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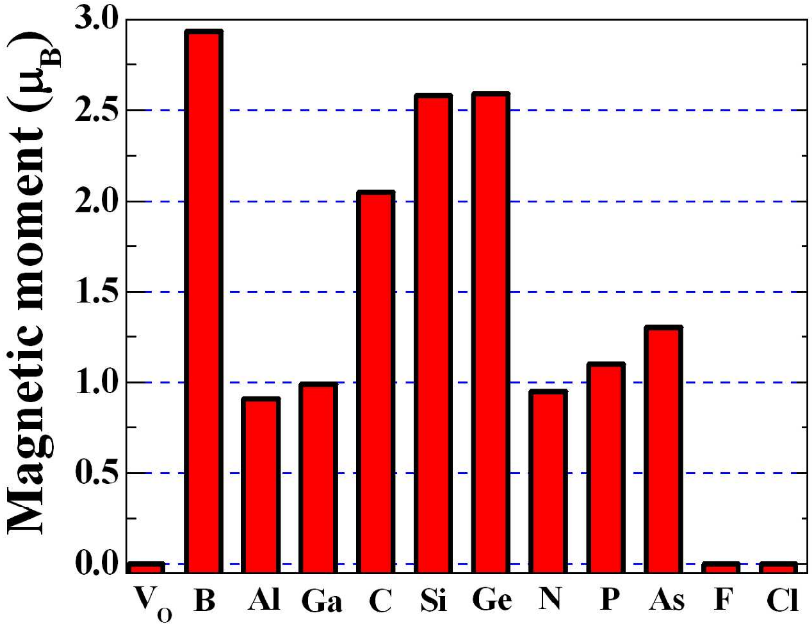

Effective magnetic moment for $Zn_{54}O_{53}X$ (X = B, C, N, F, Al, Si, P, Cl, Ga, Ge, As) system.

# *Ab-initio* calculation of magnetic properties of *p*-block element doped ZnO

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## Abstract

Recently, extensive calculations based on density functional theory (DFT) have been carried out to understand the origin of magnetism by doping ZnO, as observed experimentally. Theoretically, it has been understood that the main source of the magnetic moment arises from the unpaired 2p electrons at O sites surrounding the Zn vacancy. In the present work, we try to understand the reason of induced magnetic moment in ZnO by replacing O, using different p-block elements. We have studied the effective magnetic moments of the $Zn_{54}O_{53}X$ (X = B, C, N, Al, Si, P, Ga, Ge, As) system in the framework of density functional theory. Our calculations suggest that partial substitution of the oxygen atom by a foreign element can induce magnetism in ZnO, and the amount of induced magnetic moment depends upon the electronegativity and the size of the doping element with respect to the oxygen atom.

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Keywords: Magnetic semiconductor; Density-functional theory, Defect formation

## 1. Introduction

Zinc oxide (ZnO) is a wide-band gap semiconductor (3.37 eV at room temperature) with strong excitonic emission in the ultraviolet regime with large exciton binding energy ~60 meV.[1] ZnO has attracted a lot of research attention in the last several years, not only due to its potential application as a diluted magnetic semiconductor,[2-4] but also for the experimental observation of defect induced room temperature $d^0$ ferromagnetism.[5-7] Interestingly, defects play the most crucial role in determining the magnetic as well as optical properties of ZnO.[8] Although a large number of theoretical studies have been carried out,[9-13] the exact roles of intrinsic and extrinsic lattice defects, which largely affect the electronic and optical properties, are yet to be understood. The room-temperature ferromagnetism in undoped ZnO has been theoretically attributed to the interaction between the defects and the 3d ions of Zn[10] or Zn interstitial.[11]

Apart from theoretical studies addressing the exact mechanism of ferromagnetic ordering in undoped ZnO, several studies of such ordering in doped ZnO by different elements, e.g., Carbon,[12] Nitrogen,[13] Aluminum,[14] etc., showed interesting results. Identifying the exact mechanism of ferromagnetism in both undoped and doped ZnO is of utmost importance for its possible future applications. In the present work, we try to understand using the density functional theory (DFT), the reason of induced magnetic moment in ZnO by replacing the oxygen atom by different *p*-block elements, such as B, C, N, Al, Si, P, Ga, Ge, and As. And then we ask the question: What determines the amount of induced magnetic moment in doped ZnO? Our calculations indicate that electronegativity, valence-shell electron configuration, and the size of the dopant atom with respect to oxygen atom, determine the amount of magnetism in the doped ZnO structures.

## 2. Computational methodology

Here, the spin-polarized calculations in the framework of *ab-initio* density functional theory have been performed. The entire DFT calculations have been performed using the Vienna *ab intio* simulation (VASP) code,[15-18] along with the MedeA software package. All the systems have been studied under generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange and correlation.[19] Throughout the calculations, the size of the super cell has been considered to be 3×3×3 unit cells, i.e., with 108 atoms in a super cell. Periodic boundary conditions have been introduced along all the basis vectors. In the super cell single oxygen (O) atom has been systematically replaced by different p-block elements of the periodic table, resulting in the general form of the doped systems to be $Zn_{54}O_{53}X$, where X denotes the impurity element, such as boron, carbon, etc. Apart from $Zn_{54}O_{53}X$ complex, the magnetic property of the ZnO system with oxygen vacancy ($Zn_{54}O_{53}$) has also been studied to conclude the results. Before the commencing the DFT calculations of magnetic properties of different structures, all the structures have been geometrically relaxed until the maximum value of the unbalanced inter-atomic force component converged to values below 0.03 eV/Å. For all calculations, 400 eV mesh cut-off energy has been taken into account to expand the plane wave basis set, and $10^{-4}$ eV tolerance has been fixed as stopping criteria of the self-consistent loop to reach the electronic ground state. The Brillouin zone (BZ) of the super cells has been divided by 3×3×3 Monkhorst-Pack (MP) k-points.[20]

## 3. Results and discussion

The pristine ZnO crystal is a $sp^3$ bonded system, where each zinc atom, with ground state valence electron configuration of $3d^{10}4s^2$, contains four nearest neighbor oxygen atoms with ground state valence electron configuration of $2s^2 2p^4$, and vice-versa. Fig. 1 shows the hexagonal wurtzite structure of ZnO. In this pristine system, no excess or deficiency of electrons is present. Hence the pristine ZnO does not show any magnetic ordering in its ground state, as confirmed by the results shown in Fig. 2a. Incorporation of impurities leads to magnetism in ZnO. However, the type of impurity plays an important role in estimating the magnitude of the magnetism. It is interesting to note that all types of impurities do not give rise to magnetism in ZnO systems -- the ZnO system with oxygen vacancy ($V_O$), i.e., the $Zn_{54}O_{53}$ complex yields no magnetism (see Fig. 2b). This is because, the absence of oxygen atom in the structure does not incorporate any unpaired electron in the system as Zn atoms near the $V_O$ are in closed shell $3d^{10}4s^2$ configuration. However, replacing the oxygen atom in ZnO by some other *p*-orbital element results an effective magnetic moment in most of the cases. Moreover, the amount of the magnetism is found to be significantly dependent on the position of the elements in the periodic table. We are going to analyze the magnetic property of doped ZnO systems, oxygen replaced by p-block elements, in several cases. The defect formation energy and the obtained magnetism for ZnO with $V_{Zn}$ and ZnO with $V_O$ and for all p-block elements doped ZnO are listed in Table 1.

The DFT calculated magnetic moment in $Zn_{54}O_{53}B$ (B = Boron), where oxygen has been replaced by boron ($B_O$) is $2.93\mu_B$. The atomic ground state valence electronic configuration of B atom is $2s^22p^1$. When the O atom is replaced by B atom, the $sp^3$ hybridization bonding between the B atom and nearest Zn atoms has a deficiency of three electrons. A partial electron transfer then occurs from the nearest bonding orbitals between the Zn and O atoms, to the partially bonded Zn-B cluster, which incorporates nearly three unpaired electron in the system. As a result, this system yields a magnetic moment of nearly $3\mu_B$. In the Fig. 2c, the spin polarized density of states (DOS) has been depicted for this particular system. The asymmetric DOS for spin up and spin down states clearly indicate the appearance of an effective magnetic moment in the $Zn_{54}O_{53}B$ system.

C and N doped ZnO system are the two most studied[12,13] systems, both experimentally as well as theoretically. Present *ab-initio* calculations for these doped systems are in agreement with the earlier works.[12,13] In the earlier work[12,13] on C and N doped ZnO the predicted magnetism is in agreement with the present theoretically calculated value. The experimental value of C doped ZnO[12] is about 1.5 – 3.0 $\mu_B$. Similar to the B doped ZnO ($Zn_{54}O_{53}B$), partial charge transfer argument is valid in case of C doped and N doped ZnO. In case of C ($2s^2 2p^2$) doped system ($Zn_{54}O_{53}C$), the deficiency of electrons is two, so due to electron transfer the system contains nearly two unpaired electrons giving a magnetic moment of $2.05\mu_{B.}$, while for N ($2s^2 2p^3$) doped system $Zn_{54}O_{53}N$, one can predict a magnetic moment of near $1.0\mu_B$ resulting from deficiency of a single electron. The spin-polarize DFT results corresponding to N doped structure yield a magnetic moment of $0.95\mu_B$, strongly validating the model of electron deficiency and transfer. The spin polarized electronic DOS have been depicted for both C doped and N doped ZnO systems in Figs. 2d and 2e, respectively, which clearly indicate effective magnetic moments.

Our DFT calculations also showed induced magnetic moment in ZnO, when doped with p-block elements down the periodic table, like aluminum (Al) and gallium (Ga), which are just below Boron atom in the periodic table having valence electronic configurations of $3s^2 3p^1$ and $4s^2 4p^1$, respectively. But these two atoms when doped in the ZnO structure, yield much lower magnetic moments of about $0.91\mu_B$ and $0.99\mu_B$, respectively, in contrast with the large magnetic moment ($2.93\mu_B$) observed in case of the same group element, Boron. Although the total number of unpaired electrons determines the order of magnitude of the magnetic moment of the doped ZnO structures, the magnitude of the magnetic moments are quite different from the value corresponding to B doped system. This anomaly may be explained with the help of electronegativity of the dopants. In favour of $sp^3$ hybridized bonding of Al and Zn, electronic charge transfer has to occur from the nearest neighbor sites. The value of electronegativity for oxygen is 3.5, while for Boron it is 2, for Aluminum, 1.5, and for Gallium, 1.6. The electronegativity of Al is less than B, and hence the amount of electron transfer occurring for the $sp^3$ hybridization is smaller. Due to this reason, the total unpaired electron in Al doped ZnO is close to unity, and thus DFT predicted the magnetic moment of 0.91 $\mu_{B.}$ Similar explanation may be inferred for the Ga doped (at the oxygen site) ZnO structure.

Silicon (Si) and germanium (Ge) substituting the O atom in the ZnO system exhibit magnetic moments of $2.59\mu_B$ and $2.58\mu_B$, respectively. These two atoms have similar electronic configurations as the C atom. Surprisingly, Si and Ge doped ZnO systems yield larger value of magnetic moments than the C doped system. After formation of the $sp^3$ hybridization, these structures were expected to give rise to magnetic moments close to $2\mu_{B.}$ The atomic sizes of the Si and Ge atoms are quite large; consequently, the extension of the outer shell electrons induces magnetism to the nearest neighbor electron sites. Hence the magnetic moment of Si and Ge doped ZnO yield magnetic moments of 2.59 and $2.58\mu_B$, respectively, which are little more relative to DFT calculations.

Down the group of N atom, magnetic moments for Phosphorus (P) and Arsenic (As) have been obtained to be $1.1\mu_B$ and $1.3\mu_B$, respectively, which are more than that of the N atom. Like Si and Ge, these two elements also induce magnetism to the nearest electronic sites yielding slightly larger magnetic moments than the N doped ZnO system.

However, in the cases of Fluorine (F) and Chlorine (Cl) doped structure, no magnetism have been observed. Both F and Cl, have the common valence electronic configurations of

$ns^2np^5$. After formation of $sp^3$ bonding with the nearest Zn atoms, each of the dopants contains an extra single *p* electron. This extra single *p* electron with respect to O atom, for F and Cl in the doped structures $Zn_{54}O_{53}X$ (X = F, Cl), does not exhibit any magnetism, since this particular electron has no spin up or spin down asymmetry with respect to the fully filled valence structure.

Fig. 3 represents the net magnetic moment of different *p*-block element doped ZnO, as calculated from DFT. As depicted in the Fig. 3, the maximum magnetic moment can be achieved in case of $Zn_{54}O_{53}B$ system. It is also clear from the Fig. 3 that most of the doped $Zn_{54}O_{53}X$ structures give rise to magnetism, except F and Cl doped systems. All of these systems are not stable or energetically favourable due to quite large defect formation energy ($E_{df}$). The value of $E_{df}$ has been computed with the help of the definition:

$$E_{df} = E_d + E_O - E_P - E_X \quad , \tag{1}$$

where the terms $E_d$, $E_O$, $E_P$ and $E_X$ denote the total energies for the doped system, isolated O atom, pristine ZnO system and isolated X atom, respectively. Fig. 4 depicts the variation of $E_{df}$ for different dopants. According to Fig. 4, $E_{df}$ shows an increasing tendency *down* the column of the periodic table for a given group, as well as a decreasing tendency towards *right* along a given row. The only exceptions are F and Cl. From Fig. 4, it is clear that the most stable structure is N doped ZnO, i.e., $Zn_{54}O_{53}N$, and then F and C doped ZnO, i.e., $Zn_{54}O_{53}F$ and $Zn_{54}O_{53}C$. Since, F-doped system does not yield any magnetic moment, one can get a stable structure with an effective magnetic moment in ZnO by doping N and C. This has already been reported in a number of previous studies[12,13] and our present DFT calculations have provided an extensive and systematic theoretical reasoning.

To investigate the interaction between the magnetic moments, for a particular case, e.g., $B_O$ in ZnO, we have further carried out the calculations by specifying the spins of two boron atoms in parallel configurations i.e., with the two magnetization configurations, e.g., ferromagnetic (FM) state. The distance between the two defect ($B_O$) sites in the supercell is 3.1 Å. The atomic positions of the ferromagnetic state have been fully optimized and the total energy has been computed. It has been found that the FM state is stable with respect to the non-magnetic state. The difference of the energy is about 173 meV, which clearly indicate that the ferromagnetic state is stable even at room temperature. Magnetization density of different ZnO systems, e.g., pristine ZnO, ZnO system with Zn vacancy ($V_{Zn}$) and boron doped ($B_O$) ZnO system has been plotted in Fig. 5. It is clear from Fig. 5 that in case of pristine ZnO there is no magnetism, while in case of ZnO with $V_{Zn}$ a highly localized magnetization is noticed around Zn vacancy. Similarly, in case of ZnO with $B_O$ a localized magnetization is noticed around B atom. In Fig. 5 the top panels show the magnetization density distribution in 3d space and the bottom panels show the same on (001) plane.

## 4. Conclusion

In conclusion, we have thoroughly studied the effective magnetic moment in doped ZnO system with different *p*-block elements in the periodic table at oxygen site. The amount of magnetic moment is highly sensitive to the position of the dopant elements in the periodic table. The electronegativity, along with the valence shell electron configuration and the atomic size of the dopant, plays the key role to determine the amount of magnetism of the doped ZnO structure. Down the column of the periodic table, the magnetic moment of the doped systems increases for the dopants having $ns^2np^2$ and $ns^2np^3$ valence electron configuration, whereas an anomaly has been observed for the $ns^2np^1$ electronic configuration. However, no signature of magnetism has been observed in case of dopants like F and Cl with valence electron configuration of $ns^2np^5$.

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Table 1: Defect formation energy and obtained magnetic moment for different p-block element doped ZnO

| System | Defect formation energy (eV) | Magnetism as calculated by DFT ($\mu_B$) |
|---|---|---|
| $Zn_{54}O_{54}$ | -- | 0.00 |
| $Zn_{53}O_{54}$ ($V_{Zn}$) | 6.43 | 1.11 |
| $Zn_{54}O_{53}$ ($V_O$) | 8.76 | 0.00 |
| $Zn_{54}BO_{53}$ ($B_O$) | 5.80 | 2.92 |
| $Zn_{54}CO_{53}$ ($C_O$) | 3.20 | 2.05 |
| $Zn_{54}NO_{53}$ ($N_O$) | 1.25 | 0.94 |
| $Zn_{54}AlO_{53}$ ($Al_O$) | 9.42 | 0.91 |
| $Zn_{54}SiO_{53}$ ($Si_O$) | 7.26 | 2.59 |
| $Zn_{54}PO_{53}$ ($P_O$) | 5.20 | 1.09 |
| $Zn_{54}GaO_{53}$ ($Ga_O$) | 9.50 | 0.99 |
| $Zn_{54}GeO_{53}$ ($Ge_O$) | 8.00 | 2.58 |
| $Zn_{54}AsO_{53}$ ($As_O$) | 6.48 | 1.33 |

## Figure Captions

| | |
|---|---|
| Fig. 1 | The hexagonal wurtzite structure of ZnO. |
| Fig. 2a | Spin polarized density of states for the pristine ZnO. |
| Fig. 2b | Spin polarized density of states for the ZnO with oxygen vacancy. |
| Fig. 2c | Spin polarized density of states for the boron doped ZnO ($Zn_{54}O_{53}B$) system. |
| Fig. 2d | Spin polarized density of states for the carbon doped ZnO ($Zn_{54}O_{53}C$) system. |
| Fig. 2e | Spin polarized density of states for the nitrogen doped ZnO ($Zn_{54}O_{53}N$) system. |
| Fig. 3 | Effective magnetic moment for $Zn_{54}O_{53}X$ (X = B, C, N, F, Al, Si, P, Cl, Ga, Ge, As) system. |
| Fig. 4 | Defect formation energy for $Zn_{54}O_{53}X$ (X = B, C, N, F, Al, Si, P, Cl, Ga, Ge, As) system. |
| Fig. 5 | Magnetization density of different ZnO systems. (a) The pristine ZnO wurtzite structure showing no magnetism. (b) B doped ($O_B$) ZnO system; highly localized magnetization is noticed around B atom. (c) ZnO system with Zn vacancy ($V_{Zn}$); highly localized magnetization is noticed around Zn vacancy. In these two figures ((b) and (c)), the top panels show magnetization density distribution in 3d space and the bottom panels show the same on (001) plane. |

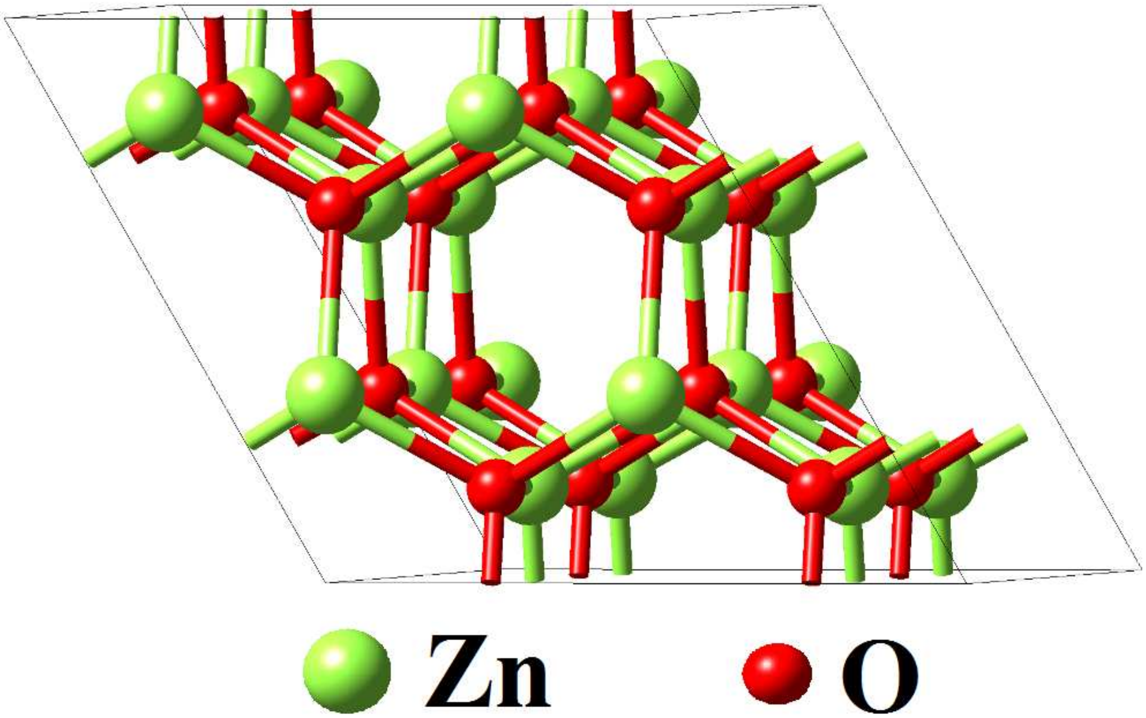

Fig.1 The hexagonal wurtzite structure of ZnO.

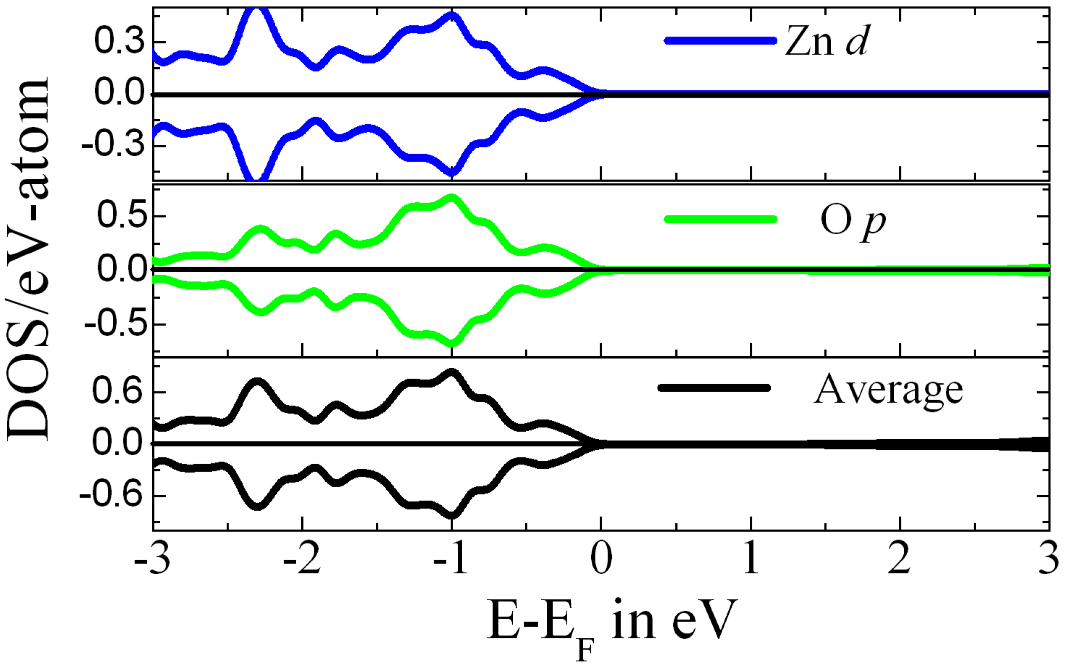

Fig. 2a Spin polarized density of states for the pristine ZnO.

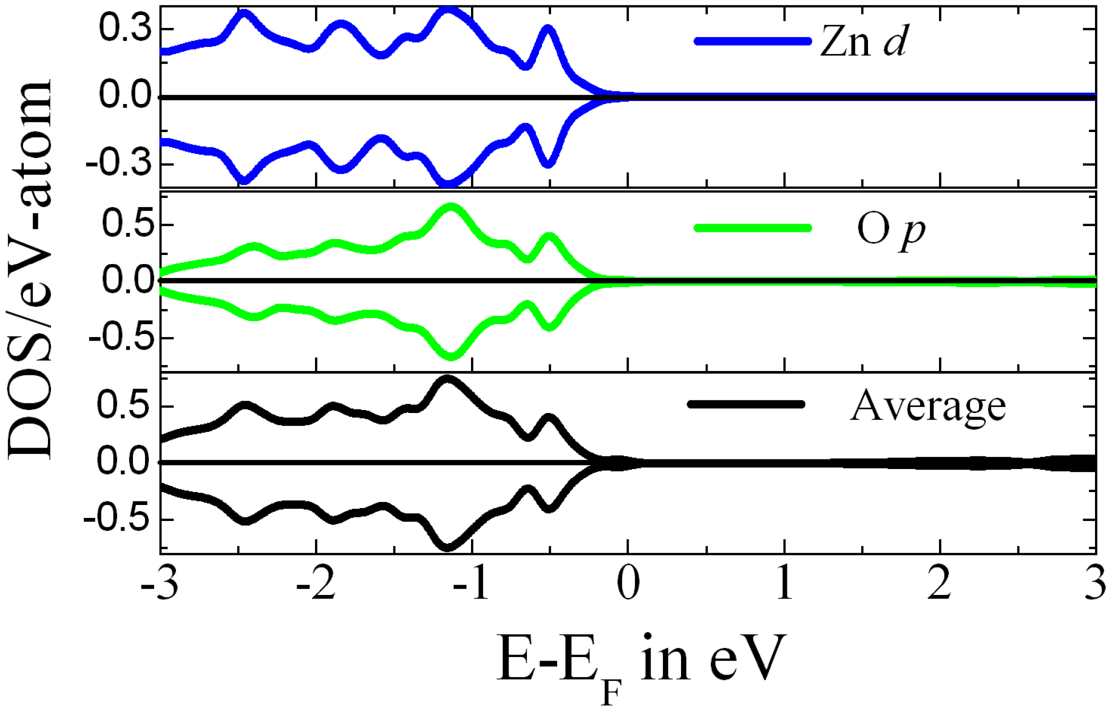

Fig. 2b Spin polarized density of states for the ZnO with oxygen vacancy.

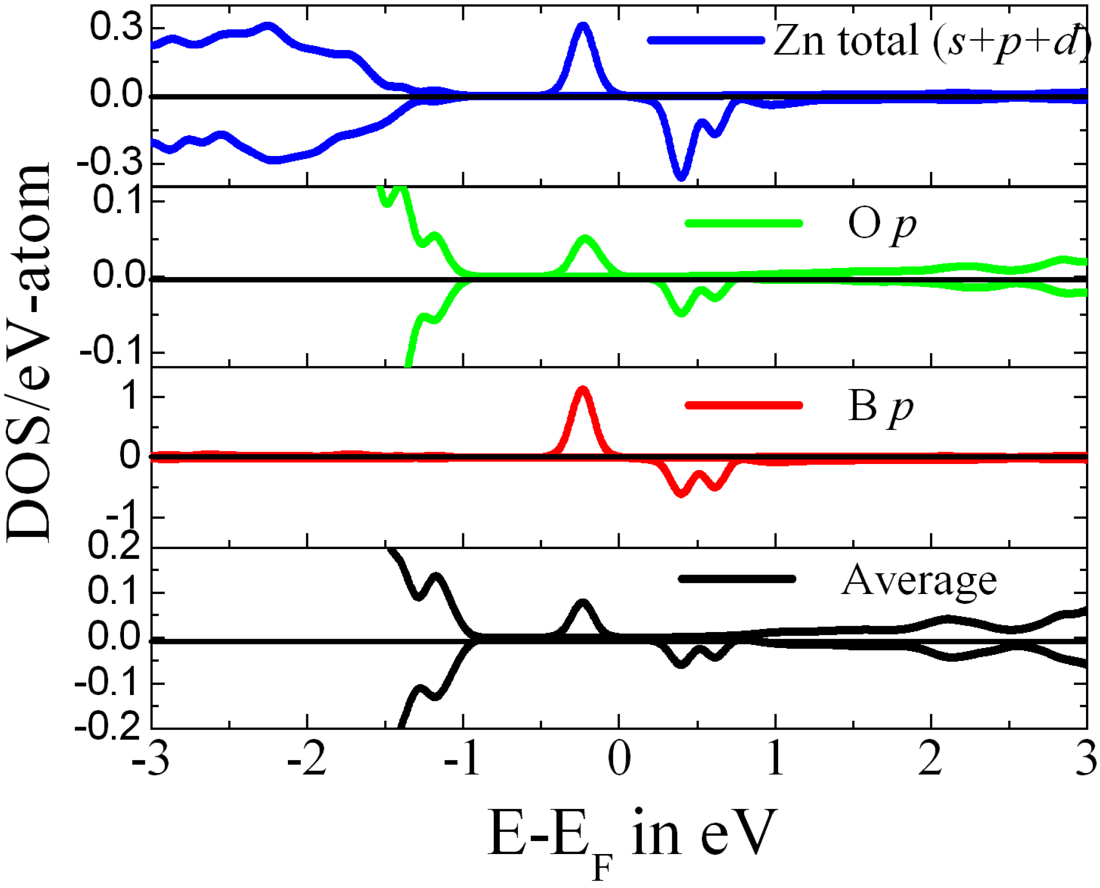

Fig. 2c Spin polarized density of states for the boron doped ZnO ($Zn_{54}O_{53}B$) system.

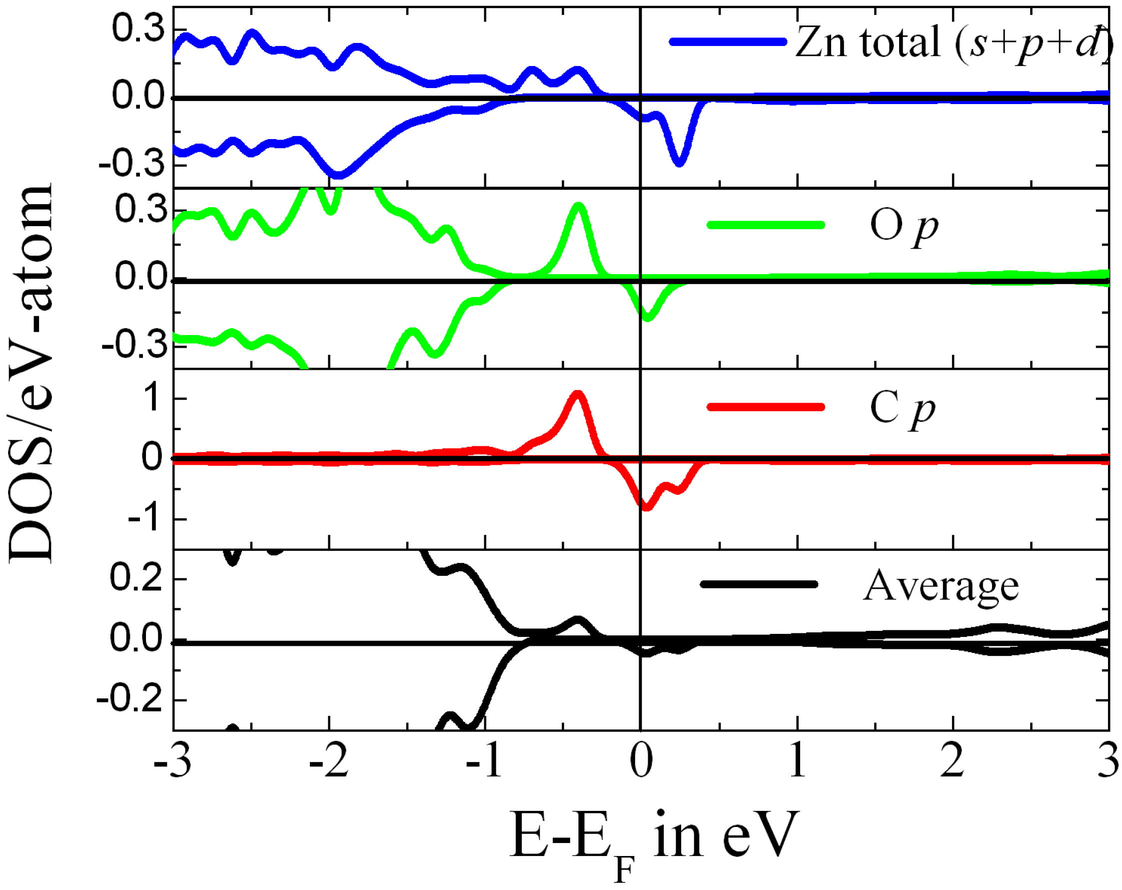

Fig. 2d Spin polarized density of states for the carbon doped ZnO ($Zn_{54}O_{53}C$) system.

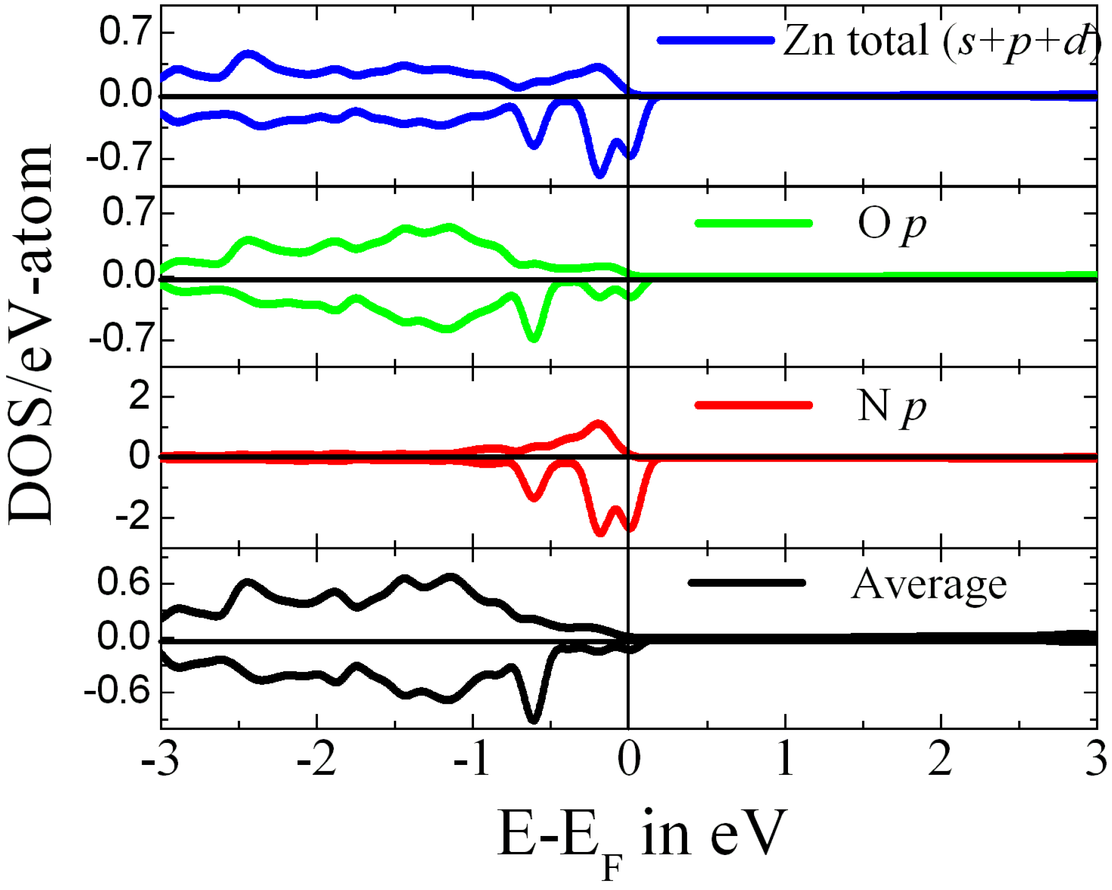

Fig. 2e Spin polarized density of states for the nitrogen doped ZnO ($Zn_{54}O_{53}N$) system.

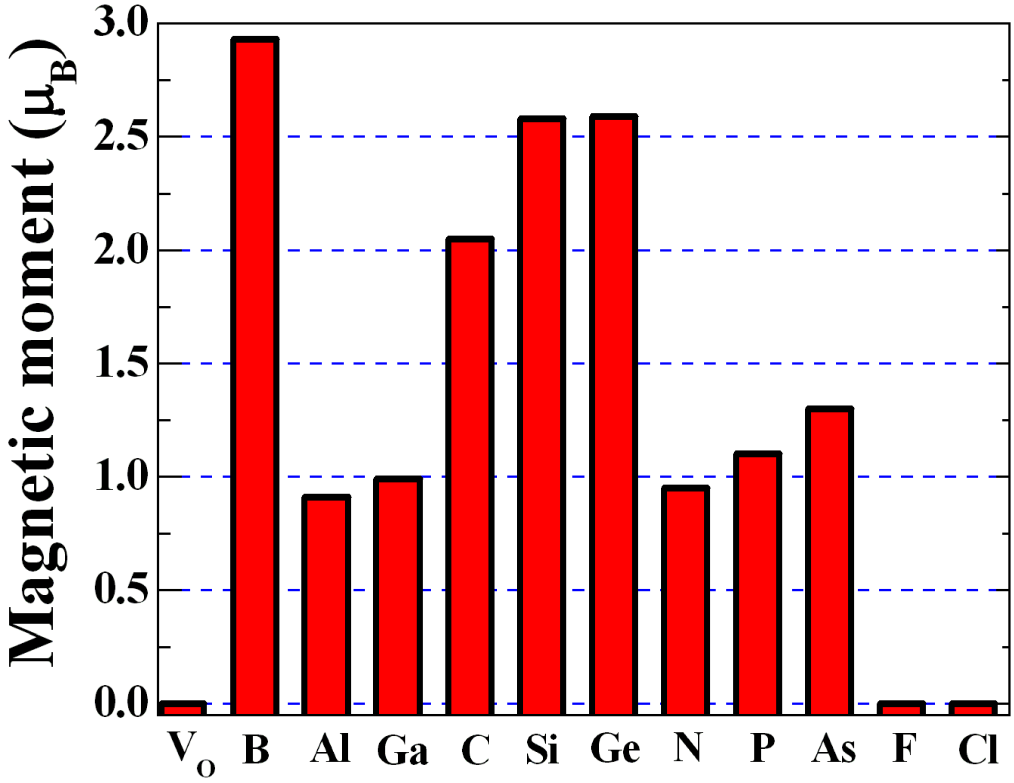

Fig. 3 Effective magnetic moment for $Zn_{54}O_{53}X$ (X = B, C, N, F, Al, Si, P, Cl, Ga, Ge, As) system.

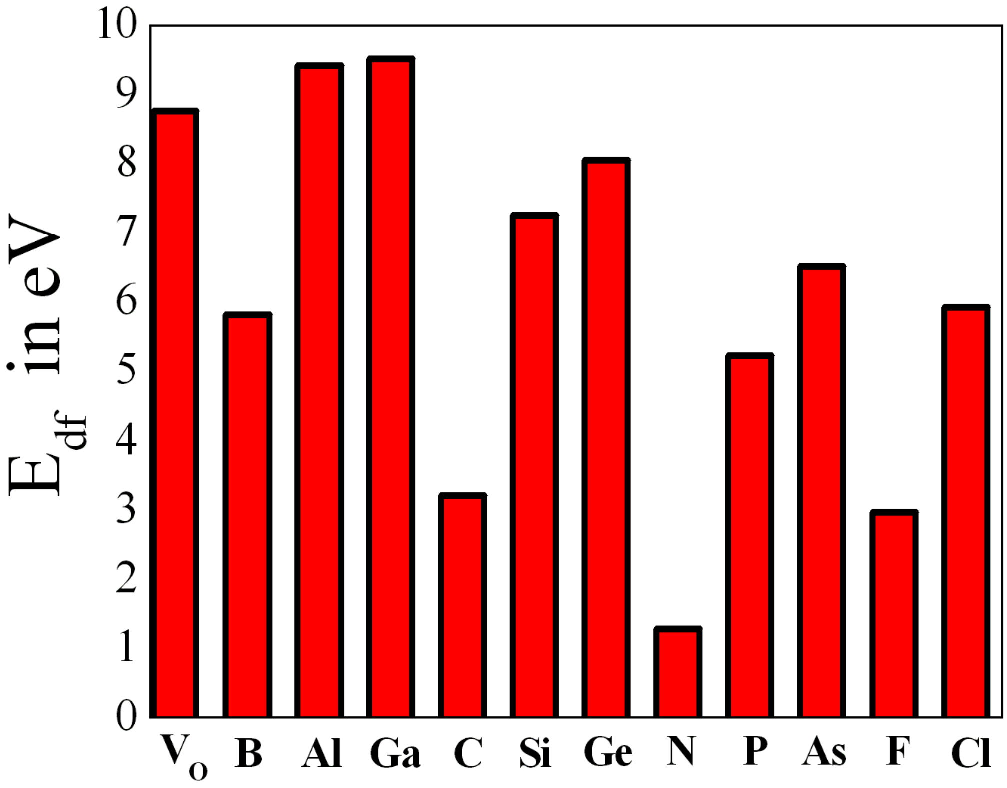

Fig. 4 Defect formation energy for $Zn_{54}O_{53}X$ (X = B, C, N, F, Al, Si, P, Cl, Ga, Ge, As) system.

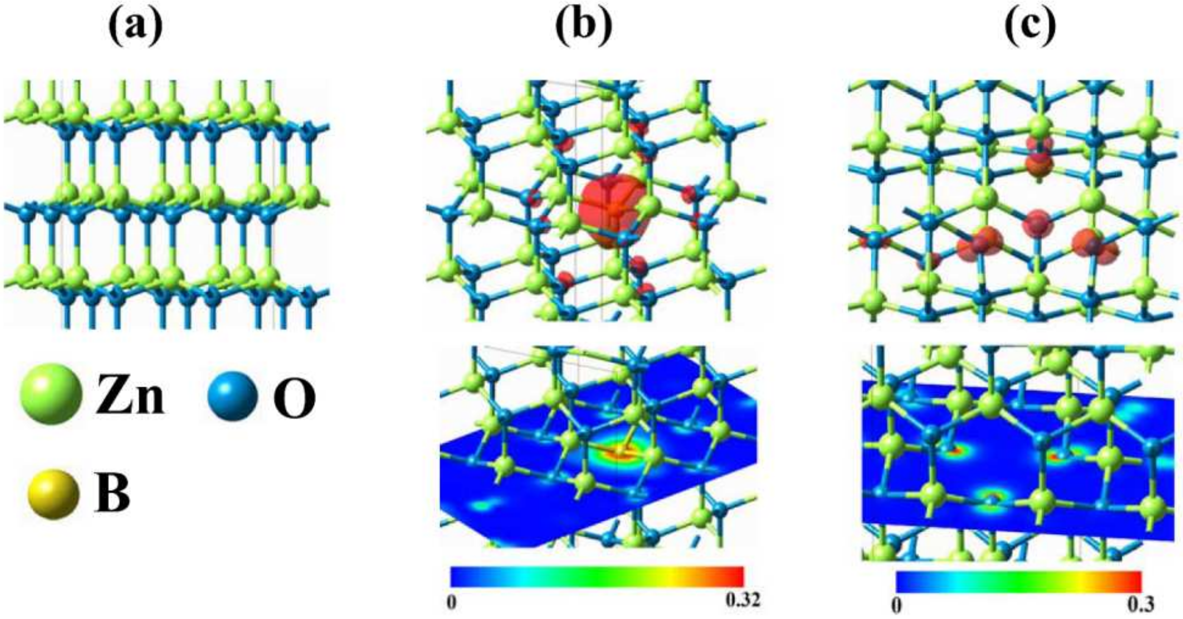

Fig. 5 Magnetization density of different ZnO systems. (a) The pristine ZnO wurtzite structure showing no magnetism. (b) B doped ($O_B$) ZnO system; highly localized magnetization is noticed around B atom. (c) ZnO system with Zn vacancy ($V_{Zn}$); highly localized magnetization is noticed around Zn vacancy. In these two figures ((b) and (c)), the top panels show magnetization density distribution in 3d space and the bottom panels show the same on (001) plane.