

Magnetism, electronic structure and half-metallic property of transition metal (V, Cr, Mn, Fe, Co) substituted Zn₃P₂ dilute magnetic semiconductors: An ab-initio study



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ABSTRACT

The ab-initio electronic structure calculations are used to investigate the half-metallic property, structural stability, spin dependent density of states and magnetism of transition metal (V, Cr, Mn, Fe, Co) substituted Zn₃P₂. Our results show the half-metallic ground state and ferromagnetic (antiferromagnetic) stability for small concentrations (2.5% and 5%) of transition metal atom substitution considered in our study. The structural and magnetic stability of the substituted compounds have been investigated through the calculation of the heat of formation and analyzing the minimum total energies corresponding to the ferromagnetic, antiferromagnetic and nonmagnetic phases. The substituted transition metal atom is found to give rise to magnetism of these compounds and half-metallic property is observed in many cases. We have used the spin, orbital and atom projected density of states to investigate this point and studied the nature of bonding in these systems using the charge density contours. We have observed from our calculations, magnetically stable phases and large values of the magnetic moments in these compounds and it suggests that these compounds may be useful materials for semiconductor spintronic devices. We have further calculated the theoretical X-ray diffraction pattern of these compounds.

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1. Introduction

Since the emergence of the field of spintronics, there is a continued interest in this field of research both in the experimental and theoretical sides [1]. Spintronics aims at revolutionizing the electronics industry by exploring the possibility of manipulating the two fundamental properties (charge and spin) of the electron simultaneously. Spintronics research has several branches. The branches that are related to the subject of the paper are the area of dilute magnetic semiconductors and half metallic ferromagnets. The unique characteristics of dilute magnetic semiconductors are the presence of magnetic property as well as semiconducting nature within the same substance and it has found an important place in the field of spintronics [2]. These materials have potential industrial applications in the magneto-transport and magneto-optical devices [3]. Half metallic ferromagnets on the other hand are materials in which one spin channel shows metallic behavior while the other channel shows an energy gap around the Fermi level. This behavior has stimulated research interest in half metallic materials

as these materials too have potential applications in spintronic devices. In 1983, de Groot and his group first reported half metallic behavior in C1_b-type Heusler alloys using the augmented-spherical-wave method [4]. Since then many half-metallic ferromagnets have been identified [5].

The simultaneous presence of magnetic and semiconducting properties was initially observed in doped and undoped Eu²⁺ based oxides and chalcogenides [6] and the spinel structured composites [7]. These materials have low Curie temperature (~50 K) and poor semiconducting properties. Further, the discovery of ferromagnetism in p-type Mn-doped IV–VI [8], III–V [9], II–VI [10] compounds has added new dimensions to the development of the field of spintronics. For spintronics applications, ferromagnetic semiconductors with T_c above 300 K are required. In 2000, Dietl et al., using Zener model predicted the existence of room temperature ferromagnetism in zinc-blende ferromagnetic semiconductors [11]. Over the past years or so, a number of transition-metal doped semiconductors with room temperature ferromagnetism such as transition metals doped TiO₂ [12], Cr doped ZnTe [13], Mn-doped ZnO [14] are reported. Further, high temperature ferromagnetism with T_c up to and above 350 K was also observed in Mn-doped chalcopyrite type ternary compounds

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$A^{\text{II}}B^{\text{IV}}C^{\text{V}}$ ($A = \text{Cd, Zn}$; $B = \text{Si, Ge}$; $C = \text{P, As}$) [15]. This observation makes these compounds more attractive in comparison with their binary analogs $A^{\text{II}}B^{\text{V}}$ and $A^{\text{III}}B^{\text{V}}$ compounds.

The pnictogens of group II elements mostly exist in the $A^{\text{II}}B^{\text{V}}$ forms [16]. These compounds have unusual transport properties and photovoltaic properties [17]. Compared to other conventional II–VI and III–V compound semiconductors, these compounds are less studied in the past and it is partially due to their complex crystal structures and large number of atoms in the unit cell. An important $A^{\text{II}}B^{\text{V}}$ compound is zinc phosphide (Zn_3P_2) and is an earth abundant, polar, mixed-valent, p-type semiconducting material. It is a low cost compound, easy to fabricate them as thin-films with great potential as a photovoltaic material. It is a direct band-gap semiconductor with E_g of about 1.5 eV, which is the optimal band gap for single-junction solar cells [18]. The unusual physical properties such as large optical absorption coefficient (above $1 \times 10^4 \text{ cm}^{-1}$), long minority carrier diffusion length ($\sim 13 \times 10^6 \text{ m}$) and large excitonic radii of this material offer promising applications in photo-voltaic industry [19,20]. In view of these interesting properties of Zn_3P_2 , there have been many works devoted to the preparation and investigation of thin-film photo-voltaic cells for solar energy applications. However, the studies on the development of magnetic semiconductors and half metallic ferromagnets from this material are not yet actively carried out. This has turned our interest towards this study and it is the primary motivation for undertaking the present work.

Since 1950, several experimental investigations on the thin-films [21,22], bulk [23–25] and nano phases of Zn_3P_2 [26,27] have been carried out by many research groups. However, from the theoretical point of view, it is a relatively little studied compound. The ab-initio studies on Zn_3P_2 and related compounds are also very limited [17,28–30]. Recently, Yin et al. [31] and Demers et al. [32] have calculated the intrinsic defects and dopability of this compound using density functional theory (DFT) with hybrid functional method. Laiho et al. carried out the preparation and study of the magnetic properties of Mn doped ZnAs_2 [33] and Zn_3As_2 [34] compounds and explained their observed properties by using the presence of MnAs nano clusters in these systems. The magnetization, susceptibility and specific heat of the semi-magnetic semiconductor Cd_3As_2 with very small concentration of Mn doping have been measured by Denissen and his group [35]. Except for these studies, as far as we know, magnetism of the transition metal substituted $A^{\text{II}}B^{\text{V}}$ binary wide band gap semiconductors have not been studied extensively even within the framework of the ab-initio methods. Therefore, it is desirable to study the magnetic and electronic properties of these compounds in detail which can enhance the understanding of the properties of these materials and their application potentials.

In this paper, we report the first-principles study of the magnetism, electronic structure, half-metallicity and phase stability of 3d transition metal (V, Cr, Mn, Fe, Co) substituted Zn_3P_2 compounds. We have considered in our study two values of the concentration of transition metal (TM) atoms and they correspond to 2.5% and 5% replacement of Zn atoms with the TM atoms. The change in electronic structure and the bonding nature of parent and substituted compounds are analyzed through the calculation of the orbital, spin and atom decomposed density of states. We have further considered in our studies, the different structural configurations that arise due to the replacement of Zn atoms with the TM atoms and carried out the full structural optimization to identify the stable configurations. We have further studied the magnetic stability and half-metallic properties of these systems too. The paper also addresses the issue of variation of crystal structure with respect to different compositions using theoretical X-ray diffraction pattern. The results are helpful to the

experimentalists in their search and growth of materials suitable for spintronic devices.

Our results are described in the following sections along with the details of calculations and the paper is organized as follows. In Sections 2 and 3, crystalline structure and the methodology of calculations are presented. Results and discussions are given in the Section 4 and the conclusions are given in Section 5.

2. Crystalline structure

2.1. Pure Zn_3P_2

Zn_3P_2 is found to exist at ambient conditions in a primitive tetragonal (Zn_3P_2) type structure with $P4_2/nmc$ space group (No. 137) [36]. The structure of the Zn_3P_2 compound was determined by von Stackelberg and his group [37]. It is a centrosymmetric crystal. The crystal structure of Zn_3P_2 is given in Fig. 1. The unit cell contains eight molecules of Zn_3P_2 and therefore the total number of atoms in the unit cell is 40. The cation (Zn) atoms are placed at the four nearly equally spaced planes perpendicular to the C axis whereas the anion (P) atoms lie between the two cation planes. The cation atoms occupy three distinct 8g symmetry positions and the corresponding atomic co-ordinates are given in Table 1. These three distinct zinc atoms occupying the respective 8g positions are referred as Zn (1), Zn (2) and Zn (3) atoms respectively. The anion atoms occupy the 4c, 4d and 8f positions of $P4_2/nmc$ space group and they are referred as P (1), P (2) and P (3) atoms which may be seen from Fig. 1. The Zn and P atoms form the tetrahedral arrangement like in zinc-blende and fluorite type structures. Each of the three different types of Zn atoms forms four bonds (tetrahedral coordination) with one P1, one P2 and two P3 atoms. The atomic coordinates of P atoms corresponding to the 4c, 4d and 8f positions are also given in Table 1 along with the experimental [36] and other theoretical results [30]. The table displays our calculated values of the atomic coordinates too and the details will be discussed later. In this table, we have given only the coordinates of the basis atoms. The symmetry considerations can be invoked to generate the coordinates of the remaining atoms.

2.2. Transition metal substituted Zn_3P_2 ($\text{Zn}_{3-x}\text{M}_x\text{P}_2$, $M = \text{V, Cr, Mn, Fe, Co}$)

In order to perform the calculations for the one TM atom substituted compound ($\text{Zn}_{2.875}\text{M}_{0.125}\text{P}_2$), it is necessary to consider all the possible configurations that will evolve when a Zn atom is replaced

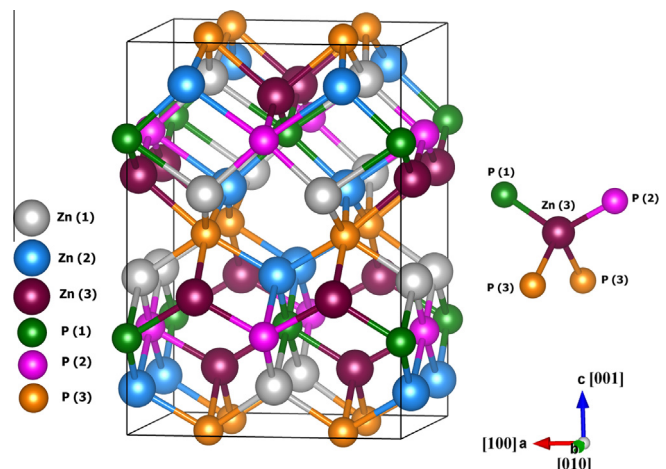


Fig. 1. Crystal structure of Zn_3P_2 .

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