# First-principles study of the structural, electronic and magnetic properties for phosphide substitutes doping of InP nanotube by V, Mn and Ni ions

Scientific research paper

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**ABSTRACT**

Structural stability, electronic and magnetic properties of armchair (5, 5) InP nanotube doped with V, Mn, and Ni are investigated using first-principles calculations. The calculations are performed by the PWscf code. The V, Mn, and Ni metals are replaced by the P position in the InP nanotube. The optimized angles between them and bond lengths are calculated. The results illustrate that the magnetic moment changes are in agreement with the predicted value of Hund's rule. The results show that Mn-doped InPNT is a ferromagnetic metal, whereas Ni-doped InPNT is a non-magnetic metal. More; importantly doping V in InPNT leads to half-metallic ferromagnetism. Thus, the present results predict that the InP nanotube doped with V is useful for industrial applications, especially in spintronic devices and Nano magnets. To identify the most stable configuration, the formation binding energy and cohesive energy are calculated for all compounds. In the end, the InP nanotube doped with Ni are more stable than others.

## 1 Introduction

Over the last few years, the study of nanotubes and nanowires has received special attention. Investigating the possibility of doping InP with transition metals to get semiconductor material with stable and good electrical properties is very important from a practical point of view [1]. Materials that form the components of electronic devices are metals, insulators, and semiconductors. In contrast, materials that constitute the foundation for spintronic are half-metals, gapless semiconductors, and dilute magnetic semiconductors (DMSs). Materials having a zero-energy band gap are a special class of these materials that illustrate some interesting and better electronic properties, in

comparison to materials with a non-zero energy gap [2]. When a fraction of the atoms of a non-magnetic semiconductor is replaced by magnetic ions, the atomic spin of these magnetic impurities creates magnetic properties in the material by interacting with the lattice carriers. As a result, this material has both semiconducting and magnetic properties, which is called dilute magnetic semiconductor (DMS). The DMS material-based spintronic devices are proposed to use both d electrons of transition metal impurities and s or p electrons of host semiconductors to perform their semiconducting and magnetic functions [3–5]. The applications of the DMSs demand a host material that can resist interstitial impurities and accommodate lots of substitute impurities. The single-walled nanotubes, in

comparison to the III–V and II–VI compound semiconductors, just have two surfaces, where the interstitial impurities can be removed more easily. Also, replacing cations with TM atoms can be easily found using the atom-by-atom substitution technique by a scanning tunneling microscope with a controlled bias voltage proposed by Kitchen et al. [6] in experiments. So, III–V nanotubes doped with 3d TM are expected to be vital in the progress of nanoscale spintronic semiconductor devices due to their unique characteristics on electron spin polarization. Indium phosphide (InP) is an interesting III–V semiconducting material which has a direct band gap of 1.35 eV at room temperature (corresponding to the near-infrared (NIR) wavelength of 923 nm). InP can be utilized as a substrate for the epitaxial growth of other III–V semiconductors [7–11]. InP is used in solar cells, light-emitting diodes, and light detectors. The structural, optical, and electronic properties of InP have been of interest to both experimentalists as well as theoreticians. InP can be synthesized using various methods such as hydrothermal, flash evaporation, co-evaporation, and chemical vapor deposition [12–16]. 1D InP-based semiconductor devices with advantageous optoelectronics and electronics properties show a quickly appearing field because of numerous interesting properties as superb electron transport and quantum effects. This makes InP nanotubes and nanowires highly appropriate alternatives for the fabrication of viable Nano-integrated circuits [17].

In this paper, the electronic, magnetic, and structural properties of three different 3d transition-metal doped armchair (5, 5) InPNT have been examined utilizing the projector-augmented-wave (PAW) potential approach to the density-functional theory (DFT) implemented in the QUANTUM-ESPRESSO package [18].

The aim of this research is an ab initio study of the magnetic, electronic, and structural properties of V-, Mn- and Ni-metal doped InPNT. This paper is organized as the following. Section II briefly illustrates the computational details regarding the method employed in calculations. In Section III, the results for the magnetic and electronic properties are presented, mainly including the spin-polarized electronic band structures, total state density (DOS) and magnetic moments. In the end, the main conclusions are given in part IV.

# 2 Calculation techniques and structure model

Our density functional theory calculations are performed by using the plane wave pseudopotential technique implemented in the Quantum-Espresso package [19]. This code is a superior alternative for the periodic systems such as nanotube arrays. In this technique, the wave functions of valence electrons are expanded into plane waves while the core electrons are treated with the pseudopotential technique. The PBE form the generalized gradient approximation to the exchange-correlation functional is used. All calculations are done in a hexagonal supercell with a vacuum width of 25Å. To reduce the numerical cost, the sampling of the Brillouin zone was done using a $1\times1\times22$ grid and the energy cut-off for the wave function and the charge density are respectively 90 Ry and 900 Ry [20]. The In $(2s^22p^3)$, P $(3s^23p^1)$ and the d-electrons of the doped TM atom are treated as the valence electrons. Convergence with respect to the plane wave cut-off energy and k-point sampling has been carefully checked. Our calculations for the local distortions resulting from different covalent radii of In and doped TM (V, Mn and Ni) atoms are based on reducing the magnitude of the calculated forces and stresses until they become smaller than the chosen convergence tolerances. All the structures have been optimized to attain the minimum energy by precise relaxation of the atomic positions up to the energy accuracy of 1mRy and forces of fewer than 1mRyBohr. We do calculations on TM (V, Mn, and Ni ) impurities doped at doped InPNT structures corresponding to 5% impurities.

# 3 Results and discussions

## 3.1 Binding energies, Cohesive energies, and Geometrical Parameters

The InP nanotube can be constructed by rolling a graphene-like sheet of InP along a specific direction, which is akin to carbon nanotubes [21].

The structure of the armchair nanotube (5,5) for pure indium phosphide is optimized firstly. The calculated In–P bond length of (5, 5) InPNT, The calculated In–P bond length, the average diameter, and the Mean bond angle (P–In–P) in accordance with previously reported

values [22-25] are about 2.52 Å, 11.49 Å, and 119.30 degrees respectively. Figure 1 displays the optimized structure models of pristine and the 3d TM (V, Mn, and Ni ) doped InPNT. The transition-metal ion replaced by an anion site (P site) in a pure (5,5) InPNT contributes three electrons to the cation (In) dangling bonds. In which the gray, yellow, and black spheres represent In, P, and TM atoms, respectively. These obtained results suggest that the method utilized in the calculations is suitable for describing the properties of InPNT. We present calculations on InPNT-based DMSs using a supercell for 3d TM-doped InPNT. $In_{10}(TM)P_9$ corresponds to 5% of 3d TM impurities, InPNT. For investigating the structural stability of the 3d TM-doped InPNT, as a comparison study, binding and cohesive energies were firstly calculated and these results are listed in Table 1.

The binding energy is defined as [26]:

$$E_{bind} = E_{InPNT-TM} - E_{InPNT} - E_{TM} + E_P,$$

where $E_{InPNT-TM}$ is the total energy of V-, Mn- ,and Ni-doped InPNT, $E_{InPNT}$ is the total energy of pure InPNT and $E_P$ is the total energy of the atom of phosphide and $E_{TM}$ is the total energy of the atom of isolated V, Mn and Ni respectively. The cohesive energy is also defined as [27]:

$$E_{coh} = E_{InPNT-TM} - 9E_{(P)} - 10E_{(In)} - E_{TM}$$

Where $E_{InPNT-TM}$ is the total energy of V-, Mn- and Ni-doped InPNT, $E_{TM}$, $E_P$ and $E_{In}$ are the total energy of atoms of isolated V, Mn, and Ni, phosphide and indium atoms, respectively.
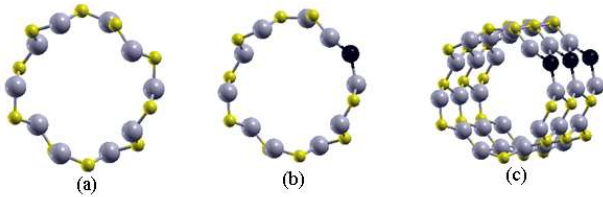


**Figure 1.** Structure model of the (a) pristine armchair InPNT (b) unit cell V-, Mn- and Ni-doped InPNT in P position and (c) supercell of V-, Mn- and Ni-doped InPNT. In which the gray, yellow and black spheres represent In, P and TM atoms, respectively.

The condition that 3d transition-metal doping InPNT system is desirable in terms of energy and stable structure is that the cohesive energy obtained a negative value. The binding energy gives data about the relative stability of the nanostructures, while the cohesive energy gives data about the overall stability of the nanostructures.

It can be seen from the calculations of the binding energies and the cohesive energy in Table1, that the cohesive energy of V and Mn replacing In atom in InPNT are larger than pure InPNT (-2.44 eV/atom). In contrast, the cohesive energy of Ni is smaller than pure InPNT. It implies that when Ni is doped in the P position, the structure is more stable than pristine INPNT, whereas the pristine InPNT is a little more stable than V- and Mn-doped InPNT. Therefore, it can be assumed that these two TM-doped InPNT stabilities are akin to the pure InPNT and they can exist.

**Table 1** The binding energy ($E_{bind}$), cohesive energy ($E_{coh}$), band-gap energy $\mathbf{E_g}$ and total magnetic moment of the pure InPNT and V-, Mn- and Ni-doped InPNT.

| specimen | μTM(Bohr) | Ebind (eV/atom) | Ecoh (eV/atom) | $E_g$(eV) |
|---|---|---|---|---|
| Pure | 0.00 | - | -2.44 | 1.46 |
| InPNT-V | 3.90 | 0.05 | -2.39 | Up 0.20, Dw 0.00 |
| InPNT-Mn | 4.80 | 0.04 | -2.41 | 0.00 |
| InPNT-Ni | 0.00 | -0.01 | -2.45 | 0.00 |

It can be clearly concluded from Table 2 that:

Firstly, compared to the pure nanotube except Mn impurity, the average In-P bond length around the TM impurity site is reduced in V- and Ni-doped InPNT. Secondly, the obtained lattice parameters for doped nanotubes are smaller than the pure nanotube and also the mean bond angle (P–TM–P) around V, Mn, and Ni metals are different and for bond angle (P–TM–P), the lowest and largest value of 99.37 and 116.63 degrees belong to the V and Mn-doped indium phosphide nanotube, respectively. Secondly all the mean TM–P bond lengths in V- , Mn-, and Ni-doped InPNT are smaller than the mean In–P bond length in the pure nanotube. Also, the largest and lowest values of the mean TM–P bond lengths of 2.82 Å and 2.49 Å revealed in the case of Mn- and Ni-doped InPNT, respectively. These results show that, obviously there is distortion

around V, Mn, and Ni impurities. So the geometric structure, because of the observed distortion around these dopants, is affected.

## 3.2. Magnetic properties

On the base of our findings from the total magnetic moments (the 1st column of Table 1), it is observed that pure InPNT has no magnetic property. Therefore the magnetic moments of the TM-doped InPNT arise from the doped TM atoms and their positions. It is interesting to note that the Ni-doped in an InPNT is nonmagnetic, while the V- and Mn-doped atoms have the largest local magnetic moment. Similar to these magnetic moments were also obtained in BP nanotube [25] doped with 3D TM.

On the base of our findings in Table 1 and as shown in Fig. 2, interestingly, the total magnetic moment changes reach the Mn-doped nanotube maximum and then the trend decreases.

**Table 2.** The calculated Lattice parameter, the small and long diameters, the mean bond lengths between nearest-neighbor of In atoms and next nearest-neighbor of P atoms ($d_{In-}$ )), local atomic bond lengths around the substitutional 3d TM impurity in InPNT, comprising the mean bond lengths between the TM atom and its nearest-neighbor In atoms ($d_{TM-P}$).

| specimen | Lattice parameter (Å) | Small Diameter (Å) | Long diameter (Å) |
|---|---|---|---|
| Pure | 4.30 | 11.45 | 11.54 |
| InPNT-V | 4.27 | 11.75 | 12.38 |
| InPNT-Mn | 4.27 | 11.43 | 11.99 |
| InPNT-Ni | 4.23 | 11.64 | 12.09 |
| specimen | Mean bond length TM-P (Å) | Mean bond Length In-P (Å) | Mean angles TM-P (degree) |
| Pure | - | 2.52 | - |
| InPNT-V | 2.81 | 2.51 | 99.37 |
| InPNT-Mn | 2.82 | 2.52 | 116.63 |
| InPNT-Ni | 2.49 | 2.51 | 101.97 |

That is, magnetic moments due to V-, Ni- and Mn-doped (5, 5) InPNT do follow Hund's rule. These changes are due to extreme hybridization among 3d orbitals of the V, Mn and Ni impurities and 2p orbitals of the nearest-neighbor In atoms of InPNT and spin-orbit coupling in the ferromagnetic states [28-30].
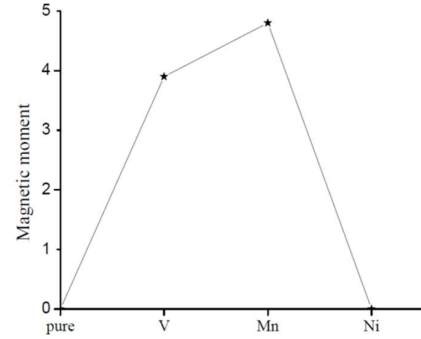


**Figure 2.** Total magnetic moments of V-, Mn-, and Ni-doped and pure InP nanotube.

## 3.3. Density of states and Band structures

The total electronic density of states (DOSs), the band structures, and the partial density of states (PDOS) are calculated to further understand the electronic and magnetic structure where in Figs. 3-5 the lower (upper) panel corresponds to the spin down (up) for pure and V-, Mn-, and Ni-doped (5, 5) InPNT. It should be noted that the Fermi level is set to zero energy which is indicated by the vertical and horizontal dashed lines in the mentioned diagrams.

However, the DOS asymmetry around the Fermi level between the minority and majority spins for V- and Mn-doped (5,5) InPNT, which is shown in the foregoing plots, indicates that the magnetic moments of the doped InPNT are due to the introduction of the TM impurities into host semiconductor.

The band structure charts and the density of states (DOSs) in Fig. 3, Fig. 4b, Fig. 3d, and Fig. 3c show that both the lower and upper spin DOSs for Mn-doped InP nanotube are asymmetric and have obvious electronic states around the Fermi energy level, As a result, that is a magnetic metal, as well as one can easily recognize that the Ni-doped InPNT is nonmagnetic metal, because both the minority and majority spin DOSs are symmetric at the Fermi level and crosses them. So, Ni impurity is not an appropriate candidate for the DMS materials.
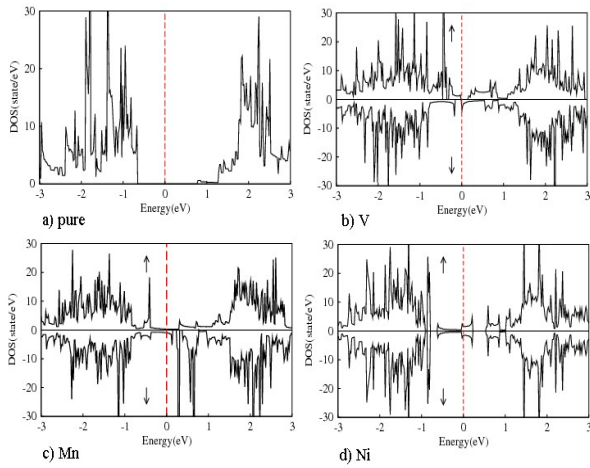
**Figure 3.** The total DOS for configuration InPNT with 5% impurity of (a) pure, (b) V, (c) Mn, and (d) Ni, instead of P atom for up-spin (majority) and down-spin (minority) states. The Fermi level ($E_F$) is set at 0 eV.
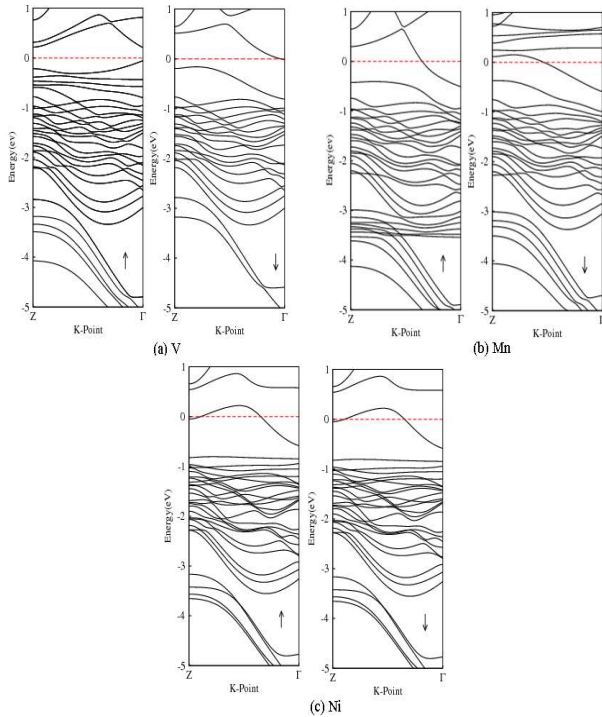


**Figure 4.** The band structures for configuration InPNT with 5% impurity of (a) V, (b) Mn and (c) Ni, instead of P atom for up-spin (majority) and down-spin (minority) states. The Fermi level ($E_F$) is set at 0 eV.

The majority of spin electronic states in Fig. 3b and Fig. 4a is semiconducting while the minority of spin electronic states cross the Fermi level and become metallic. Thus spin-polarized electronic structure of V-doped in InP nanotube shows half metal (HM) and magnetic behaviors with 100% spin polarization and may be a suitable alternative for spintronic and Nano magnet applications. Because the s orbital is the

innermost orbital, it does not make much contribution to the PDOS spectrum, so as shown in Fig. 5, the major effect on the PDOS spectrum is only due to the d orbitals of V, Mn, and Ni impurities and p orbitals of near In and P atoms of InPNT.
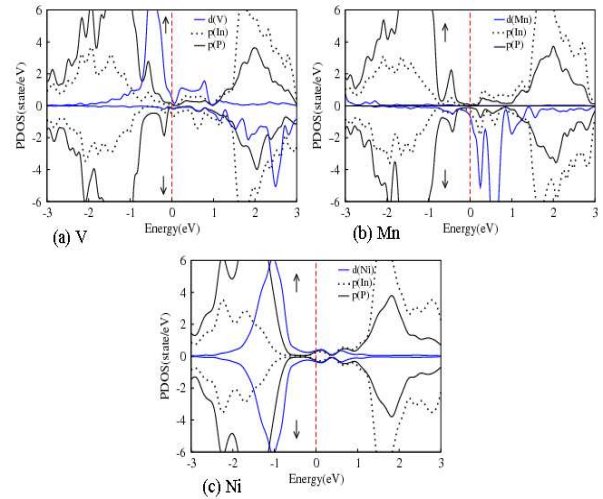


**Figure 5.** The partial density of states (PDOS) for configuration InPNT with 5% impurity of (a) V, (b) Mn, and (c) Ni, instead of P atom for up-spin (majority) and down-spin (minority) states. The Fermi level ($E_F$) is set at 0 eV

## 4 Conclusions

In summary, using the DFT method, the structural, magnetic, and electronic properties of the Indium Phosphide nanotube have been systemically studied and investigated before and after doping by 3d TM (V, Mn or Ni) atom.

According to the cohesive energies, it was found that the InP nanotube doped by V atom, Mn, or Ni has a stable structure and also Ni doped in the InP nanotube can have a more stable structure than the pure nanotube.

From the observations of the optimized structures, it is concluded that the TM atom replaced by Phosphor breaks the local symmetry of the pure nanotube and causes structural distortions around the V, Mn, and Ni impurities.

The results show that the changes of total magnetic moments induced by V-, Mn-, and Ni-doped InPNT follow Hund's rule. Also, maximum magnetic moments are observed for both states of InPNT doped with Mn and V. Therefore, they can be used in magnetic data storage devices.

## Acknowledgements

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