31] is fitted to calculate total energies to determine ground state properties of alloy. The LC and volume of compound decrease with applied pressure, but the total energy and Fermi energy of alloy have been increased as shown in Fig 1. The pure GaP has semiconductor behavior, but on doping with Cr it undergoes significant change in its electronic properties. The study of spin polarized band structures of Ga$_{0.75}$Cr$_{0.25}$P shows that compound is ferromagnetic in nature for majority spin channel and has semiconductor behavior in minority spin channel at given pressure range i.e. 0 GPa to 26 GPa as shown in Fig. 2. It is further investigated that this compound is half metallic ferromagnetic in nature with 100% spin polarization at Fermi energy level ($E_F$). The calculated results of band structures show that forbidden energy gap increases because conduction band maximum and valence band minimum undergo significant change with increasing pressure as represented in Fig 3 and calculated results are presented in Table 2.
FIGURE 1. Variation of LC, Volume, Total Energy and Fermi energy of Ga\textsubscript{0.75}Cr\textsubscript{0.25}P with pressure

TABLE 1. Lattice Constant (LC), Bulk modulus (B\textsubscript{0}) and Band gap (E\textsubscript{g}) of pure GaP

| System/Property | LC(Å) | B\textsubscript{0}(GPa) | E\textsubscript{g}(eV) |
|-----------------|-------|-----------------|------------------|
| GaP             | 5.63  | 76.51           | 2.02             |
|                 | 5.51\textsuperscript{[27]} | 88.00\textsuperscript{[29]} | 1.57\textsuperscript{[7]} |
|                 | 5.45\textsuperscript{[28]} |                 | 2.51\textsuperscript{[30]} |

FIGURE 2. Spin-polarized Band Structures of Ga\textsubscript{0.75}Cr\textsubscript{0.25}P at 0 GPa to 26 GPa pressure.

3.2. Magnetic Properties
The GaP is nonmagnetic semiconductor. On substitution of gallium atom with Cr atom having greater number of valence electrons, the unshared valence electrons of Cr occupies the impurity levels in vicinity of E\textsubscript{F} which causes magnetic states in Ga\textsubscript{0.75}Cr\textsubscript{0.25}P ternary alloy. The basic reason behind the magnetization is Cr-3d states. The calculated value of total magnetic moment of Ga\textsubscript{0.75}Cr\textsubscript{0.25}P is 3.00 \(\mu\text{B} \) at different pressure values. Due to hybridization of Cr-3d and P-3p states, there is induction of smaller values of local magnetic moments on the nonmagnetic Ga and P atoms. The local magnetic
moment developed on P have negative values that indicate induced magnetic moment is anti-parallel to spin states of Cr atom, while the positive values on Ga indicate parallel nature. The variation of total and local magnetic moments with pressure is shown in Fig. 4 and calculated values are represented in Table 2. With increase in pressure, total magnetic moments remain same at higher pressure and local magnetic moments undergo increase in case of Ga and P atoms, but the magnetic moment on Cr atom decreases with increasing pressure.

**FIGURE 3.** Variation of forbidden energy band gap (Eg) of Ga$_{0.75}$Cr$_{0.25}$P with pressure

**FIGURE 4.** Variation of total magnetic moment ($\mu_{\text{Tot}}$), local magnetic moments of Ga, Cr and P atoms of Ga$_{0.75}$Cr$_{0.25}$P with pressure
TABLE 2. Total Energy ($E_{\text{Tot}}$), Fermi energy ($E_F$), Volume (V), Lattice Constant(LC), Band gap ($E_g$), total & local magnetic moments (μB, in Bohr magneton), $E_{\text{CBM}}^\downarrow$, $E_{\text{CBM}}^\uparrow$, $E_{\text{VBM}}^\downarrow$, $E_{\text{VBM}}^\uparrow$, Valence band edge splitting ($\Delta E_V$), Conduction band edge splitting ($\Delta E_C$), Exchange constants $N_0 \alpha$ and $N_0 \beta$ of GaP$_{0.75}$Cr$_{0.25}$P at different values of Pressure.

| Property/Pressure | 0 GPa     | 5 GPa     | 10 GPa    | 15 GPa    | 20 GPa    | 26 GPa    |
|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| $E_{\text{Tot}}$(eV) | -1163.986 | -1163.921 | -1163.772 | -1163.523 | -1162.897 | -1162.280 |
| $E_F$(eV)         | -5.271    | -5.249    | -5.233    | -5.220    | -5.208    | -5.203    |
| V (Ang$^3$)       | 178.533   | 171.230   | 165.848   | 160.410   | 151.964   | 146.300   |
| LC (Ang)          | 5.631     | 5.553     | 5.494     | 5.433     | 5.336     | 5.269     |
| $E_g$             | 1.671     | 1.672     | 1.677     | 1.702     | 1.723     | 1.742     |
| $\mu_{\text{Total}}$ | 3.000    | 3.000     | 3.000     | 3.000     | 3.000     | 3.000     |
| $\mu_{\text{Ga}}$ | 0.035     | 0.048     | 0.081     | 0.099     | 0.117     | 0.132     |
| $\mu_{\text{Cr}}$ | 2.961     | 2.832     | 2.744     | 2.672     | 2.491     | 2.142     |
| $\mu_{\text{P}}$  | -1.044    | -0.976    | -0.924    | -0.880    | -0.784    | -0.720    |
| $E_{\text{CBM}}^\downarrow$ | 1.427    | 1.316     | 1.264     | 1.348     | 1.401     | 1.230     |
| $E_{\text{CBM}}^\uparrow$ | 0        | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{VBM}}^\downarrow$ | -0.244   | -0.356    | -0.413    | -0.354    | -0.322    | -0.512    |
| $E_{\text{VBM}}^\uparrow$ | 0        | 0         | 0         | 0         | 0         | 0         |
| $\Delta E_C$      | 1.427     | 1.316     | 1.264     | 1.348     | 1.401     | 1.230     |
| $\Delta E_V$      | -0.244    | -0.356    | -0.413    | -0.354    | -0.322    | -0.512    |
| $N_{0 \alpha}$    | 2.854     | 2.632     | 2.528     | 2.696     | 2.802     | 2.460     |
| $N_{0 \beta}$     | -0.488    | -0.712    | -0.826    | -0.708    | -0.644    | -1.024    |

In case of half metallic spin polarized, $N_{0 \alpha}$ and $N_{0 \beta}$ are important parameters that represent s-d exchange constant and p-d exchange constant respectively. These exchange constants are obtained by using the following formulae [32]:
where $x$ represents the concentration of Cr and $<S>$ is the half of magnetization per Cr atom, $\Delta E_c$ and $\Delta E_v$ are the band edge spin splitting of conduction band minimum and valence band maximum respectively at gamma symmetry points in band structures. Further, $\Delta E_c$ and $\Delta E_v$ are calculated from following formulae:

$$\Delta E_c = E_{CBM}^\uparrow - E_{CBM}^\downarrow$$
$$\Delta E_v = E_{VBM}^\uparrow - E_{VBM}^\downarrow$$

Where $E_{CBM}^\uparrow$ conduction band minimum of spin down state, $E_{CBM}^\downarrow$ is conduction band minimum of spin up state, $E_{VBM}^\uparrow$ is valence band maximum of spin down state and $E_{VBM}^\downarrow$ is valence band maximum of spin up state. The calculated results of these parameters are represented in Table 2.

**Conclusion**

In this paper, the effect of hydrostatic pressure on structural, electronic and magnetic properties of Ga$_{0.75}$Cr$_{0.25}$P has been studied and following results are investigated:

- The calculated structural properties show that lattice constant and volume of compounds undergo decrease along with increase in total energy of compounds with increasing pressure.
- The study of electronic structures represents that conduction band maximum and valence band minimum move downward along with increase in forbidden energy band gap ($E_g$) of these compounds with pressure.
- The analysis of electronic properties represents that compounds are half metallic ferromagnets at 0 GPa to 26 GPa with 100% spin polarization and show significant variation in electronic structure of Ga$_{0.75}$Cr$_{0.25}$P as compare to nonmagnetic pure GaP semiconductor.
- Due to p-d hybridization of Cr-3d and P-3p states, there is induction of local magnetic moments on the non magnetic Ga and P atoms. The total magnetic moment of compounds remains same, but induced local magnetic moment value on non-magnetic Ga and P increases along with decrease on Cr with applied pressure.

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