DFT Study of Effect of Hydrostatic Pressure on Structural, Electronic and Magnetic Properties of In$_{0.875}$Cr$_{0.125}$P

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Abstract. In this paper, the effect of hydrostatic pressure on structural, electronic and magnetic properties of In$_{0.875}$Cr$_{0.125}$P Diluted Magnetic Semiconductor (DMS) in Zinc Blende (B3) phase has been studied at 0 GPa to 26 GPa. The calculations have been performed using Density Functional Theory as implemented in the Spanish Initiative for Electronic Simulations with Thousands of Atoms code (SIESTA) using LDA+U (U=3) as exchange-correlation (XC) potential. The study of electronic structures and magnetic properties show that In$_{0.875}$Cr$_{0.125}$P is half metallic in nature and this behaviour is maintained at given pressure range. It is found that forbidden energy band gap increases with increase in pressure due to shifting of valence band maximum and conduction band minimum of energy levels. The investigation of structural properties shows that lattice constant and volume of compound decreases along with increase in total energy of compound with applied pressure. The study of induced local magnetic moment values show their continuous increase on non-magnetic indium and phosphorus atoms with increasing pressure.

Keywords: InP, Pressure effect, DMS, 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[1-2]. Indium phosphide (InP) semiconductor is important compound having applications in high speed electronics and optoelectronic devices i.e. resonant tunnelling diodes, advanced transistors, etc and behaves as ferromagnet at high temperature conditions. In literature, many researchers are working in this field to tune the band gap and other properties of InP to achieve the desired properties of materials. D. L. Rode investigated the electron transport properties on InSb, InAs, InP compounds [3]. D.S. Yadav and D.V. Singh have done work to study the static and dynamic properties of number of II-VI and III-V binary compounds [4]. Mohammed Ameri et. al., investigated structural and electronic properties of Al$_x$In$_{1-x}$P using FT-LMTO method [5]. H.A.Tahini et. al., studied the vacancies and defect levels in various III-V semiconductors [6]. Kanchana Somaskandan et. al., synthesized In$_{1-x}$In$_x$P (x≤0.0135) nanoparticles using isovalent doping strategy [7]. M. Schmidet et. al., studied electronic and magnetic properties of Mn doped InP nanowires [8]. Bouhemadou et. al., theoretically studied the structural, elastic, electronic and lattice dynamical properties of In$_{1-x}$Ga$_x$P quaternary alloys [9].
N. Bouarissa studied the effect of hydrostatic pressure on pure InP [10]. K. Kaur and S. Sharma theoretically studied the different properties of In$_{0.75}$Cr$_{0.25}$P using SIESTA software [11]. E. Mundy et al investigated the Cu doped InP Nanocrystals [12]. The pressure has significant effect on different properties of semiconductor materials because inter-atomic distance undergoes significant change with applied pressure. 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 In$_{0.875}$Cr$_{0.125}$P and theoretically investigated the effect of hydrostatic pressure structural, electronic and magnetic properties of In$_{0.875}$Cr$_{0.125}$P.

2. Theoretical details

In this paper, the structural, electronic and magnetic properties of In$_{0.875}$Cr$_{0.125}$P in the Zinc Blende phase at different pressure have been investigated using Density Functional Theory as implemented in SIESTA code [13]. The Local Density Approximation LDA+U (U=3) parameterized by CA was used as exchange correlation potential [14]. The super cell of sixteen atoms (eight indium atoms and eight phosphorus atoms) having 2×1×1 dimension is used to generate crystal structure of In$_{0.875}$Cr$_{0.125}$P by substituting In at (0,0,0) position with Cr. The norm-conserving pseudo-potentials in the manner of Troullier and Martins have been generated [16] 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.

3. Results and discussions

3.1. Structural and Electronic properties

First of all, crystal structure of pure InP semiconductor is generated and investigated the lattice constant (LC), bulk modulus (B$_0$) and band gap (E$_g$) values. The calculated results of pure InP are in good agreement with literature data as represented in Table 1 and the electronic band structure along with TDOS of InP is shown as Fig. 1. Then, the crystal structure of In$_{0.875}$Cr$_{0.125}$P alloy was optimized by using different values of lattice constant within the range of its experimental data. The Murnaghan’s equation of state [17] 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 2. The pure InP has semiconductor behavior, but on doping with Cr it undergoes significant change in its electronic properties. The study of spin polarized band structures of In$_{0.875}$Cr$_{0.125}$P show that compound is metallic 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. 3. 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. 4 and calculated results are presented in Table 2. This change in electronic structure of compound near the Fermi level (E$_F$) causes considerable change in alloy behavior and Cr doped InP alloy can be tuned to meet desired properties of material under specific conditions.
TABLE 1. Lattice Constant (LC), Bulk modulus ($B_0$) and Band gap ($E_g$) of pure InP

| System/Property | LC (Å) | $B_0$ (GPa) | $E_g$ (eV) |
|-----------------|--------|-------------|------------|
| InP             | 5.923  | 69.04       | 1.291, 0.5647[6] |
|                 | 6.00[6] |            |            |
|                 | 5.869[18] | 67[4]   | 0.41[6], 1.35[20] |
|                 | 5.851[19] | 79.24[6]  | 1.23[21], 1.3831[22] |

FIGURE 1. Band Structure and TDOS of pure InP

FIGURE 2. Variation of Lattice Constant (LC), Volume, Total Energy and Fermi energy ($E_F$) of In$_{0.875}$Cr$_{0.125}$P with pressure
3.2. Magnetic Properties

The InP is non magnetic semiconductor. On substitution of In with Cr atom having greater number of valence electrons, the unshared valence electrons of Cr occupies the impurity levels in vicinity of $E_F$ which causes magnetic states in In$_{0.875}$Cr$_{0.125}$P ternary alloy. The basic reason behind the magnetization is Cr-3d states. The calculated value of total magnetic moment of In$_{0.875}$Cr$_{0.125}$P is 3.00 $\mu$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 In and P atoms. The local magnetic moment developed on P have negative values as that indicate induced magnetic moment is anti parallel to spin states of Cr atom, while the positive values on In indicate parallel nature with respect to Cr 3d-states. The variation of total and local magnetic moments with pressure is shown in Fig. 5 and calculated values are

**FIGURE 3.** Variation in Spin-polarized Band Structures of In$_{0.875}$Cr$_{0.125}$P at given pressure range

**FIGURE 4.** Variation in Energy band gap ($E_g$) of In$_{0.875}$Cr$_{0.125}$P at given pressure range
With increase in pressure, total magnetic moments remain same at higher pressure and local magnetic moments undergo increase in case of In and P atoms, but the magnetic moment on Cr atom decreases with increasing pressure.

**FIGURE 5.** Variation in Total Magnetic Moment, Local Magnetic Moments on In, Cr and P of In$_{0.875}$Cr$_{0.125}$P with Pressure

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 [23]:

\[ N_0\alpha = \frac{\Delta E_C}{x(S)} \]
\[ N_0\beta = \frac{\Delta E_V}{x(S)} \]

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 [23]:

\[ \Delta E_C = E^\uparrow_{CBM} - E^\downarrow_{CBM} \]
\[ \Delta E_V = E^\uparrow_{VBM} - E^\downarrow_{VBM} \]

Where $E^\downarrow_{CBM}$ conduction band minimum of spin down state, $E^\uparrow_{CBM}$ is conduction band minimum of spin up state, $E^\downarrow_{VBM}$ is valence band maximum of spin down state and $E^\uparrow_{VBM}$ is valence band maximum of spin up state. The calculated results of these parameters are represented in Table 2.
TABLE 2. Total Energy (E_{Tot}), Volume (V), Lattice Constant (LC), Band gap (E_{g}), total & local magnetic moments (μ, in Bohr magneton), E_{CBM}^{↑}, E_{CBM}^{↑}, E_{VBM}^{↓}, E_{VBM}^{↑}, ΔE_c, ΔE_v, Exchange constants (N_{α}, N_{β}) of In_{0.875}Cr_{0.125}P at 0GPa to 26 GPa

| Property/Pressure | E_{Tot}(eV) | E_{F}(eV) | V (Ang^3) | LC (Ang.) | E_{g}(eV) | μ_{Total} | μ_{In} | μ_{Cr} | μ_{P} | E_{CBM}^{↑} | E_{VBM}^{↑} | ΔE_{c} | ΔE_{v} | N_{α} | N_{β} |
|-------------------|-------------|-----------|-----------|-----------|-----------|-----------|---------|--------|-------|-------------|-------------|--------|--------|-------|-------|
|                   | 0 GPa       | 3 GPa     | 6 GPa     | 10 GPa    | 15 GPa    | 20 GPa    | 26 GPa  |        |       |             |             |        |        |       |       |
|                   | -3766.38479 | -3766.23238 | -3763.86374 | -3762.59874 | -3761.73871 | -3761.10785 | -3758.72923 | | | | | | | | |
|                   | -5.01874    | -4.92198  | -4.79955  | -4.71583  | -4.65663  | -4.62110  | -4.60541 | | | | | | | | |
|                   | 485.64834   | 464.6776  | 441.1896  | 425.4473  | 408.9182  | 397.78245 | 389.4233 | | | | | | | | |
|                   | 6.3228      | 6.2900    | 6.1919    | 6.1123    | 5.63703   | 5.6190    | 5.4655  | | | | | | | | |
|                   | 0.15399     | 0.338     | 0.664     | 0.969     | 1.020     | 1.099     | 1.223   | | | | | | | | |
|                   | 3.00009     | 3.00000   | 3.00000   | 3.00000   | 3.00000   | 2.99999   | 3.00000 | | | | | | | | |
|                   | 0.048       | 0.063     | 0.065     | 0.086     | 0.109     | 0.141     | 0.152   | | | | | | | | |
|                   | 3.894       | 3.865     | 3.806     | 3.764     | 3.701     | 3.640     | 3.602   | | | | | | | | |
|                   | -1.276      | -1.232    | -1.128    | -1.076    | -1.001    | -0.926    | 0.152   | | | | | | | | |
|                   | 0.148       | 0.262     | 0.691     | 0.832     | 0.889     | 0.923     | 1.136   | | | | | | | | |
|                   | 0           | 0         | 0         | 0         | 0         | 0         | 0       | | | | | | | | |
|                   | -0.0059     | -0.076    | -0.278    | -0.102    | -0.131    | -0.176    | -0.087  | | | | | | | | |
|                   | 0           | 0         | 0         | 0         | 0         | 0         | 0       | | | | | | | | |
|                   | 0.148       | 0.262     | 0.691     | 0.832     | 0.889     | 0.923     | 1.136   | | | | | | | | |
|                   | -0.0059     | -0.076    | -0.278    | -0.102    | -0.131    | -0.176    | -0.087  | | | | | | | | |
|                   | 0.00925     | 0.01638   | 0.04319   | 0.05200   | 0.05556   | 0.05769   | 0.07100 | | | | | | | | |
|                   | -0.0236     | -0.304    | -1.112    | -0.408    | -0.524    | -0.704    | -0.348  | | | | | | | | |

4. Conclusion

In this paper, the effect of hydrostatic pressure on structural, electronic and magnetic properties of In_{0.875}Cr_{0.125}P has been studied and predicted the following results:

- This ternary alloy shows half metallic ferromagnetism with 100% spin polarization at 0 GPa to 26 GPa with considerable change in electronic structure of compound as compare to pure InP semiconductor.
- The analysis of electronic structures show that forbidden energy band gap of compound increases with increasing pressure as CBM and VBM move away from Fermi energy level.
- The study of magnetic properties predicts the induction of smaller values of local magnetic moments on the non magnetic In and P atoms due to hybridization of Cr-3d and P-3p states. The local magnetic moment value on In and P increases with pressure but there is decrease of magnetic moment value on Cr with pressure.
- Due to half metallic nature of this ternary alloy of InP at given pressure range, it is predicted this material can be potential candidate for spintronics at 0 GPa to 26 GPa and our calculated results will be helpful in future research in this field.
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