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Cr Induced Magnetization in Zinc-Blende ZnO Based Diluted Magnetic Semiconductors

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***Abstract*—**The capability of exploiting the electronic charge and spin properties simultaneously in a single material has made diluted magnetic semiconductors (DMS) remarkable in the field of spintronics. We report the designing of DMS based on zinc-blend ZnO doped with Cr impurity. The full potential linearized augmented plane wave plus local orbital FP-L(APW+lo) method in density functional theory (DFT) has been adapted to carry out these investigations. For treatment of exchange and correlation energy, generalized gradient approximations have been used. Introducing Cr atoms in the matrix of ZnO has induced strong magnetic moment with ferromagnetic ordering at stable ground state. Cr:ZnO was found to favor the short range magnetic interaction that reflect tendency of Cr clustering. The electronic structure of ZnO is strongly influenced in the presence of Cr impurity atoms where impurity bands appear in the band gap.

***Keywords*—**ZnO, Density functional theory, Diluted magnetic semiconductors, Ferromagnetic materials, FP-L(APW+lo).

I. Introduction

SPINTRONICS or spin electronics is fast emerging field in the current information and technology. The significance of spintronics is the simultaneous manipulation of charge of electron for logic operations and its spin degree of freedom for data storage. The giant magneto resistance (GMR) is a well-known example of spintronics devices. It has several other applications such as spin valves [1], magnetic tunnel junctions [2], spin torque effects [3], domain wall devices [4] etc. However, the complete potential of a spintronic device has not been utilized yet because of inefficient spin injection in account of difference in resistivity of the magnetic/ semiconducting interface [5], [6]. DMS are alternating potential materials where magnetic impurity atoms are doped into semiconducting host to stimulate magnetization effect [7], [8].

Thus a single material exhibiting both semiconducting and magnetic features is considered as potential material for future spintronic applications [9]. A DMS with ferromagnetic properties at room temperature along with high magnetic moment, homogenously distributed dopants is considered as ideal for spintronic applications. Establishing such properties strongly depends on the selection of proper semiconductor host and magnetic impurity dopant material.

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Among various semiconductors, GaN and ZnO doped with TM are claimed competent base material for fabrications of DMS [10]. The abundantly available and environmental friendly ZnO with its wide and direct band gap of 3.44 eV stand remarkable in this regard. Moreover, the TM has high solubility rate in the matrix of ZnO due to the nearly similar ionic radii of Zn(74pm) and other TM ions [11]. Among several other TM, Cr with ionic radii 73pm and high local magnetic moment of magnitude 4 μ_B is remarkable dopant [12]-[15].

There have been several studies carried out on Cr:ZnO to investigate the ferromagnetic properties. However, there exist controversies in most of the studies reporting the ferromagnetism. References [16] and [13], [17], [18] have reported FM in Cr:ZnO at room temperature. The absence of FM has been reported in Cr:ZnO by [19]. In recent studies [20] has reported FM in Cr doped p-type ZnO. At room temperature and pressure, ZnO crystallizes in wurtzite (W) structure that is n-type in nature. Recent studies have reported the existence of ZnO in ZB phase [21], [22]. ZnO in meta stable ZB phase is reported to have lower carrier concentration compared to W phase and is expected to solve the long standing problem to control p-type conductivity. However, DMS based on ZB-ZnO is very scarcely explored particularly Cr doped ZB-ZnO. In the present work, we are investigating Cr doped ZnO base DMS in ZB phase. To execute this study, DFT based full potential linearized augmented plane wave plus local orbital method has been adapted in the WIEN2k package. For the treatment of exchange and correlation energy, the Perdew *et al.* [24] proposed generalized gradient approximation have been used. To realize magnetic effect in ZnO, 12.5% of Cr atoms are substituted on Zn sites. Our investigations for physical properties of Cr:ZnO cover the calculation of the lattice constants, spin polarized electronic band structures, density of states, and magnetic moment.

II. Computational Details

In the present study, we performed calculations for structural, electronic and magnetic properties of Cr:ZB-ZnO using DFT with FP-L(APW+lo) method. In this approach, simulated unit cell is divided into two (Muffin-Tin (MT) and interstitial) regions. In the former region, "a linear combination of the atomic like wave functions times the spherical harmonics" are used to expand "Kohn–Sham wave functions, charge density and potential" whereas in the later region, plane waves basis set is applied. Calculations have been done in WIEN2k code [23] which is the practical

implementation of FP-L(APW+lo). To treat the exchange and correlation energy proposed GGA, [24] have been used. In our calculations, to expand the wave functions inside MT spheres l_{max} = 10 and in the interstitial region, energy cutoff K_{max} = 8.0/RMT $(Ryd)^{1/2}$ was taken into account. Similarly in MT sphere, "charge density and potential are expanded into lattice harmonics" and in the interstitial region Fourier series is applied. The RMT were chosen for Zn and Cr as 1.78 a.u , and for O as 1.58 a.u. The Fourier expanded charge density was truncated at G_{max}= 16 au^{-1}. For well convergence of energy we used 72 k points in the special irreducible Brillouin zone (BZ). To obtain better results, the total energy was converged to 10-5 Ryd /unit cell in our present self-consistent computations.

III. Results and Discussion

In the present investigations of structural, electronic and magnetic properties of Cr:ZnO a super cell of 2x2x2 configuration containing 64 atoms was constructed. To substitute Cr impurity over Zn sites at a concentration of 12.5%, we replaced four host cations by Cr such as $Zn_{28}Cr_4O_{32}$. With 2^+ oxidation state replacement of Zn by Cr does not change its 2^+ valence state. To investigate the stable magnetization state, total energies of ferromagnetic and antiferromagnetic orders are calculated and compared. To characterize the nature of short and long range magnetic interactions, two spatial arrangements C1 and C2 are investigated as defined in [13], [25]. In C1 configuration, the Cr substituent are positioned at minimum distance separated by an oxygen atom such such Cr-O-Cr. Where, in C2 configuration the Cr atoms are located at maximum distance from each other and are separated by two oxygen and one Zn atom such as Cr-O-Zn-O-Cr. The total energies of Cr:ZnO is lower in C1 than C2 suggesting that Cr:ZnO favor short range Cr-Cr magnetic interactions and has tendency of clustering together.

To investigate to effect of Cr impurities on the structural properties of ZnO, the lattice constant has been calculated in the present work. The lattice constant of $Zn_{28}Cr_4O_{32}$ is of 4.58 Å calculated with PBE-GGA. A marginal reduction has been observed in the lattice constant of Cr:ZnO compared to the lattice constant of pure ZnO calculated with same approach in our previous study [26]-[30] and experimentally measured value [31]. The reduction in lattice constant is due to small mismatching in the ionic radii of Cr (~ 73pm) and Zn (~ 74pm). However, the marginal variation in the lattice constant shows that ZnO in ZB phase is capable of absorbing the analogues cation impurity upto a high concentration. To investigate the effect of Cr on the electronic band structure, we first determined the electronic structure of undoped ZnO (Fig. 1) like [26]. ZnO exhibit an energy gap of 1.125, smaller than the real gap because of the self interaction correction problem with PBE-GGA.

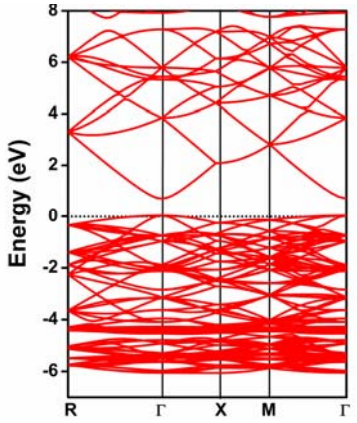

Fig. 1 The band structure of undoped ZnO in ZB phase determined with PBE-GGA

The valence band (V.B) maximum and conduction band minimum is position at high symmetry Gamma (G)-point of BZ, that reflects the direct band gap nature of ZB ZnO. The injection of Cr impurity into ZnO shows significant effect on the electronic structure, where impurity bands appeared in the in the vicinity of Fermi level (Fig. 2). In the spin polarized electronic structure of $Zn_{28}Cr_4O_{32}$ the Fermi energy was found to pass through up and down (Dn) spin states, revealing metallic behavior of Cr:ZnO system. The spin polarized electronic structures of Cr:ZnO at 12.5% of Cr concentration are found more compact and the states were slightly shifted to lower energies compared to the undoped system, showing strong interactions between atoms in the defective system because of impurity atoms. The spin splitting occurs in the vicinity of Fermi level for both majority and minority spin channels (Fig. 2). The splitting of states in the Cr defected system reveal the inducing magnetism in Cr:ZnO due Cr atoms.

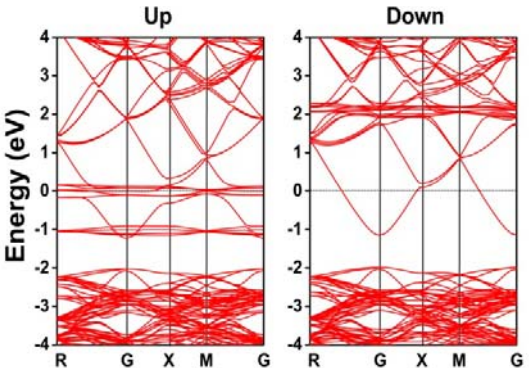

Fig. 2 The spin polarized electronic structure of Cr:ZnO determined with PBE-GGA potential

The metallic nature of Cr:ZnO is mainly caused by the Cr d-band near Fermi level that has been fused into CB states, showing that Cr dopants act as donor in ZnO. The electronic band structure calculated for Cr:ZnO in ZB phase is in good analogy to findings in ref [13], where metallic behavior has been reported for Cr:ZnO system in W phase. Moreover the

shift of Fermi level towards conduction band showing the n-type metallic [32] nature of Cr:ZnO. To further explore the details of electronic structure, the total and partial DOS have been plotted for pure ZnO and Cr:ZnO (Figs. 3, 4). The spin polarized DOS of ZnO presented in Fig. 3 exhibit a mirror symmetry for up and down spin states, showing a nonmagnetic behavior.

TABLE I
THE CALCULATED BANDS CENTERS IN CR:ZNO FOR UP AND DOWN SPIN STATES

	Zn-d	Cr-eg		Cr-t2g		O-p
		Up	Dn	Up	Dn	
Cr:ZnO	-6.32	-1.04	2.12	0.13	2.42	-3.00

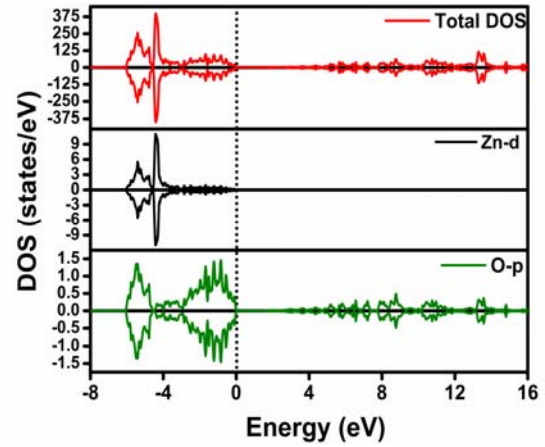

Fig. 3. The spin polarized DOS of pure ZnO

The Zn-d states are dominant in valence band at energy range -6 to -3.64 eV with marginal contribution of O-p orbitals. In the upper part of V.B (-3 eV to Fermi level), O-p states are dominant and determine the top of the valence band. In undoped system the Zn d-band is centered at -4.42 eV higher in energy compared to experimental studies because of the self interaction factors that usually exist in II-VI transition metals. Self interaction factors play a main role in the narrowing of energy gap with common exchange correlation functionals. DOS of Cr:ZnO indicate that Cr impurity atoms significantly change the arrangement of states (Fig. 4).

In the presence of Cr, the centers of Zn-d and O-p states have been pushed about 2 eV down in energies. The energies of Zn-d, Cr-d and O-p band centers as a function of impurity concentration have been listed in Table. I.

For Cr:ZnO in ZB phase, the states emerge near Fermi level are mainly formed by 3d- electrons, that exhibit a large splitting for both majority and minority spin components reflecting high spin polarization of d-band. The spin polarized charge carriers reveal ZB-Cr:ZnO as a potential material for spin polarized current applications. The Cr d-band splitting is attributed to crystal field effect mainly caused by the tetrahedral electrostatic environment induced by O atoms. In ZB configuration, each Cr atom is located in the center of anions tetrahedron (CrO_4). The d-band of Cr impurity atoms are split into two different energy levels. The splitting appears in double e_g (dz2, dx2-y2) are the bottom and triple t_{2g} (dxy, dyz and dxz) are the top three states (Fig. 5). This is in accordance to the other ZB [33], [34] and W structure studied. In tetrahedral environment, t_{2g} orbitals are at higher energies than e.g. states. The up spin e.g. orbitals are centered below Fermi level in V.B (Table I), where for down spin they are located in C.B.

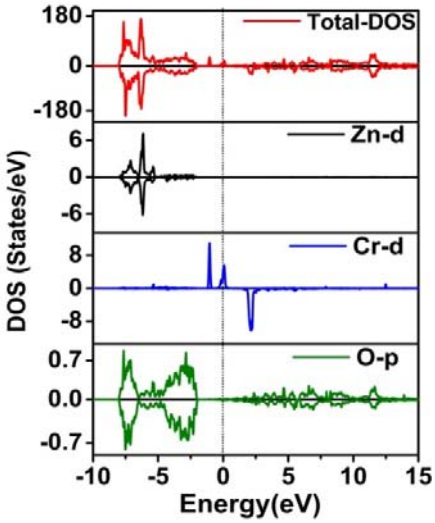

Fig. 4 The spin polarized DOS of Cr:ZnO. The states plotted along negative energies represent the minority spin states and the states along positive energies represent majority spin states

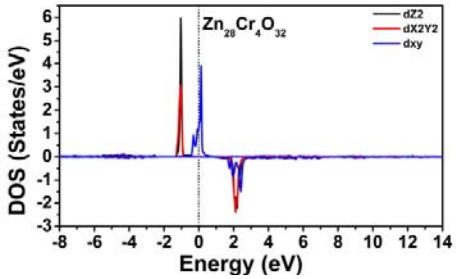

Fig. 5 The Cr d-band splitting has been schematically shown for majority and minority spin carriers

The magnetic properties of Cr:ZnO have been investigated in the present work. It is evident from the DOS profile of ZnO that pure form is nonmagnetic, as the symmetrical up and down spin states cancel out the effect of each other. However, Cr:ZnO exhibit high magnetic moment of magnitude 15.02 μ_B and 14.34 μ_B per supercell in both C1 and C2 configurations respectively. The magnetization is mainly contributed by Cr impurity. Cr ion exhibits a local magnetic moment of 2.88 μ_B, for $Zn_{28}Cr_4O_{32}$ in C1 configuration. In C2 the local MM per Cr ion in $Zn_{28}Cr_4O_{32}$, is 2.94μ_B [28]. The nearest neighbors O-ions to Cr atoms have local magnetic moment of magnitude 0.20μ_B in C1 and 0.21 μ_B in C2 [28]. The left over oxygen and Zn atoms in the supercell have local magnetic moment less than the closest neighbors Oxygen atoms to the Cr. To

investigate the nature of magnetism in Cr:ZnO system, we calculated the total energies of supercell in both the FM and AFM spin mode. To investigate the nature of magnetization in the ground state, the FM and AFM energies per formula unit are investigated and the difference in the energies of FM and AFM spin states ($\Delta E = E_{AFM} - E_{FM}$) is used as an indicator. The positive value of ΔE suggests the FM as the ground state and vice versa. In line to our previous studies, present study shows the FM ordering in ground state C1 and C2 (Table II).

TABLE II
TOTAL ENERGIES PER FORMULA UNIT OF CR:ZNO IN FM AND AFM ORDERING

Cr:ZnO	E_{FM}	E_{AFM}	ΔE	coupling
C1	-3556.4825	-3556.4817	0.0007	FM
C2	-3556.4820	-3556.4814	0.0007	FM

By equating the energy difference ΔE to the thermal energy k_BTc by following the Heisenberg model and mean field theory [35], we estimated the room temperature FM in Cr doped ZnO materials at energy difference $\Delta E \sim 39$ meV. There exist several models presenting the origin of ferromagnetism in DMS. Our analysis for electronic band structure shows that FM in Cr:ZnO in ZB phase is defined by the double exchange mechanism that explain the FM if the impurity bands appear at the band gap.

IV. CONCLUSION

In conclusion density functional theory has been to study the effect of Cr doping on the physical properties of ZnO in zinc-blende phase, using FP-L(APW+lo) method. The results show that ZB-ZnO in the presence of Cr impurity atoms exhibit high magnetic moment. Cr impurity atoms do not show significant variation in the lattice parameters of ZnO. Cr:ZnO system favors ferromagnetism in ground stable state. The observed highly spin polarized conduction carriers reflect Cr:ZnO in ZB phase as a potential material for polarized spin current application and other spintronic devices.

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