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An *ab initio* study on electronic and magnetic properties of Cr, V doped Cd and Zn nitrides for spintronic applications

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ABSTRACT

The half-metallic ferromagnetic property of Cr, V doped CdN and ZnN has been investigated by the electronic band structure calculations using Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. The host compounds of CdN and ZnN were doped with Cr and V in the concentration of 37.5% to replace Cd and Zn atoms. The compounds CdN and ZnN doped with Cr are found to exhibit half-metallic ferromagnetism and the results are compared in GGA and GGA+U (Hubbard) method. In this present work, electronic band structure, density of states, magnetic properties and spin polarization were studied. The p-d hybridization in the doped transition metal-d bands and N-p bands that causes exchange splitting was discussed to bring out the differences in the half-metallic character of the doped compounds. The degree of half-metallic nature in terms of spin polarizations has been predicted for Cr-doped CdN and ZnN. The calculated magnetic moments for the doped compounds are found to increase with the increase in Hubbard potential U for Cr-doped compounds. The Cr-doped CdN and ZnN are found to exhibit direct band gap in spin down direction.

1. Introduction

The half-metallic ferromagnetism (HMFs) were theoretically and experimentally predicted in some Heusler alloys in the year 1983 by de Groot et al. [1,2]. Since then, the focus has turned on to the study of half-metallic compounds. Half metallic ferromagnets (HMF) are known to be excellent candidates for spintronic applications. In these materials, one spin channel is conducting while the other is semiconducting and hence, 100% spin polarization at E_F can be expected. The science of spintronics uses the two separate spin channels of HMFs (with conducting and semiconducting) in electronic devices. Extensive research is being carried out in search of materials exhibiting half-metallic nature in the ferromagnetic phase. In this respect, dilute magnetic semiconductors (DMS) are found to be potential candidates. DMS obtained by substituting transitional metals having partial filled d-states such Cr, Mn, Fe, Co have been extensively studied for spintronic applications. Among these, nitride based DMSs have been reported to be half-metallic materials. Sheik et al. [3] have recently reported HMF in Fe (Mn)-doped CdN and ZnN. Houari et al. [4] have done theoretical study on half-metallic ferromagnetism in Pt and Pd nitrides. They reported half-metallicity in Pt and Pd nitrides by substituting Mn(Fe). Doumi et al. [5] did some investigations on the half-metallic property for (Al, Ga, In)$_{1-x}$M$_x$N where x=Mn,Fe. The objective of the present work is to investigate the existence of half-metallic ferromagnetism in Cr and V doped ZnN and CdN. Transition metal nitrides such as Zinc nitride and Cadmium nitride are known to be narrow gap semiconductors even though there is some discrepancy in considering CdN as semiconducting or metallic. However, these materials when doped with 3d metals can become potentially half-metallic. Su-Hyun Yoo et al. [6] have done theoretical work on zinc nitride and predicted the material to have a band gap ranging from 0.95 eV to 1.15 eV. Futsuhara et al. [7] have done experimental preparation of ZnN by RF-magnetron sputtering and according to them, ZnN is an n-type semiconductor with direct band gap of 1.23 eV. Zong et al. [8] have experimentally prepared ZnN by RF-magnetron sputtering and reported an optical band gap of 2.12 eV. The intrinsic value of band gap for zinc nitride is still a matter of controversy and debate according to another group of researchers [9–14]. This takes us to believe that a definite band gap either direct or indirect for ZnN is yet to be arrived at. The other compound CdN, as already mentioned, is also less known as a semiconductor. Gupta et al. [15] have studied using first principles the structural and dynamical stability of cadmium nitride and reported no study on band gap. Zhao et al. [16] investigated the structural, mechanical, electronic properties of 4d transition metal mono nitrides. They have reported in their work that CdN exhibits a kind of metallic behavior. Korir et al. [17] did first principles study on the bulk properties of 4d-transition metal nitrides using GGA which included CdN. Ateser et al. [18] studied structural and mechanical properties

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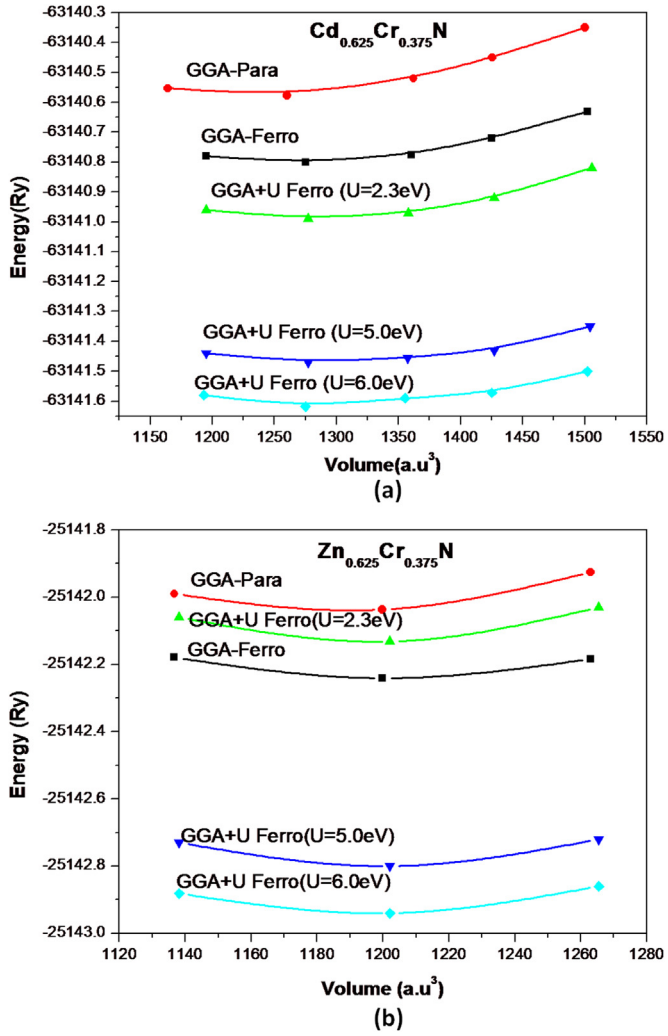

Fig. 1. Volume optimization of (a) $Cd_{0.625}Cr_{0.375}N$ and (b)$Zn_{0.625}Cr_{0.375}N$ in GGA and GGA+U methods.

of CdN and have shown that the compound stabilized in NaCl rock salt structure. Ghemid et al. [19] studied the bulk modulus of CdN compound and compared that with bulk modulus of constituent atoms. Not much of theoretical and experimental works were done on CdN with respect to finding its band gap, electronic and magnetic properties. Essentially, no report for DMS studies on Cr (V) doped CdN and ZnN are found in the literature to the best knowledge of authors. This has motivated us to do theoretical investigations on half-metallic ferromagnetism for these compounds by doping with Cr and V atoms.

The paper is organized as follows. In Section 2, methodology used in the calculations was discussed. Section 3 largely deals with the results and discussion that include electronic properties and magnetic properties. Electronic properties section is then divided into electronic structure, band structure, density of states (DOS) and spin polarization. Section 4 reports the conclusion.

2. Method of calculation

A spin polarized Full Potential Linear Augmented Plane Wave (FP-LAPW) method was used for the first principles calculations within the density functional theory [20,21]. The electronic properties were studied using WIEN2k code [22–24] which employs the full-potential linearized augmented plane wave plus local orbitals method. The generalized gradient approximation (GGA) [25] proposed by Perdew et al. [26–28] was used for exchange and correlation potentials. The exchange correlation effect U by Hubbard Model has been applied for Cr doped CdN and ZnN as Cr doped compounds are favourable to exhibit half-metallic characteristics. The DFT+U calculations were carried out in order to include the effects due to orbital dependent exchange and Coulombic interactions between the electrons. To incorporate the U-term with existing approximations, Hubbard Model approach was utilized as implemented in an FP-LAPW+lo method using WIEN2k coding. The Hubbard potential of $U=2.3$ eV, 5.0 eV and 6.0 eV with $J=0$ were used for Cr atoms which are doped into the host compounds of CdN and ZnN. The FP-LAPW+lo method expands the Kohn–Sham orbitals in atomic like orbitals inside the muffin –tin (MT) atomic spheres and plane waves in the interstitial region. The importance of this method is that near an atomic nucleus the potential and wave functions are similar to those in an atom which mean that they strongly vary but are nearly spherical. But, between the atoms the potential and wave functions are smoother [29]. In this method, the potential and charge density are treated without shape approximation and core electrons are treated relativistically. The plane wave cutoff for the basis function was set to $RK_{max}=7.0$. The electronic structures of Cr (V) doped ZnN and CdN were studied by constructing super cells. The primitive unit cells of ZnN and CdN have NaCl rock salt structure. Both the structures belong to cubic ($Fm3m$) space group. The lattice constants for the primitive unit cells of CdN and ZnN were theoretically found out to be 4.72 A° and 4.50 A° respectively. The Cr and V atoms are doped into the host ZnN such that the super-cells are formed as $Zn_{0.625}Cr_{0.375}N$ and $Zn_{0.625}V_{0.375}N$. Similarly, for CdN, super cells of $Cd_{0.625}Cr_{0.375}N$ and $Cd_{0.625}V_{0.375}N$ were created with $x=37.5\%$ for all the cases. Unit cells of M_8N_8 (M=Zn, Cd) were constructed using the configuration of $2\times2\times2$ cubic super-cell. The super-cell structure which consists of eight smaller *fcc* unit cells has lattice constants as 9.46 A^o and 9.00 A^o for the CdN and ZnN based compounds respectively. Doped Cr (V) atoms occupy structural positions of (0 0 0), (½ 0 0) (¼ ¼ 0) in the basis of their respective super cells $Zn_{0.625}Cr_{0.375}N$, $Zn_{0.625}V_{0.375}N$, $Cd_{0.625}Cr_{0.375}N$ and $Cd_{0.625}V_{0.375}N$.The crystalstructures of Cr (V) doped ZnN and CdN are shown in the Fig. 2 (a)–(d). The radii of Cd and Zn atoms were set at 1.52 A^o and 1.37 A^o while for Cr and V radii were 1.26 A^o for each. Radius of nitrogen atom was set at 0.74 A^o in all the unit cells. The self consistent calculations were found to converge when the total energy of the system is stable within 10^{-4} Ry. The integration over the irreducible Brillouin Zones was done on the grid of 63k points generated for super-cells using the Monkhorst-Pack scheme [30].Fig. 1.

3. Results and discussions

3.1. Electronic structure and optimization

Using VESTA software [31], the crystal structures of $Cd_{0.625}Cr_{0.375}N$, $Cd_{0.625}V_{0.375}N$, $Zn_{0.625}Cr_{0.375}N$, and $Zn_{0.625}V_{0.375}N$, were plotted as shown in Fig. 2. The positions of the atomic sites of Cr and V replacing Zn and Cd atoms of the host compounds are shown in the figure. Three Cr and three V atoms are substituted into the host compounds which form the super cell structure of new compounds $Cd_{0.625}Cr_{0.375}N$, $Cd_{0.625}V_{0.375}N$, $Zn_{0.625}Cr_{0.375}N$, and $Zn_{0.625}V_{0.375}N$ respectively. Replacing the 4d transition metal atoms (Cd) with 3d atoms (Cr), the cubic symmetry of doped compound are subject to change. Substitution of 3d-Cr,V in the host compounds may require the performance of relaxation process using WIEN2k to check the cubic symmetry of the doped compounds. Interestingly, the cubic symmetry of the compounds was not found to be in deviation relative to the atomic positions of un-doped lattice.