Effect of partial Ti substitution at Zn sites on the Structural, Electronic and Magnetic Properties of Zn_3P_2

G. Jaiganesh* and S. Mathi Jaya

Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam – 603102, India.

Abstract

Using the *ab-initio* calculations based on density functional theory, we have investigated the structural, electronic and magnetic properties of Ti-substituted Zn_3P_2 compound. One and two Ti atom replacements in the unit cell of Zn_3P_2, which contain eight molecules per formula unit (40 atoms), are considered in the study. Our results show that the ferromagnetic phase is favored for the single Ti atom substitution, as the total energy corresponding to the ferromagnetic phase is lower than that of the nonmagnetic phase. A considerable value of the magnetic moment at the Ti site is obtained from our calculations.

Keywords: Density Functional Theory, *Ab-initio* calculations, Ti-based compounds, Heat of formation, Zn_3P_2

PACS: 71.15.Mb; 31.15.A-; 71.20.Lp; 71.15.Nc

*Corresponding author E. Mail: drjaiganesh15@gmail.com

1. INTRODUCTION

Magnetic semiconductors are promising materials in magneto-electronic devices as they offer the possibility of manipulating the charge and spin of the electron simultaneously [1, 2]. Intensive research in this area has led to identifying several transition metal substituted magnetic semiconductors [3]. Best available diluted magnetic semiconductors with room temperature ferromagnetism belong to the III-V, II-VI, and IV-VI groups [4]. The formation of magnetism in semiconductors by introducing nonmagnetic elements is an exciting feature in this area, and it has acquired considerable interest in recent years [5, 6].

Our present study focuses on the partial substitution of nonmagnetic element Ti in Zn_3P_2, an essential semiconducting compound in the II_3-V_2 group. Zn_3P_2 is a low cost and earth-abundant material. It is a direct bandgap semiconductor with many application potentials [7]. Many experimental investigations in bulk, thin-film, and nano phases of Zn_3P_2 have been carried out by many research groups, whereas the theoretical studies are relatively less [8-13].

We have reported the magnetism, and half-metallic property of transition metal (V, Cr, Mn, Fe, Co) substituted Zn_3P_2 using *ab-initio* techniques [14]. The present work's primary interest is to investigate the ferromagnetism and its stability in nonmagnetic element substituted Zn_3P_2 using the *ab-initio* computations. In this work, we report the investigations of the electronic and magnetic properties of $Zn_{3-x}Ti_xP_2$ with $x = 0.125, 0.25$.

2. CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The crystal structure of Zn_3P_2 is a primitive tetragonal lattice (Space Group No.: $P4_2/nmc$, 137) at ambient conditions [15]. The unit cell contains 40 atoms (24 Zn and 16 P atoms). In the Zn_3P_2 unit cell, the zinc atoms occupy three distinct 8g symmetry positions characterized, and the respective 8g positions are referred to as Zn(1), Zn(2), and Zn(3) atoms, respectively. The phosphorus (P) atoms occupy the 4c(P1), 4d(P2), and 8f(P3) positions of the $P4_2/nmc$ space group. More details about this structure may be found in Reference [14]. The structure optimizations of Ti-substituted Zn_3P_2 and their electronic and magnetic properties are studied using the *ab-initio* techniques based on the density functional theory, as implemented in the Vienna *Ab-initio* Simulation Package [16-18]. The Projector Augmented Wave (PAW) method [19] and PE functional were used for the required pseudo-potentials,

and the $3d^{10}4p^2$, $4s^1\ 3d^3$, and $3s^2\ 3p^3$ valence electrons configurations for Zn, Ti, and P atoms are used in our calculations.

A plane wave cutoff energy of 525 eV is used throughout the calculations. The Monkhorst-Pack scheme with 6×6×4 k-point mesh is used for the Brillouin zone integration [20-21]. The structure's optimization was done using the conjugate gradient scheme, and the convergence of forces on atoms is taken as 0.01 eV/Å. Vosko *et al.* [22] spin interpolation scheme was used for the spin polarization calculations. To study the doping effects, we have replaced one Zn atom with one/two Ti atoms in the unit cell. We have further considered the different possibilities of substituting the one or two Ti atoms at the Zn sites in the unit cell of Zn_3P_2. Magnetic stability is obtained from the unit cell's total energy difference (ΔE) between ferromagnetic/antiferromagnetic and nonmagnetic configurations.

3. DISCUSSION OF RESULTS

To perform the calculations for the one/two Ti atoms substituted Zn_3P_2, considering all the possible configurations that will evolve when a Ti atom replaces a Zn atom is required. It is already mentioned that the Zn atoms occupy three distinct 8g positions. A Ti atom can be substituted among any three distinct 8g positions, and hence we have three different configurations for the Ti atom substituted Zn_3P_2. However, the replacement of two Zn atoms by Ti atoms gives rise to 342 configurations. Thus, it becomes a complex task of considering all configurations for our calculations. Hence we have decided to avoid the difficulties and considered 7 cases of replacing two Zn atoms within the positions represented by specified 8g symmetry by two Ti atoms and 15 cases of replacing two Zn atoms at positions by two distinct 8g symmetries with two Ti atoms. The second case of replacing two Ti atoms is taken at random. We have considered all these configurations for our calculations, and we have performed the structural optimization for all these structures. Details of the optimized structures are presented in the following section that describes our results.

The calculations were carried out for all the configurations mentioned above with and without the inclusion of spin polarization as our primary goal is to study the magnetism in these systems. Full structural optimization for the configurations having energy close to that of the minimum among these configurations is performed, and the total energies corresponding to both the magnetic and nonmagnetic cases were also

obtained. From the calculated results (Table 1), it is observed that the ferromagnetic ordering is energetically favorable for the case of one Ti-substituted Zn_3P_2, whereas the two Ti atoms substituted Zn_3P_2 favors nonmagnetic phase.

The optimized structures obtained from our calculations for one/two Ti atom substituted Zn_3P_2 were used in the further calculations of the spin-dependent band structure and spin, orbital, atom decomposed, and integrated density of states. The calculated spin-dependent band structure for one Ti atom substituted Zn_3P_2 is shown in Figure 1. It may be observed from the figure that the system prefers ferromagnetic ordering. Moreover, the densities of states of the one and two Ti atom substituted Zn_3P_2 systems are shown in Figure 2. It may be seen from the figures that the one Ti atom substituted systems prefer ferromagnetic ordering while the two Ti atoms replaced Zn_3P_2 shows nonmagnetic nature. We further observed from our calculations that one Ti atom replaced Zn_3P_2 system acquires significant magnetic moment too, and the calculated values of the magnetic moments are given in Table 1. Our calculations also found that the Zn and P atom in these systems acquires a small magnetic moment.

The atom decomposed and integrated density of states shown in Figure 3 corresponds to the one Ti atom substituted Zn_3P_2 system. It may be observed from the figure that the strong exchange splitting is present in the density of states of Ti atom, and it leads to a significant magnetic moment in this system. It clearly shows that the one Ti atom substitution induces ferromagnetic ordering in the system. It may be further observed from the integrated density of states that the system's magnetic moment originates mainly from the d-electrons of the substituted Ti atom.

The charge and magnetization density contours of one Ti atom substituted Zn_3P_2 are calculated and are given in Figure 4. The substitution of one Ti atom in Zn_3P_2 leads to a reduction in the charge density localization, enhancing conduction. The magnetization density contour explores that the magnetic moment of this system originates mainly from the *3d*-electrons of the Ti atom.

4. CONCLUSIONS

In this work, we have studied the influence of Ti atoms' partial substitution at Zn sites on the electronic structure and magnetic properties of Zn_3P_2 using the *ab-initio* techniques. We found that a single Ti atom substitution can induce magnetic property in the Zn_3P_2 semiconductor. The single Ti atom substituted Zn_3P_2 is more

stable in the ferromagnetic phase and the magnetic moment of the Ti atom is 0.707 μ_B while the net magnetic moment for the unit cell is 1.22 μ_B.

ACKNOWLEDGMENTS

One of the authors (G. Jaiganesh) wishes to thank the Council of Scientific and Industrial Research, New Delhi, India, to award Senior Research Associateship through the Scientist Pool Scheme (No. 13(8928-A)/2017-Pool). I want to thank Dr. C. Lakshmanan, Materials Physics Division, IGCAR, for his timely help.

CONFLICT OF INTEREST

We have no conflict of interest to declare.

REFERENCES

1. T. Dietl, in (Diluted) Magnetic Semiconductors, edited by S. Mahajan. Handbook on Semiconductors, Vol. **3** (North-Holland, Amsterdam 1994), pp. 1251-1342.
2. "Magnetoelectronics," edited by Mark Johnson, 1st Edition, Elsevier Academic Press, Amsterdam, 2004.
3. "Handbook of Spintronic Semiconductors," edited by Weimin and Irina Buyanova, Singapore: Pan Stanford Publishing, 2010.
4. T. Dietl and H. Ohno, Reviews of Modern Physics, Vol. **86**, 187-251 (2014).
5. Jiji Antony et al., IEEE Transactions on magnetic, Vol. **42**, No. 10, 2697-2699 (2006).
6. G. Jaiganesh and S. Mathi Jaya, Journal of Alloys and Compounds, Vol. **665**, 311-318 (2016). & G. Jaiganesh and S. Mathi Jaya, AIP Conf. Proc. **1665**, 130013 (1-3) (2015).
7. Wan-Jian Yin and Yanfa Yan, J. Appl. Phys. Vol. **113**, 013708 (1-5), (2013).
8. Gregory M. Kimball, Astrid M. Müller, Nathan S. Lewis, and Harry A. Atwater, Appl. Phys. Lett. Vol. **95**, 112103 (1-3) (2009).
9. D. M. Stepanchikov and G. P. Chuiko, Condensed Matter Physics, Vol. **12**, 239-248 (2009).
10. A. M. Hermann et al., Solar Energy Materials and Solar Cells, Vol. **82**, 241-252 (2004).
11. I. G. Stamov, N. N. Syrbu, and A. V. Dorgan, Physica B, Vol. **408**, 29-33 (2013).
12. P. J. Lin-Chung, Phys. Stat. Sol. (b), Vol. **47**, 33-39, (1971).

13. K. Sieranski, J. Szatkowski, and J. Misiewicz, Phys. Rev. B, Vol. **50**, No. 11, 7331-7337, (1994).
14. G. Jaiganesh, S. Mathi Jaya, Computational Materials Science, Vol. **102**, 85-94 (2015).
15. P. Villars and L. D. Calvert, "Pearson's handbook of Crystallographic Data for Intermetallic Phases" Materials Park, OH: ASM International, Vol. **4,** 4864 (1991).
16. G. Kresse and J. Furthmuller, Phys. Rev. B, Vol. **54**, 11169 (1996).
17. W. Kohn and L. Sham, Phys. Rev. Vol. **140**, B1133 (1965).
18. http://www.vasp.at/
19. P. E. Blochl, Phys. Rev. B, Vol. **50**, 17953 (1994).
20. H. J. Monkhorst and J. D. Pack, Phys. Rev. B. Vol. **13,** 5188 (1976).
21. P. E. Blochl, O. Jepsen and O. K. Anderson, Phys. Rev. B, Vol. **49,** 16223 (1994).
22. S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. Vol. **58,** 1200 (1980).

Figures

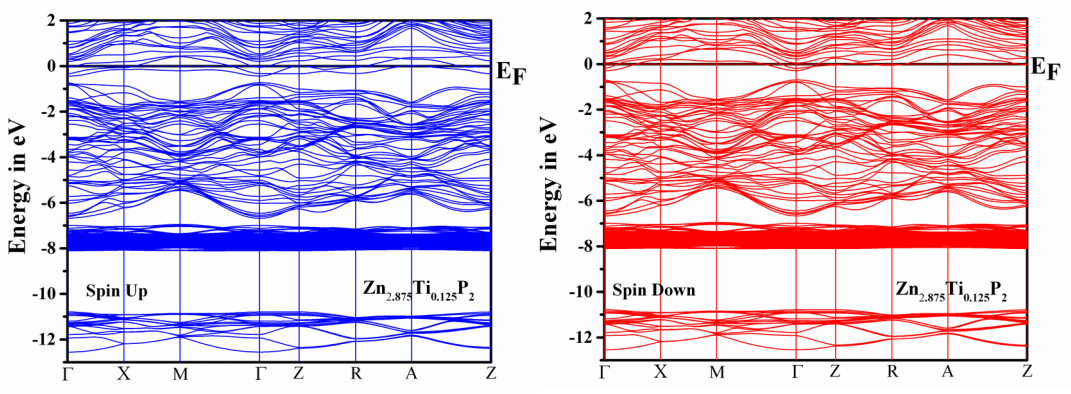

FIGURE 1. Spin-dependent electronic band structure of one Ti atom substituted Zn_3P_2

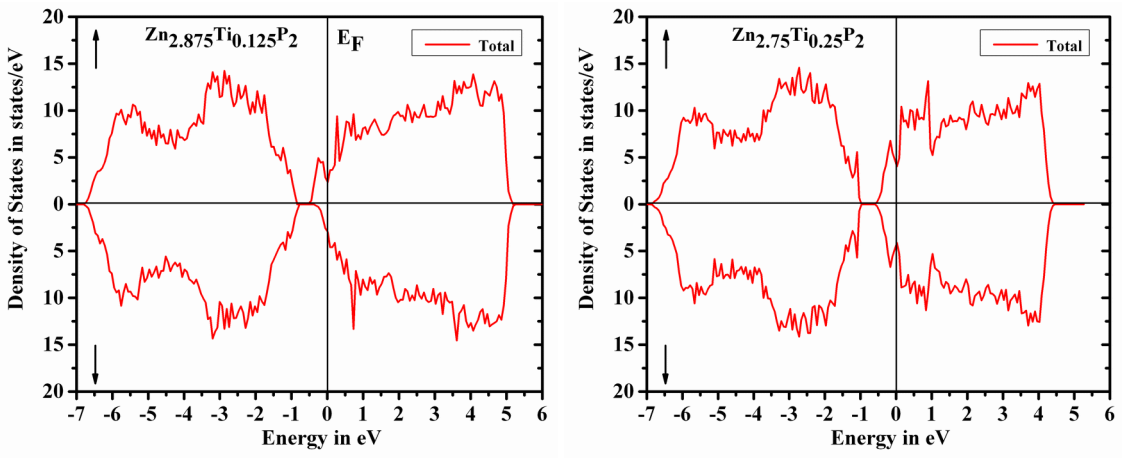

FIGURE 2. Total density of states of one and two Ti atom substituted Zn_3P_2

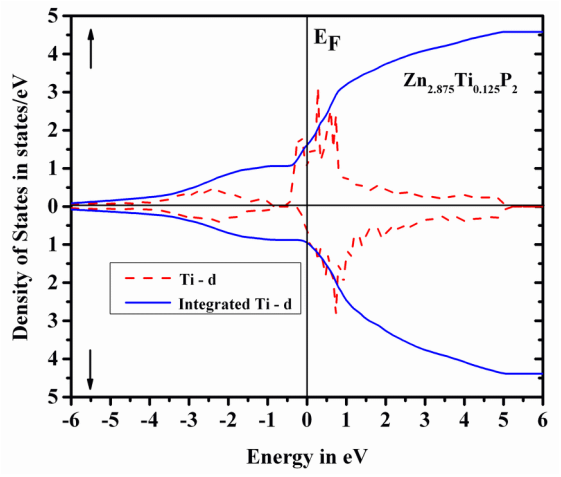

FIGURE 3. Integrated and atom decomposed of the density of states of one Ti atom substituted Zn_3P_2

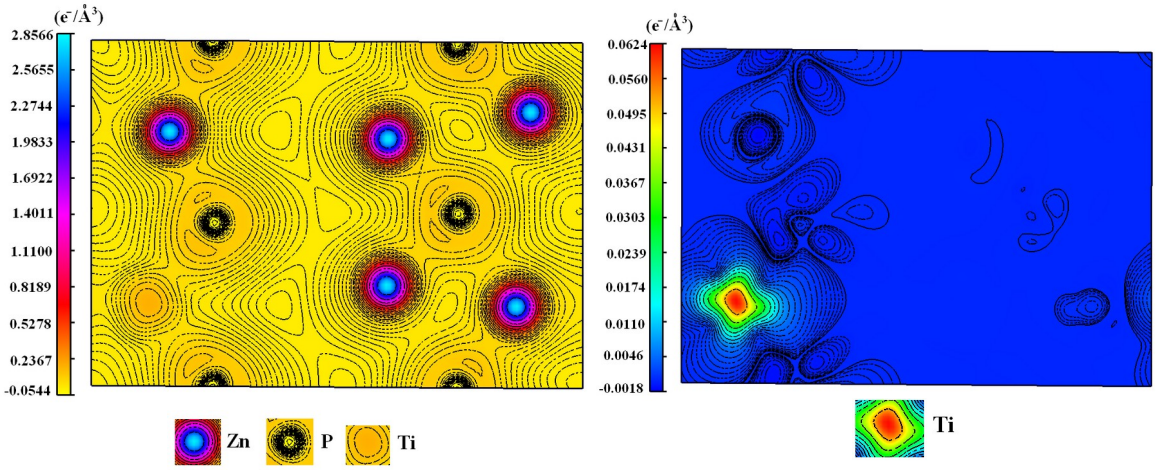

FIGURE 4. Charge and magnetization density contours of one Ti atom substituted Zn_3P_2 in (010) plane

Table

TABLE 1. Calculated total energy differences (**ΔE**) in eV, the heat of formation (**ΔH**) in eV and net magnetic moment in μ_B.

Compound	ΔE	ΔH	Net Magnetic Moment
$\mathbf{Zn_{2.875}Ti_{0.125}P_2}$	0.0122	-0.208	1.22
$\mathbf{Zn_{2.75}Ti_{0.25}P_2}$	0.0	-0.211	-