Magnetic properties of nitrogen doped ZnO*

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Using the first principle method based on density functional theory, this paper studies the electronic structure and the ferromagnetic stability in N-doped ZnO. The calculated results based on local density approximation (LDA) and LDA+U method show that ferromagnetism coupling between N atoms is more energetically favourable for eight geometrically distinct configurations. The dominant ferromagnetic interaction is due to the hybridization between O 2p and N 2p. The origin of the ferromagnetic state in N doped ZnO is discussed by analysing coupling between N 2p levels. We also analyse N dopant concentration and lattice strain effect on ferromagnetism.

Keywords: first principles, semiconductor, ferromagnetism, strain

PACC: 7000, 7115M, 7550P

1. Introduction

Diluted magnetic semiconductors (DMSs) are compounds with intermediate properties between a non-magnetic semiconductor and a magnetic element. They can usually be obtained by doping a non-magnetic semiconductor with transition metal (TM) elements.[1] The DMSs have attracted broad interest for their promising applications in spintronics because the charge and spin of the carriers can be simultaneously controlled. After the seminal discovery of ferromagnetism (FM) in (Ga, Mn)As with Curie temperature as high as 110 K,[2] there is a worldwide interest in III-V DMSs. The ferromagnetic Curie temperature of III-V DMSs is too low to realize practical application.[3,4] The realization of practical commercial or mobile devices will require these materials with room temperature FM. As a result, significant research effort has been focused on developing the DMSs with higher Curie temperature. The ZnO has a direct band gap of 3.3 eV and a large exciton binding energy of 60 meV,[5,6] which makes it more suitable for blue lasers, ultraviolet lasers, and light emitting diodes than GaN. Now, ZnO-based DMSs have attracted a lot of attention because of their unique properties. During the past years, a large number of papers have been published to discuss the room-temperature FM of TM-doped ZnO.[7−10] Even though ferromagnetism has been observed in a number of systems, experimental studies on TM-doped ZnO have produced inconsistent results and the mechanism of FM in TM-doped ZnO remains unclear. It is speculated that TM-doped ZnO easily forms clusters or secondary phase, which are unfavourable for application of DMSs. As a result, this stimulates an extensive experimental and computational search for non-TM doped ZnO.[11−13] The magnetic properties of N-doped ZnO are different from TM-doped ZnO. First, p orbits of N elements have not unpaired spins because they usually full in ionic state. Second, valence electrons in p states are delocalized in comparison with d or f states, which may produce a long-range exchange coupling interactions. Third, the interaction between spin and orbit is weak for p states.

Recently, Shen *et al.* studied FM in N-doped ZnO.[14] They proposed that alignment of magnetic moments in N-doped ZnO is achieved through the interaction between impurity p states and the host p states. However, effects of N configuration, dopant concentration and lattice strain on FM properties of N-doped ZnO still need investigation. The origins of the magnetic properties in N-doped ZnO are not fully understood because of lack of systematic studies for characterization of samples. In this paper, we will investigate possible geometrical configurations affecting FM coupling. We will demonstrate that the FM originates from the p–p coupling between N atoms. In addition, we also investigate the effect of N concentration and lattice strain on FM of N-doped ZnO. We hope that our work can offer some help for the applications of the new type of DMSs.

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2. Computational details

The calculations are performed by using the CASTEP code, which is based on density function theory (DFT) and plane-wave pseudopotential method.[15] Exchange–correlation function is adopted in the local density approximation (LDA). In addition, LDA+U method is also used to investigate ferromagnetism of N-doped ZnO. Here, U is the Hubbard parameter. The basic idea of LDA+U is that the delocalized states (s and p) are treated as LDA, and the potential of the local states (d and f) are treated as $+U$. Another important parameter in the LDA+U method is J, which is defined as Hund's rule exchange parameter.[16] In this paper, we use an effective $U_{\rm eff}$ instead of the separate U and J. The LDA+U corrections have been proved to be an effective improvement of LDA results for either magnetic or nonmagnetic systems.[17,18] The interaction between valence electron and ion core is described by ultrasoft pseudopotential. The valence electron configurations for N, Zn and O are considered as $2s^2 2p^3$, $3d^{10} 4s^2$ and $2s^2 2p^4$, respectively. In order to approach realistic experimental dopant concentration, we used a periodic 3×3×2 wurtzite supercell of ZnO, which consists of 72 atoms in a unit cell. Substitution of two O atoms by N then gives a dopant concentration of 5.6%.

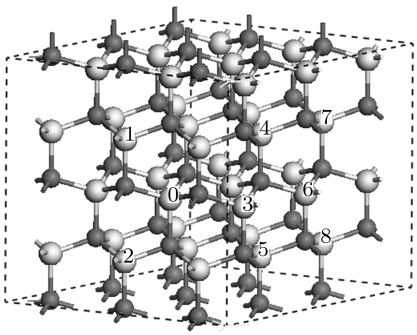


Fig. 1. The schematic 72 atom supercells used in the calculation. The undertone big balls and fuscous small balls stand for O and Zn atoms, respectively.

Figure 1 shows the supercell $Zn_{36}N_2O_{34}$ and eight configurations. Among these configurations, we substitute one N for O_0, and the other N for O atom in the range from O_1 to O_8, which is named as code from configuration 1 to configuration 8, respectively. The convergence tests of the total energy with respect to the plane wave cut-off energy and k-points sampling have been carefully examined. The final set of the cut-off energy is 340 eV, and the integration is performed by using 2×2×2 k-point sampling which is generated by the Monkhorst–Pack scheme.

The experimental lattice parameters of wurtzite ZnO, $a = 3.246$ Å (1 Å = 0.1 nm) and $c = 5.200$ Å,[19] are employed, and the internal coordinates and lattice parameters are fully relaxed throughout this work. The optimization will finish if the convergence criterion is satisfied (Maximum force between atoms is 0.03 eV/Å. Maximum stress is 0.05 GPa. Maximum displacement is 10^{-3} Å. Maximum energy change is 10^{-5} eV/atom).

3. Results and discussion

3.1. Magnetic properties of N-doped ZnO

Figure 2(a) shows the density of states (DOS) for B4 ZnO, which is calculated within LDA. We can find from Fig. 2(a) that the main peak of Zn 3d state is located at –4.4 eV below the valence band maximum, which is in worse agreement with the experimental results. The experimental result shows that Zn 3d state is located at –8.8 eV below the valence band maximum.[20] The origin of this error mainly comes from the inappropriate treatment of the Zn 3d states within LDA scheme. The DOS peaks of Zn 3d will shift if we change the value of U. When the position of the Zn 3d peak is in good conformity with that of experiment, the effective U is obtained. The optimized U is about 10 eV in the present paper. The DOS of B4 ZnO for $U = 10$ eV and $U = 20$ eV is shown in Figs. 2(b) and 2(c), respectively. The Zn 3d peak will shift toward lower level and exhibit local characteristic with increasing U.

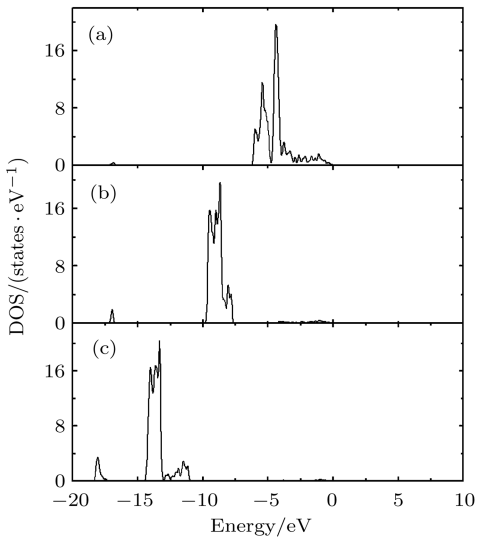


Fig. 2. The DOS of ZnO calculated with different approximations: (a) LDA; (b) LDA+U with $U = 10$ eV; (c) LDA+U with $U = 20$ eV.

For N-doped ZnO, in order to investigate spin polarization and ideal positions of N atom, we first substitute only one oxygen atom with one nitrogen atom. We choose five different configurations of nitrogen ions (see Table 1 and Fig. 1). The total energies of supercell of spin polarization and non-spin polarization are calculated, respectively. During the calculation, the total energy of spin polarized system for configuration 1 is chosen as an energy reference. The calculated results are shown in Table 1. It is found that the total energy of the supercell for configuration 1 is lower than other configurations, which indicates that N atom exhibits site preference. The total energies of supercell for spin polarized system are lower than those for non-spin polarized system, indicating that replacing O by N in ZnO can produce spontaneous spin polarization. The magnetic moment of N hardly changes with positions of N. We can also find that the values of magnetic moment obtained from LDA method are smaller than those obtained from LDA+U method.

Table 1. The energy (meV) and magnetic moment ($\mu_{\rm B}$) of N atoms. The calculation is carried out in relaxed 3×3×2 supercell structures with replacing one O by one N. E_1 is the energy of spin polarized system, E_2 is the energy of non-spin polarized system. The ΔE is defined as the energy difference between E_1 and E_2. The energy of spin polarized system for configuration 1 is chosen as an energy reference.

configuration	N position	LDA				LDA+U			
		E_1	E_2	ΔE	M_n	E_1	E_2	ΔE	M_n
1	0	0	41.2	–41.2	0.38	0	8.2	–8.2	0.48
2	1	5.2	48.1	–42.9	0.40	0.1	13.2	–13.1	0.48
3	2	5.0	48.0	–43.0	0.40	2.9	13.0	–10.1	0.48
4	7	6.6	49.4	–42.8	0.38	5.5	13.0	–7.5	0.48
5	8	6.8	47.8	–41.0	0.40	1.4	12.8	–11.4	0.48

In order to investigate whether FM coupling between N atoms exists in ZnO supercell, we calculated eight geometrically distinct configurations. For configurations from 1 to 3, the two N atoms are separated by one Zn atom, forming –N–Zn–N–. For configurations 4, 5 and 6, the two N atoms are separated by two Zn atoms, forming –N–Zn–O–Zn–N–. For configurations 7 and 8, the two N atoms are separated by three Zn atoms, forming –N–Zn–O–Zn–O–Zn–N–. For each configuration in Fig. 1, the total energies of the ferromagnetic ($E_{\rm FM}$) and antiferromagnetic ($E_{\rm AFM}$) spin configurations are calculated by using LDA and LDA+U methods. The magnetic coupling strength can be obtained from the energy difference between FM and AFM (antiferromagnetic) states ($\Delta E = E_{\rm FM} - E_{\rm AFM}$). We can estimate which state is more energetically favourable from the ΔE. Negative ΔE means that FM state is lower in energy than the AFM state, indicating that the FM state is more favourable. In order to make the total energy comparison among different configurations, the energy of FM states for configuration 3 is chosen as an energy reference. Therefore in the new scale, the energy of FM states of configuration 3 is equal to zero. The calculated results are shown in Table 2.

Table 2. The energy (meV), magnetic moment ($\mu_{\rm B}$) and distance (Å) between N atoms in relaxed 3×3×2 supercell structures for eight FM/AFM configurations. The energy of FM states for configuration 3 is chosen as an energy reference. The ΔE is defined as the energy difference between FM and AFM states.

configuration	N position	LDA					LDA+U					distance
		FM	AFM	ΔE	M_0	$M_{\rm n}$	FM	AFM	ΔE	M_0	$M_{\rm n}$	
1	0, 1	165	176	–11	0.50	0.50	166	214	–48	0.60	0.58	3.172
2	0, 2	169	182	–13	0.52	0.50	167	223	–56	0.60	0.58	3.184
3	0, 3	0	36	–36	0.52	0.52	0	68	–68	0.60	0.60	3.219
4	0, 4	345	401	–56	0.38	0.38	426	505	–79	0.44	0.46	4.554
5	0, 5	350	403	–53	0.38	0.38	428	493	–65	0.44	0.44	4.564
6	0, 6	209	281	–72	0.42	0.40	267	365	–98	0.50	0.48	5.628
7	0, 7	345	402	–57	0.38	0.38	426	502	–76	0.44	0.46	7.240
8	0, 8	350	403	–53	0.38	0.36	429	507	–78	0.46	0.46	7.245

The energies for configurations from 1 to 3 are lower than those for the configurations from 4 to 8, which indicate that N atoms in ZnO have a clear clustering tendency. The clustering tendency has been reported in TM-doped ZnO.[21] The FM energy of configuration 3 is lowest among configurations that two nitrogen atoms are separated by one Zn atom (see configurations 1–3). It is clearly observed from Table 2 that the FM energy of configuration 6 is lowest among configurations that two nitrogen atoms are separated by two Zn atoms (see configurations 4–6). The two N atoms are located on a–b plane for configurations 3 and 6. This result indicates that N atom prefers to reside on a–b plane, similar to what had been found in TM atoms-doped ZnO.[22]

From Table 2, it is found that the N-doped ZnO system possesses FM stability for eight geometrically distinct configurations. As two N atoms are separated far away by 7.2 Å in the configuration 7, the calculation based on LDA shows that the energy of FM state is 57 meV lower than that of AFM state. The calculation based on LDA+U shows that the energy of FM state is 76 meV lower than that of AFM state, indicating that N-doped ZnO may possess room temperature FM, which is in agreement with the report in Ref. [14]. These results also indicate that FM interaction between N atoms could be regarded as long-range coupling. The N 2p states are more delocalized than d or f states of TM, which could promote long-range coupling. The total magnetic moment is $2\mu_{\rm B}$ per $Zn_{36}N_2O_{34}$ supercell in FM configuration. The calculated results show that magnetic moment is mainly dominated by N, the rest magnetic moment mainly comes from spin polarized neighbouring Zn and second nearest neighbouring O.

In order to analyse long-range coupling order in N-doped ZnO, we calculated spin partial DOS in configuration 7. Figure 3 shows the partial spin DOS for ferromagnetic $Zn_{36}N_2O_{34}$ in configuration 7. The vertical dot line in Fig. 3 is Fermi energy. Figure 3(a) presents the results within LDA scheme. Since the energy level of the Zn 3d state is close to that of the O 2p state in valence band, and shape of DOS for Zn 3d and O 2p is similar, so the two states show a strong hybridization. The N 2p hybridizes with O 2p near valence band top, which introduces p-type carriers in system and results in spin redistribution. It is observed that the electronic states at the Fermi energy are spin-polarized. These electronic states at Fermi level are dominated mainly by minority spin states of N 2p, O 2p. Figure 3(b) presents the results within LDA+U scheme. It is clearly observed from Fig. 3(b) that the DOS of Zn 3d shifts to lower energy region compared to LDA method. The Zn 3d hardly hybridizes with O 2p in valence band. We can make a conclusion that LDA method will overestimate the interaction between O 2p and Zn 3d. Thus, the quantitative results obtained by LDA+U calculations are more reliable.

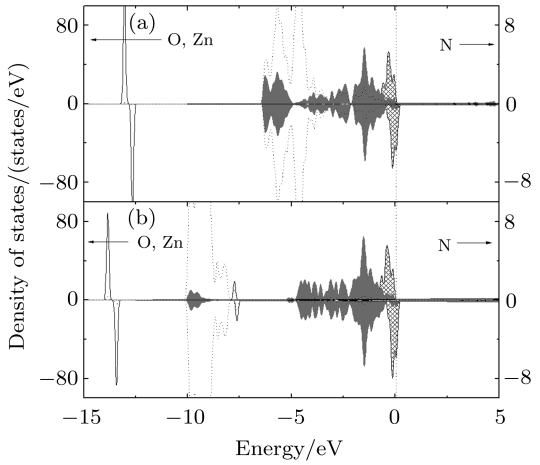


Fig. 3. The partial spin DOS for ferromagnetic $Zn_{36}N_2O_{34}$ in configuration 7. Figure (a) shows calculation results based on LDA. Figure (b) shows calculation results based on LDA+U. The solid lines show N 2s. The dot lines show Zn 3d. The dark gray regions show O 2p states. The reseau regions show N 2p states. The left scale denotes O, Zn. The right scale denotes N.

Here, we give a concise physical picture to explain the origin of the FM state in N-doped ZnO. We propose holes mediation as the mechanism of FM coupling in N-doped ZnO. Substitution of O atoms by N will introduce holes in O 2p states, which will couple with O 2p by p–p interaction, similar to p–d hybridization in TM-doped ZnO.[23] Alignment of magnetic moments can be achieved through interaction of N energy levels, similar to d–d interaction in TM doped ZnO.[24] We suppose that a nitrogen atom will obtain about two electrons from zinc atoms by substitution of N atom at O sites in ZnO. The roughly $T_{\rm d}$ crystal field splits the N ion into lower single state s and upper triply degenerate p states. All majority spin states (s_1 and p_1) and minority spin states s_2 will be occupied. However, minority spin states p_2 will be partially occupied. Figure 4 shows the schematic plot of N level. Figures 4(a) and 4(b) denote FM and AFM interactions between N atoms, respectively. The Δ_1 and Δ_2 denote the energy gap between N 2s and N

2p in FM and AFM couplings, respectively. For fully occupied majority spin states s_1, p_1 and minority spin states s_2, one level is pushed up due to FM coupling, and the other is pushed down by the same amount, therefore, there is no net energy gain (see Fig. 4(a)). The FM interactions between partial occupied minority spin states p_2 can result in energy gain because the electrons push down and occupy lower level. For AFM interaction, the s and p of one N ion with majority spin (minority spin) couple with the s and p of another N ion with the same spin. The AFM coupling will result in p_2 level increasing, which is unfavourable for system stability. Therefore, the FM coupling is more energetically favourable. This may explain why the FM state is more stable for N or C-doped ZnO.[11–14]

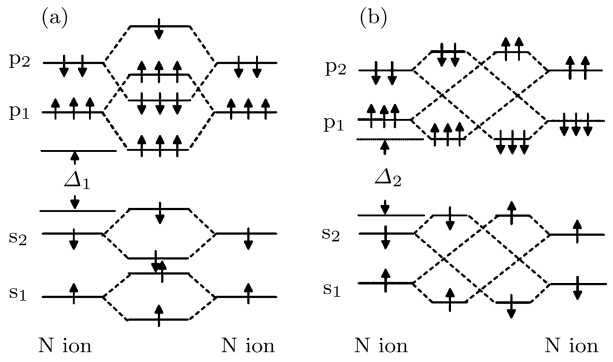


Fig. 4. Coupling between the N energy levels. Figure 4 (a) denotes FM coupling. Figure 4 (b) denotes AFM coupling.

3.2. Effect of N dopant concentration on magnetic properties

To study the effect of N concentration on magnetic properties, we performed extensive calculations on 3×3×3, 2×2×3, 2×2×2, 2×2×1 wurtzite supercell of ZnO, which consists of 108, 48, 32 and 16 atoms in a unit cell, respectively. Substitution of two O atoms by N then gives a dopant concentration of 3.7%, 8.3%. 12.5%, 25%, respectively. It is found from Table 2 that FM energy of configuration 6 is lowest among these configurations that two nitrogen atoms are separated by two Zn atoms, forming –N–Zn–O–Zn–N–. Therefore, the calculation is carried out in configuration 6.

The calculated results are shown in Fig. 5. Our calculations indicate that FM coupling is preferable to the AFM for different nitrogen concentration. The calculations based on LDA/LDA+U methods show that the FM is lower in energy by –75/–104, –72/–98, –29/–55, –17/30 and –1/–11 meV than the AFM states for ZnN_xO_{1-x} with x = 0.037, 0.056, 0.083, 0.125 and 0.25, respectively. The ΔE obtained from LDA method is larger than those values obtained from LDA+U. The FM coupling stability will be enhanced with decreasing N concentration, this fact indicates that nitrogen is a novel dopant for ZnO dilute magnetic semiconductor materials. Since the energy associated with thermal electronic fluctuations is in the order of k_BT, which is approximately equal to 26 meV for T = 300. The values of ΔE for N concentration of 12.5% and 25% do not guarantee any effective FM coupling at room temperature. The magnetic moments per nitrogen atoms obtained from LDA/LDA+U are 0.42/0.46, 0.41/0.49, 0.22/0.74, 0.22/0.26 and 0.12/0.28 μ_B for nitrogen concentration with x = 0.037, 0.056, 0.083, 0.125 and 0.25, respectively. The behaviour of magnetic moment results obtained from LDA+U method shows existence of a maximum value of 0.74μ_B. Although LDA method could give a very accurate lattice constant, the results strongly underestimated the band gap due to overestimation of the hybridization between Zn 3d and O 2p states.[25] The LDA method will result in electronic transition between Zn 3d and O 2p due to hybridization between Zn 3d and O 2p. As Hubbard parameter U is introduced into the calculation, the Zn 3d peak will shift toward lower level and exhibit local characteristic. Mulliken charge shows that electrons transition from Zn 3d to N 2p will disappear with U introduction into calculation, which results in increasing magnetic moment of N atoms.

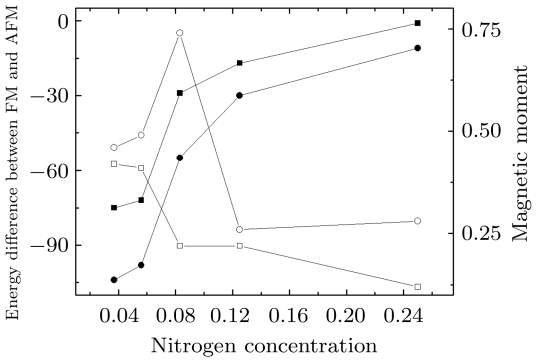


Fig. 5. The energy difference ΔE and magnetic moment vs. N concentrations. Solid symbols denote the energy difference between FM and AFM. Hollow symbols denote magnetic moment of N per atom. Circle symbol denotes the calculation results obtained from LDA+U method. Square symbol denotes the calculation results obtained from LDA. Energy unit is meV. Magnetic moment unit is μ_B.

3.3. Strain affecting FM and AFM properties of N doped ZnO

Because of lattice mismatch between the film and the substrate, lattice strain exists inevitably in films. Strain engineering offers the opportunity to enhance the physical properties of a chosen material. It has been found that a strain-induced break in symmetry has a great influence on the single spin and the corresponding magnetic behaviour of typical DMSs such as Mn:GaAs.[26] Therefore, it is important to investigate strain affecting FM coupling for N-doped ZnO. The axis strain is defined as, $\varepsilon = (C - C_0)/C_0 \times 100\%$, where C is the lattice constant (a, b, c) of strained $Zn_{36}N_2O_{34}$ for configuration 7 in FM/AFM state. The C_0 is the lattice constant of unstrained $Zn_{36}N_2O_{34}$ for configuration 7 in FM/AFM state. For tensile strain, ε is larger than zero. For stress strain, ε is smaller than zero. The calculation is carried out in the a-axis and c-axis strain changing in the range from –0.15 to 0.15 in intervals of 0.05.

The calculated results from a-axis and c-axis strain are shown in Tables 3 and 4, respectively. We find from Tables 3 and 4 that the calculated results based on LDA are different from those based on LDA+U. Because LDA method overestimates the interaction between O 2p and Zn 3d, therefore the results obtained by LDA+U calculations are more reliable. In this paper, we only analyse the results based on LDA+U method. For LDA+U method, the energy difference ΔE between FM and AFM is increased to –45, –14, –13, –12 and –5 meV as a-axis strain ε = –0.15, –0.10, –0.05, 0.10 and 0.15, this fact indicates that the FM stability of N-doped ZnO will decrease. As a-axis strain $\varepsilon = 0.05$, the energy difference ΔE between FM and AFM is decreased to –81 meV, indicating that FM coupling is enhanced. For c-axis strain, FM stability of N-doped ZnO is decreased as c-axis strain ε = –0.15, –0.10, –0.05, 0.10 and 0.15. The FM coupling will be strengthened as c-axis strain $\varepsilon = 0.05$. The change of magnetic moment (μ_B) of N atoms is small as lattice strain changes. The FM coupling variation reflects complexity of the hybridization and anisotropy of spin density distributed in space. It is well known that the energy of the system will rise with increasing strain. Tables 3 and 4 also show that energy of N-doped ZnO depends on the axial strain. Previously, Li *et al.*[27] pointed out that band gap of ZnO can be tuned by strain. Liu *et al.*[28] found that the FM enhancement in $Zn_{0.95}Co_{0.05}O$ films originates from a combination of an increase in Co–O bond length and an increase in the number of defects induced by lattice strain. These results indicate that lattice deformation plays a significant role in the TM-doped ZnO.

Table 3. The energy (eV), energy difference ΔE (meV) and N magnetic moment (μ_B) under a axial strain. The energy of FM states for unstrained configuration 7 is chosen as an energy reference.

a-axis strain	LDA					LDA+U				
	FM	AFM	ΔE	M_0	M_7	FM	AFM	ΔE	M_0	M_7
–0.15	19.041	19.080	–39	0.38	0.40	20.940	20.985	–45	0.48	0.48
–0.10	5.482	5.481	1	0	0	6.987	7.001	–14	0.48	0.48
–0.05	0.289	0.289	0	0	0	1.345	1.358	–13	0.46	0.48
0	0	0.057	–57	0.38	0.38	0	0.076	–76	0.44	0.46
0.05	3.699	3.749	–50	0.40	0.42	3.275	3.356	–81	0.48	0.50
0.10	9.936	9.975	–39	0.44	0.46	9.380	9.392	–12	0.52	0.52
0.15	17.468	17.475	–7	0.48	0.48	16.844	16.849	–5	0.54	0.54

Table 4. The energy (eV), energy difference ΔE (meV) and N magnetic moment (μ_B) under c axial strain. The energy of FM states for unstrained configuration 7 is chosen as an energy reference.

c-axis strain	LDA					LDA+U				
	FM	AFM	ΔE	M_0	M_7	FM	AFM	ΔE	M_0	M_7
–0.15	22.245	22.247	–2	0	0	23.749	23.782	–33	0.44	0.44
–0.10	6.766	6.794	–28	0.34	0.34	8.157	8.174	–17	0.42	0.42
–0.05	0.401	0.456	–55	0.36	0.36	0.971	0.989	–18	0.44	0.44
0	0	0.057	–57	0.38	0.38	0	0.076	–76	0.44	0.46
0.05	3.181	3.246	–65	0.38	0.38	2.375	2.457	–82	0.46	0.46
0.10	9.189	9.225	–36	0.40	0.40	8.602	8.612	–10	0.46	0.48
0.15	15.673	15.694	–21	0.42	0.42	14.415	14.434	–19	0.52	0.46

4. Summary

In this paper, we investigated the magnetic properties of N-doped ZnO by the first principles. By investigating eight geometrically distinct configurations, we found that energies of FM are lower than those of AFM, indicating that FM state is more energetically favourable. We propose that p–p interaction between N atoms can be regarded as long-range FM coupling. The origin of the FM state in N-doped ZnO can be discussed by coupling between N 2p levels. The results also show that FM coupling is preferable to the AFM for different nitrogen concentrations. The FM stability will be enhanced with decreasing N concentration. Because complexity of the hybridization and anisotropy of spin density distributed in space, the FM coupling can be tuned by lattice strain.

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References

[1] Pan F, Song C, Liu X J, Yang Y C and Zeng F 2008 *Mater. Sci. Eng.* R **62** 1

[2] Matsukura F, Ohno H, Shen A and Sugawara Y 1998 *Phys. Rev.* B **57** R 2037

[3] Schallenberg T and Munekata H 2006 *Appl. Phys. Lett.* **89** 042507

[4] Nazmul A M, Sugahara S and Tanaka M 2003 *Phys. Rev.* B **67** 241308

[5] Shi L B, Kang L, Jin J W and Chi F 2009 *Chin. Phys.* B **18** 4418

[6] Shi L B, Cheng S, Li R B and Li M B 2009 *Acta Phys. Sin.* **58** 6446 (in Chinese)

[7] Wang Q, Sun Q, Jena Puru and Kawazoe Y 2009 *Phys. Rev.* B **79** 115407

[8] Wakano T, Fujimura N, Morinaga Y, Abe N, Ashida A and Ito T 2001 *Physica* C **10** 260

[9] Yin Z, Chen N, Yang F, Song S, Chai C, Zhong J, Qian H and Ibrahim K 2005 *Solid State Commun.* **135** 430

[10] Snure M, Kumar D and Tiwari A 2009 *Appl. Phys. Lett.* **94** 012510

[11] Herng T S, Lau S P, Wang L, Zhao B C, Yu S F, Tanemura M, Akaike A and Teng T S 2009 *Appl. Phys. Lett.* **95** 012505

[12] Zhou S Q, Xu Q Y and Potzger K 2008 *Appl. Phys. Lett.* **93** 232507

[13] Pan H, Yi J B, Shen L, Wu R Q and Yang J H 2007 *Phys. Rev. Lett.* **99** 127201

[14] Shen L, Wu R Q, Pan H, Peng G W, Yang M, Sha Z D and Feng Y P 2008 *Phys. Rev.* B **78** 073306

[15] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045

[16] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev.* B **44** 943

[17] Novák P, Boucher F and Greeier P 2001 *Phys. Rev.* B **63** 235114

[18] Mohn P, Persson C, Blaha P and Schwarz K 2001 *Phys. Rev. Lett.* **87** 196401

[19] Yang Y, Qi J, Zhang Y, Liao Q, Tang L and Qin Z 2008 *Appl. Phys. Lett.* **92** 183117

[20] Ley L, Pollak R A, Mcfeely F R, Kowalczyk S P and Shirley D A 1974 *Phys. Rev.* B **9** 600

[21] Lu Z L, Hsu H S and Tzeng Y H 2009 *Appl. Phys. Lett.* **94** 152507

[22] Kan E J, Yuan L F and Yang J 2007 *J. Appl. Phys.* **102** 033915

[23] Dalpian G M, Yan Y and Wei S H 2006 *Appl. Phys. Lett.* **89** 011907

[24] Walsh A, Silva J L F and Wei S H 2008 *Phys. Rev. Lett.* **100** 256401

[25] Zhou G C, Sun L Z, Zhong X L, Chen X, Wei L and Wang J B 2007 *Phys. Lett.* A **368** 112

[26] Yakunin A M, Silov A Y, Koenraad P M and Tang J M 2007 *Nature Materials* **6** 512

[27] Li Y F, Yao B, Lu Y M, Cong C X, Zhang Z Z, Gai Y Q and Zheng C J 2007 *Appl. Phys. Lett.* **91** 021915

[28] Liu X J, Song C, Zeng F, Pan F, He B and Yan W S 2008 *J. Appl. Phys.* **103** 093911