Ferromagnetism in pure wurtzite zinc oxide

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The discovery of unexpected magnetism in HfO2 thin film1 has triggered a debate on the origins of the ferromagnetism in the undoped diamagnetic oxide. Experiments have shown that ferromagnetism may be universal in the nanoparticles2 or films3,4 of diamagnetic oxides. Moreover, ab initio calculations have predicted that ferromagnetism may be induced by Hf vacancy in HfO2,5 or by O vacancy in TiO2.6 In the diamagnetic oxides showing d^0-magnetism, zinc oxide (ZnO) has drawn great interest. Experiments have discovered room-temperature ferromagnetism in undoped ZnO nanoparticles7 and films,8 and in carbon-doped ZnO films.9 Moreover, ab initio calculations have shown that magnetism may be induced by C substitution in ZnO,9 or by Zn vacancy in zinc chalcogenides with zinc blende structure.10 In this paper, we study the ferromagnetism induced by the intrinsic point defects in wurtzite ZnO (w-ZnO) using ab initio calculation based on density functional theory. We choose wurtzite structure because most films and nanoparticles of ZnO prepared in the experiments are in this structure.

The ab initio calculations are performed on the defect supercells, which are derived from the prototypical supercell by removing (or adding) a Zn (or O) atom. The prototypical supercell is a 2×2×2 supercell consisting of 16 chemical formulas (Zn_{16}O_{16}). The calculation is performed in two steps: the structural relaxation is followed by the calculation of properties. In the first step, both lattice parameters and atomic positions are relaxed by using Perdew-Wang 91 (PW91) generalized gradient approximation (GGA) exchange correlation and ultrasoft pseudopotential. This step is numerically accomplished by the vasp code with a 4×4×3 k-mesh and the accuracy up to 10^{-3} and 10^{-4} eV for the ionic and electronic loops, respectively. In the second step, electronic structure and magnetic properties are calculated by using Perdew-Burke-Ernzerhof (PBE) GGA exchange-correlation and full-potential linear augmented plane wave method. This step is numerically accomplished by the wienn2k code with a 5×5×3 k-mesh and the accuracy up to 10^{-6} Ry. In both steps, the spin polarization options are enabled.

We investigate oxygen vacancy (V_O), oxygen interstitial (I_O), zinc vacancy (V_Zn), and zinc interstitial (I_Zn) as the possible sources of the magnetic moment.11 We depict the relaxed local structures in Fig. 1, where the I_O is located inside a cage-shaped Zn_{16}O_{16} molecule and the V_Zn is located inside a tetrahedral O_4 molecule. For the convenience of further discussion, we define the defect molecule consisting of the defect and the first-shell O ions. The defect molecule is an octahedral O_7 molecule for I_O or a tetrahedral O_4 molecule for V_Zn.

The total and site-projected magnetic moments are estimated from the spin populations. The total magnetic moments of I_Zn and V_O vanish, but those of I_O and V_Zn are 2.00 and 1.77μB, respectively (Table I). In both cases of I_O and V_Zn, there is little magnetic moment in the interstitial region or on the Zn ions, and most of the magnetic moment is

FIG. 1. (Color online) (a) and (b) show the relaxed local structures and spin isosurfaces of I_O and V_Zn, respectively. The O, Zn, and V_Zn are colored red, blue, and green, respectively. (c) shows the simplified electronic configuration for the defect molecules. (d)–(f) show the antiferromagnetic and ferromagnetic superexchanges, and double exchange, respectively. The impurity band corresponding to the minority LUMO of the defect molecule is colored gray in (f).

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localized on the defect molecule. To visualize the detailed distribution of magnetic moments, we plot the calculated spin isosurfaces in Fig. 1. The distributions of magnetic moment strongly suggest that the magnetic moment is originated from the O-p orbitals of the defect molecules.

To examine the stability of the local magnetic state, we calculate the energy difference between the diamagnetic and ferromagnetic states. The energy differences show that in both cases of \( I_0 \) and \( V_{Zn} \), the ferromagnetic state is more stable than the diamagnetic state (Table I). To examine the exchange coupling between the defect molecules, we calculate the energy difference between the antiferromagnetic and ferromagnetic states (Table I). To do the calculation, we induce two \( I_0 \) or \( V_{Zn} \) in the prototypical supercell. We first relax the structure, and then calculate the total energies of the ferromagnetic and antiferromagnetic states, respectively. In both cases of \( I_0 \) and \( V_{Zn} \), the ferromagnetic state is lower in energy than the antiferromagnetic state, which suggests that exchange coupling between the defect molecules is ferromagnetic.

We calculate the density of states (DOS) of \( w-ZnO \) with \( I_0 \) and \( V_{Zn} \), respectively, and plot them in Fig. 2. We also calculate the DOS for perfect \( w-ZnO \) as the reference. In both cases, the defect induces the impurity bands around the Fermi level. The projected DOS shows that the impurity bands are mainly formed by the O-p orbitals of the defect molecule. In the case of \( V_{Zn} \), the DOS is a ferromagnetic metal, where both majority and minority DOS at the Fermi level are nonzero but not equal to each other. In the case of \( I_0 \), the DOS is a ferromagnetic semiconductor, where the minority band gap is much narrower than the majority one.

As the defect molecules may play the key role in the \( d^0 \)-magnetism of \( w-ZnO \), we perform ab initio calculations to study the electronic configurations of the defect molecules. The calculations are performed on the defect molecules, \( O_2 \) molecule in the case of \( I_0 \) and \( O_4 \) molecule in the case of \( V_{Zn} \). To simulate the charge-compensating effect in the solid, the \( O_2 \) molecule is charged as \( O_7^{12} \) and the \( O_4 \) molecule as \( O_4^{2-} \). The calculations are performed by using Becke-Lee-Yang-Parr (BLYP) GGA exchange-correlation and double numerical plus d-functions basis set, and numerically accomplished by the DMOL3 code with the accuracy up to \( 10^{-6} \) Hartree.

In the calculation, we first ignore the structural relaxation temporarily. Thus, the defect molecule is in high symmetry \( O_h \) for \( I_0 \) (or \( T_d \) for \( V_{Zn} \)). The spin-restricted calculation shows that the highest occupied molecular orbital (HOMO) is triply degenerated \( T_{1u} \) for \( I_0 \) (or \( T_2 \) for \( V_{Zn} \)). Since two electrons are removed from the defect molecule due to the charge-compensating effect, the HOMO is partially occupied by four electrons. The spin-unrestricted calculation shows that the majority and minority levels will split. The majority levels will be fully occupied by three electrons and the minority levels will be partially occupied by one electron. Thus, the defect molecule exhibits a magnetic moment of \( 2 \mu_B \). When the relaxed structure given by the supercell approach is used in the calculation, the degeneration of the majority (or minority) levels will be lifted. The simplified electronic configuration is depicted in Fig. 1(c). For the convenience of further discussion, we denote the energy difference between the majority HOMO and the minority lowest unoccupied molecular orbital (LUMO) as \( U_1 \) and that between the minority HOMO and LUMO as \( U_2 \).

By comparing the simplified electronic configuration [Fig. 1(c)] to the DOS [Figs. 2(a) and 2(b)], it is obvious that the three minority levels in the simplified electronic configuration are corresponding to the minority impurity bands around the Fermi level. Thus, we may explain the total magnetic moment, electronic structure, and ferromagnetism based on the simplified electronic configuration.

In the case of \( I_0 \), the impurity band corresponding to the minority HOMO is higher than the valence band maximum (VBM) [Fig. 2(c)]. The electron occupation of the defect molecule will hold true. Thus, the total magnetic moment is \( 2 \mu_B \). The spin-unrestricted calculation using the relaxed structure given by the supercell approach shows that \( U_2 \sim 0.5 \) eV for the \( O_2 \) molecule. The large \( U_2 \) of the \( O_2 \) molecule results in the minority band gap in the DOS [Fig. 2(a)]. Thus, \( w-ZnO \) with \( I_0 \) is a ferromagnetic semiconductor.

The ferromagnetism of \( w-ZnO \) with \( I_0 \) may be attributed to the superexchange interactions between the defect molecules. The simplified electronic configuration implies both ferromagnetic and antiferromagnetic superexchanges between the defect molecules. The virtual transfer between the occupied majority (or minority) levels of a defect molecule and the unoccupied minority levels of another defect molecule will result in antiferromagnetic (or ferromagnetic) superexchange [Figs. 1(d) and 1(e)]. The dominant contribution to the antiferromagnetic (or ferromagnetic) superexchange is due to the virtual transfer between the majority (or

<table>
<thead>
<tr>
<th>( m ) (( \mu_B ))</th>
<th>( \Delta E_1 ) (meV)</th>
<th>( \Delta E_2 ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_0 )</td>
<td>2.00</td>
<td>18.83</td>
</tr>
<tr>
<td>( V_{Zn} )</td>
<td>1.77</td>
<td>7.67</td>
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</tbody>
</table>

FIG. 2. (Color online) (a) and (b) show the DOS of \( w-ZnO \) with \( I_0 \) and \( V_{Zn} \), respectively. The black and red lines are the total DOS and the DOS projected to the O-p orbitals of the defect molecule, respectively. The Fermi level is aligned to 0 eV. (c)–(e) show three cases depending on the position of the impurity band corresponding to the minority HOMO relative to the host VBM. The host valence band and the impurity bands induced by the defect molecule are colored green and red, respectively.
minority HOMO and the minority LUMO. The spin-unrestricted calculation using the relaxed structure given by the supercell approach shows that the spatial distributions of the minority and majority HOMOs are almost identical, which implies that the transfer integrals corresponding to the dominant ferromagnetic and antiferromagnetic superexchange are approximately equal. Thus, the relative strength of the dominant superexchange interactions will be determined by the effective on-site Coulomb repulsion energies, which are $U_1$ and $U_2$ for the antiferromagnetic and ferromagnetic superexchanges, respectively.\(^\text{13}\) We estimate $U_1 \sim 0.5$ eV and $U_2 \sim 0.25$ eV from the DOS [Fig. 2(a)]. Thus, the dominant ferromagnetic superexchange is about two times stronger than the dominant antiferromagnetic superexchange. As a result, the total superexchange interaction between the defect molecules is ferromagnetic in $w$-ZnO with $I_0$.

In the case of $V_{\text{zn}}$, the impurity band corresponding to the minority HOMO is lower than the VBM (but not too much) [Fig. 2(d)]. The electrons will relocate from the host valence band (both majority and minority) to the minority impurity band corresponding to the minority LUMO of the defect molecule. Thus, the total magnetic moment is less than $2\mu_B$. If the impurity bands are much lower than the VBM, the total magnetic moment will vanish due to the relocation of electrons [Fig. 2(e)]. The relocation results in the finite spin densities in both majority and minority directions at the Fermi level in the DOS [Fig. 2(b)]. Thus, $w$-ZnO with $V_{\text{zn}}$ is a ferromagnetic metal.

The ferromagnetism of $w$-ZnO with $V_{\text{zn}}$ may be attributed to the double exchange interaction between the defect molecules. In fact, the impurity band corresponding to the minority LUMO in the DOS [Fig. 2(b)] is partially filled due to the relocation. In another picture, the minority spins itinerate between the LUMOs of the defect molecules and interact with the local spins via the on-site exchange interaction [Fig. 1(f)]. As a result, the local magnetic moments of the defect molecules are aligned by the itineration. We may also understand the ferromagnetism of $w$-ZnO with $V_{\text{zn}}$ following the idea of charge-transfer ferromagnetism.\(^\text{12}\) The charge reservoir in our case is the host instead of the doped cations. The relocation (or transfer) of electrons from the host valence band to the impurity bands raises the Fermi level to the peak of DOS corresponding to the LUMO, which results in Stoner split of the impurity bands and, consequently, the spontaneous Stoner ferromagnetism.

In conclusion, we have shown by ab initio calculation that both $I_0$ and $V_{\text{zn}}$ may induce ferromagnetism in $w$-ZnO. However, $w$-ZnO with $V_{\text{zn}}$ is a ferromagnetic metal and $w$-ZnO with $I_0$ is a ferromagnetic semiconductor. We have proposed the simplified electronic configuration for the defect molecules, based on which we have explained the calculated results including the total magnetic moment, electronic structure, and ferromagnetism.

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