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# Explanation of ferromagnetism origin in N-doped ZnO by first-principle calculations

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**Abstract.** **By *ab-initio* calculations, the possible source of ferromagnetism in N-doped ZnO compound was systematically studied. The electronic structure and magnetic properties of N-doped ZnO with/without ZnO host and N defects were investigated using the Korringa–Kohn–Rostoker method combined with coherent potential approximation. It was shown that Zn vacancy and the presence of N defects (substitutional, interstitial or combination of both) induce the ferromagnetism in N-doped ZnO. From density of state analysis, it was shown that p–p interaction between 2p-elements (N,O) is the mechanism of ferromagnetic coupling in N-doped ZnO.**

**Keywords.** **C-doped ZnO; diluted magnetic semiconductors; DOS.**

## 1. Introduction

Diluted magnetic semiconductor (DMS) is a compound obtained by doping a non-magnetic semiconductor with transition metal (TM) elements [1–3]. DMS is the most promising material for novel spintronic devices because the charge and spin of the carriers can be simultaneously controlled. In particular ZnO-based systems have attracted much attention owing to its abundance and environment-friendly nature and also because of its both wide band gap 3.3 eV and high exciton binding energy (60 meV) [1]. Moreover, ZnO doped with 3d TM elements has been studied widely since the model calculation by Dietl *et al* predicted the possibility of ferromagnetism in ZnO with a small amount of Mn as an impurity [4]. However, TM doping often suffers from the problems related to precipitates or secondary phase formation undesirable for practical applications. A possible way to avoid the problem related to magnetic precipitates is to dope semiconductors with nonmagnetic elements instead of TM, which is referred as sp or $d^0$ magnetism since the magnetism is not induced by the localized unpaired electrons in d or f states of TM or rare-earth metals. Moreover, the magnetic properties arising from non-magnetic elements doped ZnO are different from TM-doped ZnO [5]. First, p orbital of non-magnetic elements are usually full in ionic state. Therefore, they do not have unpaired spins. Second, the interaction between spin and orbit is weak for p states compared with the d states of TM. Third, valence electrons in p states are delocalized, and have much larger spatial extension, which may produce a long-range exchange coupling interactions. In recent times several works have been investigated on C- and N-doped ZnO [5–12]. The origin and mechanism of ferromagnetism in 2p element-doped oxides are still in debate. Shen *et al* reported that the local moments in N-doped ZnO are mainly localized on dopant N and equals to 1.0 $\mu_B$ atom$^{-1}$ [5]. Also the long-range magnetic coupling on N-doped ZnO can be attributed to p–d exchange-like p–p coupling. Moreover, Chen *et al* investigated systematically the electronic structure and magnetic properties of N-doped ZnO with and without Zn vacancy [11]. They have also attributed ferromagnetism in such compounds to the hole-mediated double exchange interaction. In this work, an attempt was made to give some insights into possible source of ferromagnetism in N-doped ZnO. Therefore, the experiment was performed on the ZnO bulk first-principle spin-density functional calculations, using the Korringa–Kohn–Rostoker (KKR) method combined with the coherent potential approximation (CPA). The KKK-CPA method is one of the most efficient band structure calculation methods for treating disorder systems like DMS.

## 2. Electronic and magnetic structure calculations

Electronic structure calculations were performed using the KKR method within the density functional theory (DFT) [13]. To solve the DFT one-particle equations multiple-scattering theory was used, i.e., KKR Green's function (KKR-GF) method for the dilute impurity limit and the KKR coherent-potential approximation (KKR-CPA) for concentrated alloys. This method consists in solving the multiple

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scattering problem in two steps. The first one is to solve the single-site (noted $n$) scattering problem leading to its corresponding $t$-matrix operator $\hat{t}^n$ which allows us to determine the Green function operator (GF) $\widehat{G}^n$ by the explicit expression [14]

$$\widehat{G}^n(E) = \widehat{G}^0(E) + \widehat{G}^0(E)\,\hat{t}^n(E)\,\widehat{G}^n(E)$$

with $G^0$ is the Green function for free system. The last step consists to decompose the multiple scatterings process into sequences of single-site scattering events represented by single-site $t$-matrix. The resulting $\widehat{T}(E)$ matrix operator is giving by

$$\widehat{T}(E) = \sum_{nn'} \widehat{\tau}^{nn'}(E),$$

where $\widehat{\tau}^{nn'}$ is the scattering path operator [15–17] which is defined to transfer all the outgoing electronic wave functions from site $n$ into incoming electronic wave function at site $n'$. In the angular momentum representation $(L : (l, m))$, the equation that give us $\widehat{\tau}^{nn'}$ is as follows:

$$\tau^{nn'}_{LL'}(E) = t^n_{LL'}(E)\,\delta_{nn'} + t^n_{LL'}(E) \sum_{k \neq n} G^{0nk}_{LL'}(E)\,\tau^{kn'}_{LL'}(E).$$

One found the $\tau(E)$ matrix by inversing the KKR matrix $M$ given by

$$\tau(E) = \left[t^{-1} - G^{0^{-1}}\right]^{-1} = M^{-1}.$$

For disordered system $A_{1-x}\,B_x$ as in the present study, the coherent potential approximation (CPA) supposes that such system is an assembly of the fictitious atoms characterized by the average $t$-matrix $\tau^{\mathrm{CPA}\,nn}$ given by

$$(1-x)\,\tau^{Ann} + x\tau^{Bnn} = \tau^{\mathrm{CPA}nn},$$

where $\tau^{A(B)nn'}_{LL'}(E) = \left[\left(t^{A(B)}_{LL'}\right)^{-1} - \left(t^{\mathrm{CPA}}_{LL'}\right)^{-1} - \left(\tau^{\mathrm{CPA}}_{LL'}\right)^{-1}\right]^{-1}.$

Such method is the so-called KKR-GF-CPA. The KKR-CPA code MACHIKANEYAMA2002v08 package produced by Akai of Osaka University was used [18]. The Morruzi, Janack, Willaims (mjw) parameterization of exchange-correlation energy functional was used [18]. The form of the crystal potential is approximated by a muffin-tin potential, and the wave functions in the respective muffin-tin spheres were expanded in real harmonics up to $l = 2$, where $l$ is the quantum angular momentum number defined at each site. Spin polarization, relativistic effect and spin–orbit interaction were taken into account. Higher $K$-points up to 450 in the irreducible part of the first Brillouin zone were used. To ensure high accuracy in the performed computations, the convergence criterion was chosen to be the total energy and set at $10^{-6}$ Ry. ZnO crystallize in the hexagonal wurtzite (space group P63mc) and zinc blende phases (space group F43Mm). The normal phase of ZnO shows a wurtzite structure, which consist of hexagonal Zn and O planes stacking alternatively along the $c$-axis. In this structure, the unit cell contains two Zn atoms placed at (2/3, 1/3, 0) and (1/3, 2/3, 1/2) and two O atoms placed at (2/3, 1/3, 3/8) and (1/3, 2/3, 1/3). In the original cell, the O sites are randomly occupied by N atoms with appropriate occupancies. Each Zn atom is surrounded by four O atoms at the corners of a tetrahedral and *vice versa*. This structure is derived from hexagonal-close-packed array of anions. It was assumed that the N-doping do not affect much more the experimental lattice constants ($a = 3.25$ Å, $c = 5.21$ Å) for ZnO [20]. Internal coordinate for the ZnO wurzite structure $u = 0.345$ is used.

## 3. Results and discussion

In order to investigate the origin of ferromagnetism in N-doped ZnO systems, systematic studies are carried out for the $ZnN_{0.0625}O_{0.9375}$ compound using the KKR-CPA method. Different types of N substitution (at O sites $N_O$, Zn sites $N_{Zn}$ and interstitial $N_I$) and host defects (Zn ($V_{Zn}$) and O ($V_O$) vacancies) have been investigated. It is found that $ZnN_{0.0625}O_{0.9375}$ compounds with $N_{Zn}$ and $V_O$ [12] are non-magnetic. In contrast to other theoretical works, it is also found that $ZnN_{O_{0.0625}}O_{0.9375}$ with nitrogen at O sites ($N_O$) is non-magnetic with total and N magnetic moments (MMs) equal to 0. However, $ZnN_{0.0625}O_{0.9375}$ system is found to be magnetic when nitrogen atoms are placed into interstitial sites ($N_I$) or the ZnO host matrix contains Zn vacancies ($V_{Zn}$) [11]. Calculations of magnetic moments on $ZnN_{O_{0.0625}}O_{0.9375}$ (N at O sites), $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}O_{0.9375}$ (10% of Zn vacancies), $ZnN_{I_{0.0625}}O_{0.9375}$ (N at interstitial sites) and $ZnN_{O_{0.03125}}N_{I_{0.03125}}O_{0.9375}$ (50% of $N_O$ and 50% of $N_I$) were performed. The results are reported in table 1. The total energy calculations are also performed for all cases and reported in table 2. The results listed in this table, give evidence that the system $ZnN_{I_{0.0625}}O_{0.9375}$ has the lower total energy. From results listed in table 2, it is found that the total and local magnetic moments (MMs) are zero for $ZnN_{O_{0.0625}}O_{0.9375}$. In figure 1a, the total DOS

**Table 1.** Magnetic moments of atoms, interstitials and vacancies in $ZnN_{0.0625}O_{0.9375}$, $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}$ $O_{0.9375}$, $ZnN_{I_{0.0625}}O_{0.9375}$ and $ZnN_{O_{0.3125}}N_{I_{0.3125}}O_{0.9375}$.

| MMs ($\mu_B$) | $M_T$ | $M_{NO}$ | $M_{NI}$ | $M_O$ | $M_{Zn}$ | $M_{Vzn}$ |
|---|---|---|---|---|---|---|
| $ZnN_{O_{0.0625}}O_{0.9375}$ | 0 | 0 | — | 0 | 0 | 0 |
| $Zn_{0.9}V_{Zn_{0.1}}N_{O_{0.0625}}O_{0.9375}$ | 0.33 | 0.91 | — | 0.08 | 0.02 | 0.006 |
| $ZnN_{I_{0.0625}}O_{0.9375}$ | 0.09 | — | 0.34 | 0.02 | 0.002 | — |
| $ZnN_{O_{0.3125}}N_{I_{0.3125}}O_{0.9375}$ | 0.09 | 0.07 | 0.62 | 0.002 | 0.003 | — |

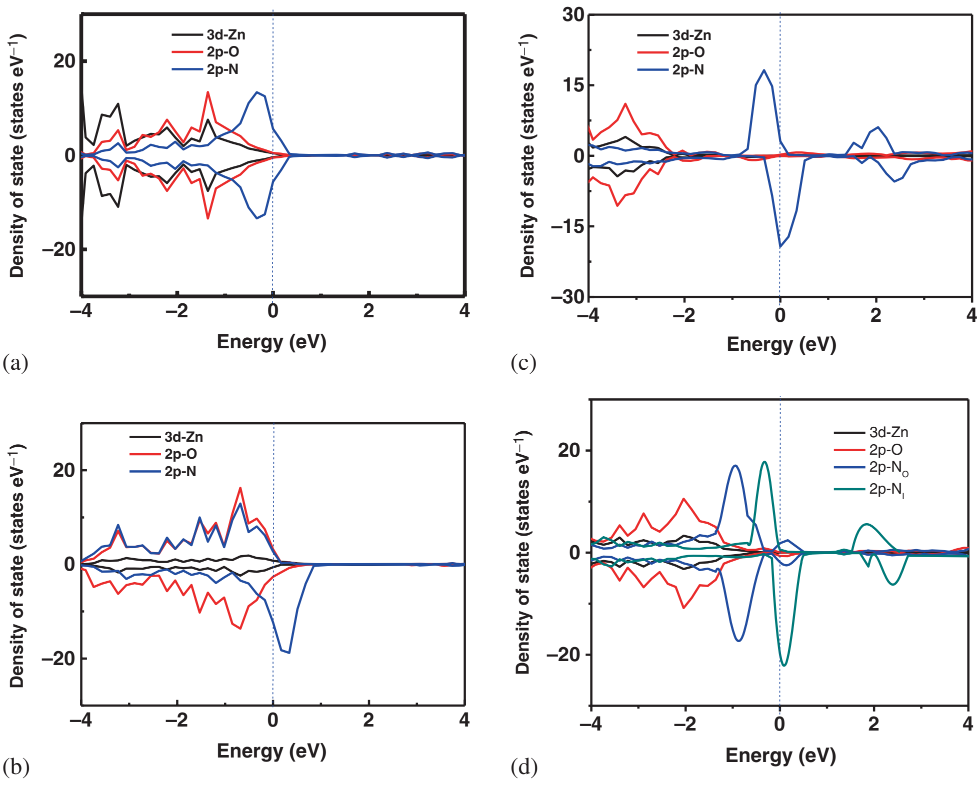
for $ZnN_{O_{0.0625}}O_{0.9375}$ is plotted. It gives evidence that this compound exhibits metallic character. Moreover, symmetry of minority and majority spin at Fermi level confirms non-magnetic behaviour. Also, from calculations of partial DOS displayed in figure 2a it is noted that the 2p-N orbitals exhibit symmetry at the Fermi level confirming that nitrogen do not carry a magnetic moment. By *ab initio* calculations, Anh Pham *et al* reported that $N_O$ shows no sign of localized magnetic moment which is confirmed by our calculations [12]. For $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}O_{0.9375}$ system it is found that the total, the local N and O MMs are 0.33, 0.93 and 0.02 $\mu_B$, respectively, whereas the magnetic moments of Zn and Zn vacancy are very weak (see table 1). Trying to better understand this, the total and partial DOS calculations are performed. In figure 2b, it is noted that at Fermi level almost 100% spin polarized of DOS exhibiting a half-metallic character of $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}O_{0.9375}$ system. On the other hand, the partial DOS of zinc, oxygen and carbon are computed and plotted in figure 2b. By comparing with figure 1a, it is noted that

(i) In the presence of cations vacancies the minority spin of 2p-N states cross the Fermi level and become unoccupied while the majority spin states are partially occupied and dyssymmetry between the minority and majority states at Fermi level takes place pointing out to that the atom nitrogen has a magnetic moment.
(ii) The 2p-O states are more shifted towards the Fermi level.

**Table 2.** Total energy of $ZnN_{0.0625}O_{0.9375}$, $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}O_{0.9375}$, $ZnN_{I_{0.0625}}O_{0.9375}$ and $ZnN_{O_{0.3125}}N_{I_{0.3125}}O_{0.9375}$.

| Systems | Total energy (Ry) |
|---|---|
| $ZnN_{O_{0.0625}}O_{0.9375}$ | −7466.4029054 |
| $Zn_{0.9}V_{Zn_{0.1}}N_{O_{0.0625}}O_{0.9375}$ | −6748.4405864 |
| $ZnN_{I_{0.0625}}O_{0.9375}$ | −7484.9778571 |
| $ZnN_{O_{0.3125}}N_{I_{0.3125}}O_{0.9375}$ | −7475.6051925 |

These two facts can be explained by broken bonds of anions near cations vacancies. Moreover, as seen in figure 1b a high degree of overlap pointing out to the hybridization between 2p-N and 2p-O orbitals around the Fermi level is noted. The mechanism of such hybridization is presented in figure 3a. This probable 2p-N–2p-O interaction generates a ferromagnetic (FM) coupling inducing a total magnetic moment that is found equal to 0.33 $\mu_B$. The value of N MM is 0.93 $\mu_B$ which is much closer to the predicted one (1 $\mu_B$). For $ZnN_{I_{0.0625}}O_{0.9375}$ system, the total, the local N and O MMs are 0.09, 0.34 and 0.02 $\mu_B$, respectively. In order to explain such values, we have reported the partial and total DOS in figures 1c and 2c, respectively. The total DOS shows a metallic character of system. By comparing the partial DOS with that in figure 1a, it can be noted that the majority spin-density



(a) (c)

(b) (d)

**Figure 1.** Partial DOS of 3d-Zn, 2p-N, 2p-O and $V_{Zn}$ of (**a**) $ZnN_{O_{0.0625}}O_{0.9375}$, (**b**) $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}O_{0.9375}$, (**c**) $ZnN_{I_{0.0625}}O_{0.9375}$ and (**d**) $Zn\ N_{I_{0.03125}}N_{O_{0.03125}}O_{0.9375}$.

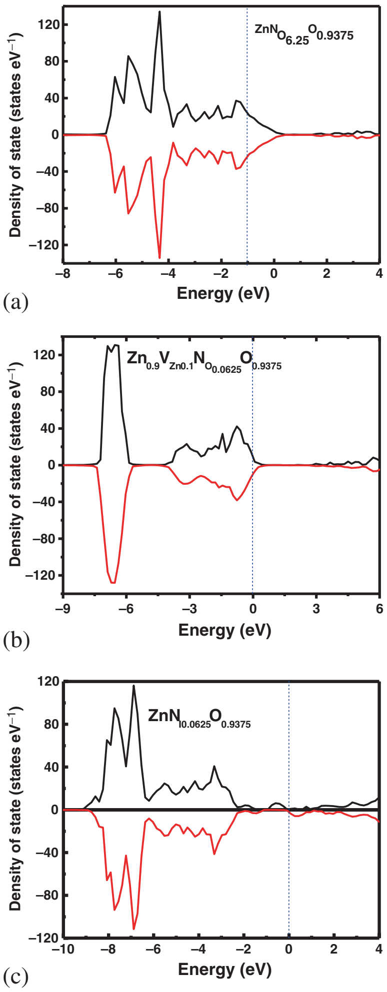


**Figure 2.** Total DOS of (**a**) $ZnN_{O_{0.0625}}O_{0.9375}$, (**b**) $Zn_{0.9}V_{Zn_{0.1}}N_{0.0625}O_{0.9375}$ and (**c**) $ZnN_{I_{0.0625}}O_{0.9375}$.

of 2p-N moves to lower energies and becomes fully occupied whereas those of minority spin moves to the highs energies. Moreover, since a net overlap between 2p-N and 2p-O states cannot be seen, this dyssymmetry between the majority and minority spin-densities of 2p-N is attributed to p–p interaction between N atoms. The value of local N MM (0.34 $\mu_B$) is much smaller than the predicted one (1 $\mu_B$) and consequently demonstrate that there is coexistence of FM and AFM couplings between N atoms as shown in figure 3b and c. The low value of N MM shows that the AFM coupling (figure 3c) is the prevailing mechanism in this case. A combination of both substitutional and interstitial nitrogen-doped ZnO via $ZnN_{O_{0.03125}}N_{I_{0.03125}}O_{0.9375}$ system is the last case studied. It was found (see table 1) that $N_I$, $N_O$ and total MMs are 0.62, 0.07 and 0.02 $\mu_B$, respectively. In this case the value of $N_I$ (0.62 $\mu_B$) MM is greater than that is found in the previous case (0.34 $\mu_B$). This is due to the additional interaction between $N_I$ and $N_O$ atoms which can be explained by net overlap between 2p-$N_I$ and 2p-$N_O$ spin band states as well seen in figure 2d. The mechanism of such interaction is presented in figure 3d. In general, the calculated values of nitrogen MMs in this work are similar to those reported in the previous theoretical calculations [5–11]. But in this work it is attributed on the origin of ferromagnetism in N-doped ZnO to the defects in host matrix (Zn vacancies) or to the defects in incorporation/implantation of nitrogen atoms in ZnO ($N_I$). These defects favour p–p exchange between N atoms in one hand or N and O atoms on the other hand. This p–p exchange coupling is like p–d exchange in TM-doped ZnO is the principal mechanism of ferromagnetism in N-doped ZnO which is called $d^0$ magnetism.

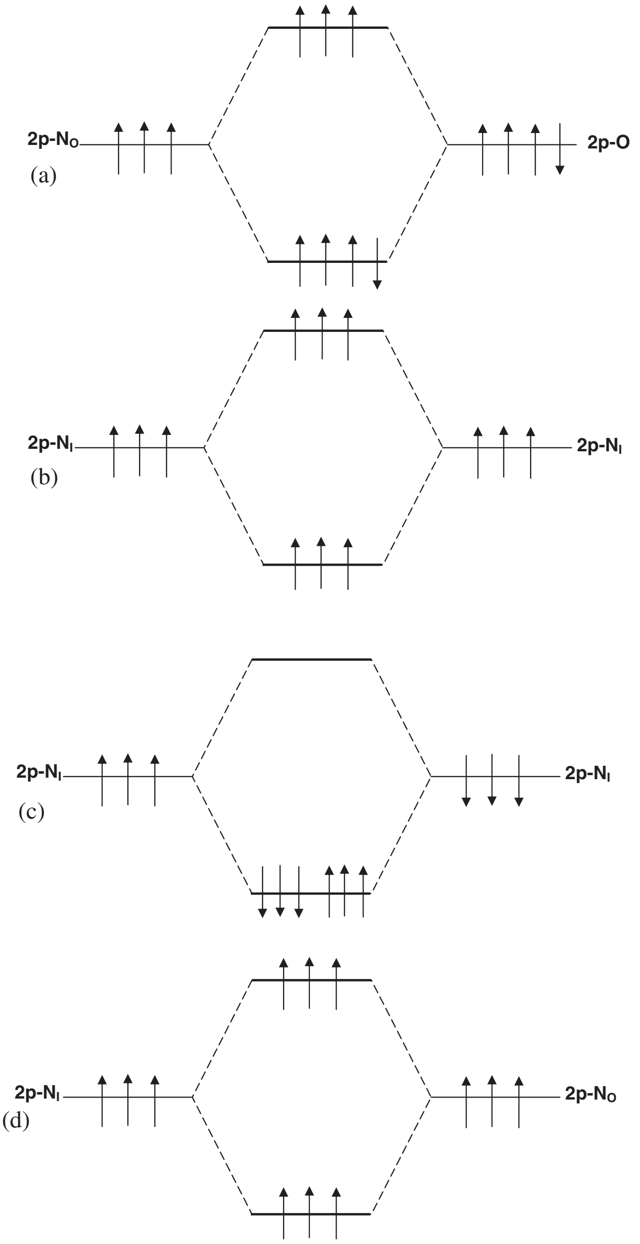


**Figure 3.** Mechanism of p–p interaction between 2p-elements (N,O).

## 4. Conclusion

In summary, the electronic structure and magnetic properties of N doped in ZnO have been studied by the first-principle calculations. The results show that N-doped ZnO exhibits ferromagnetism only when ZnO contains Zn vacancies or N atoms are logged in interstitial sites. The values of calculated N MMs are in good agreement with those reported in the literature. However, our results give insights into the origin of ferromagnetism in N-doped ZnO. From the DOS calculations, ferromagnetism in terms of p–p interaction between N atoms and/or between nitrogen and oxygen atoms was explained.

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