

Mechanism of ferromagnetism in nitrogen-doped ZnO: First-principle calculations

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Based on our first-principle calculations, ZnO doped by a nonmagnetic $2p$ light element (N) is predicted to be ferromagnetic. The local magnetic moments that are mainly localized on doped N atoms introduced total moments of $1.0\mu_B/\text{atom}$. The long-range magnetic coupling of N-doped ZnO can be attributed to a p - d exchange-like p - p coupling interaction involving holes, which is derived from the similar symmetry and wave function between the impurity (p -like t_2) and valence (p) states. We also propose a codoping mechanism, using beryllium and nitrogen as dopants in ZnO, to enhance the ferromagnetic coupling and to increase the solubility and activity.

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Magnetic $3d$ transition-metal ($3d$ TM)-doped dilute magnetic semiconductors (DMSs) based on III-V and II-VI hosts have been extensively studied due to their potential applications in spintronics.¹ However, despite considerable theoretical and experimental efforts, the origin of ferromagnetism observed in some DMSs is still under debate,² and the ferromagnetic (FM) property arises from the doped magnetic TM ions, which were observed to form magnetic clusters or secondary phases, is still not clear. These extrinsic magnetic behaviors are undesirable for practical applications. A possible way to avoid problem related to magnetic precipitate is to dope semiconductors or oxides with nonmagnetic elements instead of magnetic TM. Following this idea, room-temperature ferromagnetism has been demonstrated in Cu- and Ti-doped GaN (Refs. 3 and 4) and ZnO.^{5,6} Besides cationic impurities, theoretical studies predicted that anion substitutions in IIA oxide can also lead to ferromagnetism.^{7,8} This represents another concept in the search for potentially useful DMSs. Work done so far along this line has been confined to IIA oxides, and the mechanism for ferromagnetism in such anion-doped magnetic materials is still not understood. Recently, experimental magnetic moments and room-temperature ferromagnetism in N-doped ZnO and C-doped ZnO have been reported.⁹⁻¹¹ The existing theories of DMSs cannot be applied because they are based on d and f orbitals, but there are no such orbitals in these $2p$ light-element ($2p$ LE)-doped materials. There are several important differences between the $2p$ and the $3d$ orbitals which determine the different magnetic properties of DMSs doped with $2p$ LE (anion) and $3d$ TM (cation). First, the anion $2p$ bands of the light element are usually full in ionic states, leaving no room for unpaired spins compared to $3d$ bands of TM. Second, the spin-orbit interaction of p states is considerably reduced compared to that of d states since it scales with the fourth power of the atomic number. Consequently, spin relaxation of DMSs doped with $2p$ light elements is expected to be suppressed by up to two orders of magnitude in comparison with $3d$ cation-doped DMSs.¹² Third, valence electrons in p states are more delocalized than those in d or f states and have much larger spatial extensions which could promote long-range exchange coupling interactions. There-

fore, despite suffering from low solubility,^{10,11,13,14} DMSs doped with $2p$ light elements can be weak ferromagnets in a highly ordered and low doping concentration. For example, the N-doped ZnO with the N concentration of 0.10 at. % showed a weak ferromagnetism (~ 0.2 emu/cm³).¹⁰

In this Brief Report, we explore the origin of ferromagnetism in N-doped ZnO by first-principle calculations and propose that ZnO, which has been widely investigated both theoretically and experimentally for applications in optoelectronics as a wide band-gap semiconductor, is a potential host material for $2p$ LE anion-doped DMSs. Results of calculations predict that nitrogen-doped ZnO (ZnO:N) is ferromagnetic with the magnetic moment of $1.0\mu_B/\text{atom}$. Surprisingly, almost all magnetic moments reside on the p states of anionic nitrogen and its neighboring anionic oxygen. Compared to the conventional $3d$ TM cation-doped DMSs, nitrogen (a $2p$ LE anion)-doped DMSs can provide a possible way to resolve the clustering problem of magnetic elements, and it will open another avenue for producing potentially useful DMSs. Since N-doped ZnO typically has a low doping concentration but enough mobile carriers, and only $2p$ electrons of dopants and hosts contribute to the magnetism, the origin of ferromagnetism in it challenges our current understanding of ferromagnetism of DMSs. Therefore, a comprehensive understanding of the physics of N-doped ZnO is essential for further exploration of another $2p$ LE-doped DMS. We provide a physical insight into the ferromagnetic mechanism of N-doped ZnO.

In addition, we propose a codoping mechanism to enhance the ferromagnetism of N-doped ZnO. Such approach has been used to solve the asymmetry doping problem of ZnO. For example, a codoping approach¹⁵ was demonstrated to be effective in enhancing the N solubility and reducing the ionization energy of ZnO:N-based materials such as ZnO:N+Ga and ZnO:N+Be.^{16,17} Recently, it was found that ferromagnetism in DMS can be enhanced by codoping. For example, Sluiter *et al.*¹⁸ used this approach to promote the FM state and increase the Curie temperature (T_c) of ZnO-based ferromagnets. Based on the results of our first-principle calculations, we predict that FM coupling in ZnO:N can be enhanced by codoping with Be, and we propose that

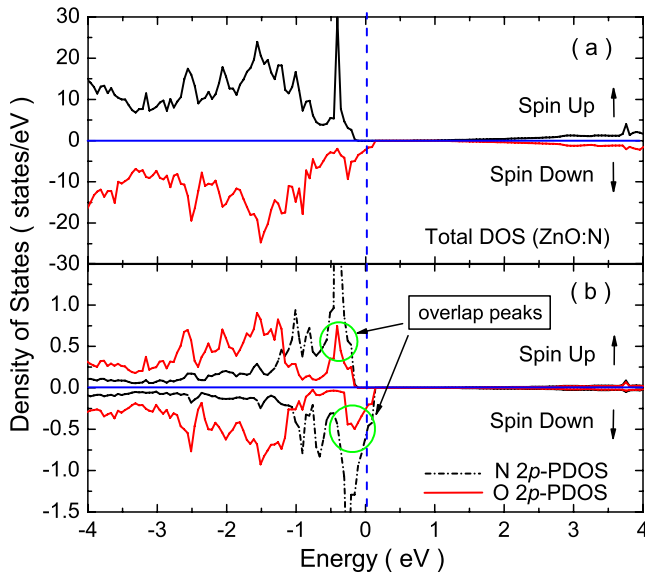


FIG. 1. (Color online) Total DOS (a) and partial DOS (b) of N-doped ZnO. One dopant is incorporated into the 108-atom supercell which corresponds to a doping concentration of 1.85 at. %. The Fermi energy is set to zero.

N-doped ZnO has a possible application in spintronics besides optoelectronics, which has been studied extensively.

We performed band-structure and total-energy calculations using first-principle method based on the density-functional theory (DFT). The calculations were carried out using the VASP program,¹⁹ with the generalized gradient approximation,²⁰ and projector augmented wave method. The energy cutoff was 400 eV and a k mesh of $2 \times 2 \times 2$ was used for a 108-atom ZnO host supercell ($3a \times 3a \times 3c$). All atoms were allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.01 eV/\AA .

We consider first a single anion substitution (N_O), which is modeled by replacing an oxygen atom in the supercell by a nitrogen atom. This corresponds to a doping concentration of 1.85 at. %, comparable to experimental doping level. Based on the calculated total energy, N_O favors a spin-polarized state and its total energy is 23 meV lower than that of the nonspin-polarized state. Each N dopant introduces a total magnetic moment of $1.0\mu_B$ ($\sim 0.4\mu_B$ from N itself, $\sim 0.4\mu_B$ from its 12 second-neighboring O atoms, and $\sim 0.1\mu_B$ from its four nearest-neighboring Zn atoms). Figures 1(a) and 1(b) show the calculated total density of states (DOS) and partial DOS of the $2p$ states of nitrogen and a second-nearest-neighboring oxygen, respectively. As can be seen, the N $2p$ states overlap significantly with those of O $2p$ near the Fermi level, suggesting a strong interaction between them. This strong interaction results in the splitting of the energy levels near the Fermi energy. The spin-up states are fully occupied but spin-down states are partially filled. The corresponding spin-density distribution is shown in Fig. 2(a). Different from $3d$ TM doping in wurtzite host semiconductors where the spin is exclusively localized in a tetrahedron formed by the four nearest-neighboring anions of an impurity $3d$ cation,³ most of the spin density in the N-doped ZnO are localized on the dopant itself and its 12 second-

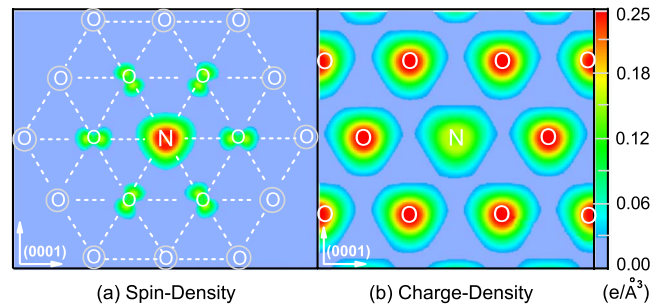


FIG. 2. (Color online) The spin density (a) and charge density (b) of N-doped ZnO. Most of the spin density is localized on the doped N atom and its 12 second-neighboring O atoms. The spin density around the nearest-neighboring Zn atoms, which are not in the plane shown here, is much smaller.

neighboring O anions, with a minor contribution from the nearest-neighboring Zn atoms. Therefore, the magnetic moment in N-doped semiconductors is mainly contributed by the anions, and it is resulted mainly from the delocalized $2p$ orbitals. The large spatial extension of the $2p$ states can be clearly seen in Fig. 2(b).

After understanding the local magnetic-moment formation in N-doped ZnO, we will go on to investigate the long-range coupling interaction of these magnetic moments. To investigate the magnetic coupling between N impurities, a pair of N atoms are incorporated into the same ZnO supercell by substituting two O atoms which are separated by 3.249, 6.136, and 9.252 \AA , respectively. This corresponds to a doping concentration of 3.7 at. %. Results of our calculations show that the magnetic moments of the two N dopants favor FM coupling in each of the three configurations, and the energy of the FM state is 7, 22, and 10 meV lower than that of the corresponding antiferromagnetic (AFM) state, respectively. This indicates that ZnO:N is a weak ferromagnet in a low nitrogen concentration. Figure 3 shows the magnetic coupling between the two N ions separated by 6.136 \AA . As can be seen, the near anions between impurity N atoms mediate the magnetic coupling. We believe that charge carriers localized around the anions between these N ions are polarized and have the same spin orientation as that of the N ions. Consequently, these polarized charge carriers mediate the long-range ferromagnetic coupling between the N ions.

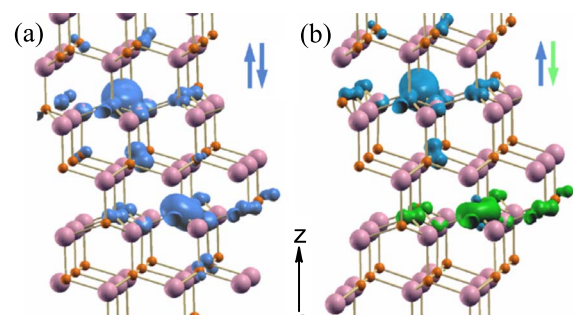


FIG. 3. (Color online) The spin density due to two N dopants separated by 3.136 \AA . (a) FM coupling and (b) AFM coupling. The FM state is most stable than the AFM state. Blue and green isosurfaces correspond to up- and down-spin densities, respectively.

Although no theoretical consensus on the mechanism of ferromagnetism in DMSs has been reached, it is now well established that spin-polarized carriers (holes or electrons) are crucial for the ferromagnetism in DMSs, either free or localized. Such an understanding of FM origin can be based on band-structure models.^{1,21,22} If the localized d states of impurities reside in the band gap of GaN- and ZnO-based DMSs, the double-exchange interaction, competing with the antiferromagnetic superexchange interaction, is responsible for the dominant ferromagnetism.²¹ However, both double-exchange and superexchange interactions cannot account for the long-range magnetic order at low doping concentrations of a few percent. On the other hand, if the d states of the impurity states are within the valence band, such as in GaAs:Mn and GaN:Gd, it was confirmed both theoretically^{1,23} and experimentally²⁴ that ferromagnetic correlations of impurity ions are mediated by free carriers via a strong p - d hybridization exchange interaction. Additionally, some studies in the opposite limit of strongly localized carriers, which are bound to impurity bands, known as bound magnetic polarons have been proposed.²⁵ These theories have been used, to some degree of success, to explain the ferromagnetism in $3d$ or $4f$ TM-doped DMSs. However, for the $2p$ LE-doped DMS, the mechanism should be different since such materials have special magnetic properties such as long-range FM coupling, high hole concentration, and only p orbitals contributing to the magnetism.

Here, we propose that alignment of magnetic moments in N-doped ZnO is achieved through a p - d hybridization-like p - p coupling interaction between the impurity p states and the host p states at the top of the valence band. This interaction follows essentially from quantum-mechanical level repulsion, which “pushes” the minority states upward, crossing the Fermi level [see Fig. 1(a)]. Consequently, the p states split into more stable threefold t_2 states which are either fully occupied or completely empty. The symmetry and wave function (p -like t_2) of the impurity $2p$ state are similar to those of the top valence band of zinc oxide which consists mostly of anion p orbitals. Therefore, a strong p - p coupling interaction between the impurity state and valence-band state is allowed near the Fermi level. Substitution of N in ZnO introduces impurity moments as well as holes. Different from Mn ions in GaAs:Mn which polarizes spin of holes in opposite direction, the spin density near each anion impurity in N-doped ZnO tends to align parallel to the moment of the impurity ion under the p - p interaction as illustrated in Figs. 3(a) and 4(a). The strong p - p interaction leads to stronger coupling between impurity and carrier spin orientations. Sufficiently densed spin-polarized carriers are able to effectively mediate an indirect long-range ferromagnetic coupling between the N dopants as illustrated in Fig. 4(b). High density of charge carriers has been experimentally observed both in N-doped ZnO (Refs. 26 and 27) and C-doped ZnO.¹¹ The spatially extended p states of the host and the impurity are able to extend the p - p interaction and spin alignment to a large range and thus to facilitate long-range magnetic coupling between the impurities. The extended tails of wave functions have also been proposed to mediate long-range magnetic interactions between defect-induced moments in cation-vacancy-induced magnetism in GaN and BN.²⁸ There-

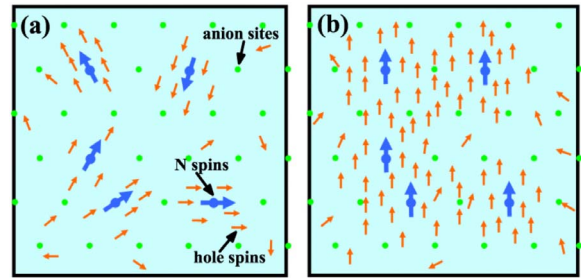


FIG. 4. (Color online) Schematic showing ferromagnetic coupling between spins of doped N impurities. (a) The magnetic moment of N polarizes carriers and aligns the spins of the carriers in the same direction as that of the N dopant. (b) If the carrier concentration is sufficiently high, it is able to effectively mediate indirect ferromagnetic coupling among nearly all doped N ions due to the long-range p - p interaction. Cation is not shown in the diagram.

fore, our model gives a reasonable explanation to the experimentally observed ferromagnetism in ZnO doped with a small amount of nitrogen^{9,10} and carbons.¹¹

N has limited solubility in ZnO (1–3%),^{13,14} and ZnO:N is observed experimentally to be a weak ferromagnet.¹⁰ To increase the N solubility and enhance ferromagnetism in ZnO:N, we propose a codoping approach. The conventional codoping concept was proposed by Yamamoto and Katayama-Yoshida¹⁵ to solve the problem of doping asymmetry in ZnO. Two acceptors are combined with a donor or an isovalent impurity to form an acceptor defect complex. By choosing the codoping element carefully, the acceptor defect complex can increase the solubility of the desired dopants and reduce the acceptor defect level. Following this concept, Be-N codoped ZnO was demonstrated, both theoretically and experimentally, to be a promising p -type ZnO.^{29,30} The concentration of N dopants was increased from 1% to 7% with 4% Be codoping.³⁰ Furthermore, the ionization energy of the N dopants was reduced from 0.4 eV in ZnO:N (Ref. 31) to 0.12–0.22 eV in (Be,N)-codoped ZnO.²⁹

Besides its high solubility in ZnO, Be was chosen as a candidate for codoping of ZnO:N in the present study because it is nonmagnetic and it does not have its own p electrons. Therefore it would not interfere with the magnetic ordering in ZnO:N. Based on the experimental ratio of Be to N concentration³⁰ and the codoping theory, a defect complex consisting of one Be atom and two nitrogen atoms (Be+2N) is considered. Results of our first-principle total-energy calculations indicate that the most stable configuration of the Be+2N defect complex in ZnO is a N-Be-N structure in which the Be atom, substituting a cation, is between two satellite N atoms occupying the nearest-neighbor O sites, similar to the Ga+2N complex in ZnO.¹⁶ The calculated ionization energy of this complex is 0.2 eV, which is in good agreement with results of earlier DFT–local-density approximation calculations (0.12–0.22 eV).²⁹ More importantly, this value is smaller than that of ZnO:N (0.4 eV).³¹ Furthermore, our calculations show that the codoping with Be stabilizes the FM state within the same structure. The FM state of the two N dopants in the Be+2N defect complex is energetically favored over the AFM state by 54 meV which is larger than that of the same configuration but without Be

codoping (7 meV). The enhancement of the FM state in ZnO:Be+2N may be attributed to the decrease in the ionization energy of ZnO:N and lowering of the acceptor level by codoping. This leads to an enhancement of the p - p coupling interaction. Moreover, the carrier concentrations should be increased with the decreasing energy level of acceptor impurities. It is noted that both effects play a key role in the FM coupling of the $2p$ LE-doped DMSs. Moreover, the ZnO:Be+2N can be expected to have a higher Curie temperature than ZnO:N due to the enhanced p - p coupling interaction in the former.¹

In summary, N-doped ZnO was studied and proposed to be a potential candidate for dilute magnetic superconducting

materials, which broadens the horizon of currently known magnetic systems. Based on results of our first-principle calculation, we propose p - p coupling interaction as the origin of long-range ferromagnetic coupling in this DMS. Furthermore, Be-codoped ZnO:N was investigated as a possible approach to stabilize and enhance the FM state of ZnO:N. Therefore, N-doped ZnO and (Be,N)-codoped ZnO may find possible applications in spintronics besides optoelectronics.

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