Erratum

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Inducing and manipulating magnetization in 2D zinc–oxide by strain and external voltage

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Abstract

Two-dimensional (2D) structures that exhibit intriguing magnetic phenomena such as perpendicular magnetic anisotropy and its switchable feature are of great interests in spintronics research. Herein, the density functional theory studies reveal the critical impacts of strain and external gating on vacancy-induced magnetism and its spin direction in a graphene-like single layer of zinc oxide (ZnO). In contrast to the pristine and defective ZnO with an O-vacancy, the presence of a Zn-vacancy induces significant magnetic moments to its first neighboring O and Zn atoms due to the charge deficit. We further predict that the direction of magnetization easy axis reverses from an in-plane to perpendicular orientation under a practically achievable biaxial compressive strain of only ~1–2% or applying an electric field by means of the charge density modulation. This magnetization reversal is mainly driven by the strain- and electric-field-induced changes in the spin–orbit coupled d states of the first-neighbor Zn atom to a Zn-vacancy. These findings open interesting prospects for exploiting strain and electric field engineering to manipulate magnetism and magnetization orientation of 2D materials.

Keywords: magnetization switching, magnetic anisotropy, 2D structure, first-principles calculations

(Some figures may appear in colour only in the online journal)

1. Introduction

During the past [52] [53] [54] [55] [56] two decades since the successful isolation of graphene from graphite [1, 2], the exploration of two-dimensional (2D) layered materials has received much attention and is likely to remain one of the leading topics in material science into foreseeable future. Although there have been a number of experimental successes and theoretical predictions on discovering 2D materials, including graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs) [1–5], their potentials in spintronic applications have been limited by the lacks of spin orders and possibilities of magnetization flip. Hence, the current research in this field primarily focuses on seeking a novel 2D material with intriguing magnetic properties [6–9], which would offer great advantages for exploring the internal quantum degrees of freedom of electrons and their potentials in nanoscale down spin-based electronic applications.

Zinc oxide (ZnO), as a 2D material, can possibly be a promising candidate in the same regard, since it has been recently reported that a (0001) oriented ultrathin ZnO film can be transformed into a new form of stable graphite-like structure [10–14]. One to three or four atomic layers of ZnO(0001) have been successfully synthesized on a (1 1 1) surface of Ag [10] and Au substrates [15–17], where Zn and O atoms are arranged in the lateral lattice as a honeycomb shape, similar with the h-BN structure. Theoretical studies have also predicted that thin films of ZnO prefer a graphite-like layered structure when the thickness is less than three atomic layers [12, 13], and the stability of even thicker graphitic layers can be improved by an epitaxial strain [14]. More remarkably, an epitaxial growth of ZnO monolayer on graphene has been very recently demonstrated in atomic resolution transmission electron microscopy (ARTEM) measurements [18].

Numerous reports, on the other hand, have already shown that intrinsic defects and impurities can readily give rise to
magnetism in ZnO allotropies, including monolayer, graphitic layers, thin films, nanowires and nanoribbons [19–29]. For instance, nonmetal (C, B, N, and K)- [27, 29] and rare-earth metal (Ce, Eu, Gd, and Dy)-doped ZnO monolayer [28] exhibits magnetic instability via first-principles calculations. Moreover, it has been shown by both experimentally [20, 22, 26] and theoretically [19, 23, 24] that the Zn vacancy induces ferromagnetism in either thin films [20, 22, 24, 26] and graphitic layers [19, 23] of ZnO without the need of magnetic impurities.

In this article, we perform first-principles calculations to reveal the synergistic effect of biaxial strain on magnetism and its spin direction of a graphene-like single layer of ZnO induced by a Zn-vacancy. Through the analyses of the spin–orbit Hamiltonian matrix elements and atom- and orbital-decomposed magnetic anisotropy energy (MAE), we elucidate the underlying mechanism of magnetization reversal, which occurs at the compressive biaxial strain of only ~1–2%, in terms of the strain-induced changes in the spin–orbit coupled d states of the vacancy-neighbored Zn atom. Moreover, this anisotropic magnetism is identified to even be reversible upon the change in charge carrier density, suggesting the possibilities of chemical doping or magnetoelectric control of magnetization reorientation.

2. Computational details

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) with plane-wave basis set [30, 31]. Projector augmented wave (PAW) potentials [32] were used to describe the core electrons, and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was adopted for
exchange-correlation energy \cite{33}. As illustrated in figure 1(a), a $4 \times 4$ lateral unit cell of the hexagonal lattice was chosen as a model geometry of a single-layer ZnO. We also consider an intrinsic defect of an oxygen vacancy (figure 1(b)) as well as a zinc vacancy (figure 1(c)) in ZnO monolayer, which occurs notably often during sample preparation and treatments \cite{34–40}. In order to avoid spurious interactions between periodic images of ZnO layer, a vacuum spacing perpendicular to the plane was employed to be no less than 15 Å. An energy cutoff of 500 eV and a $5 \times 5 \times 1$ $k$ mesh were imposed for the ionic relaxation, where the change in total energy between two ionic relaxation steps is smaller than $10^{-5}$ eV. The MAE is obtained based on the total energy difference when the magnetization directions are in the $xy$ plane ($E_{\parallel}$) and along the $z$ axis ($E_{\perp}$), $\text{MAE} = E_{\parallel} - E_{\perp}$. To obtain reliable values of MAE, the Gaussian smearing method with a smaller smearing of 0.05 and dense $k$ points of $15 \times 15 \times 1$ were used in noncollinear calculations, where convergence with respect to the $k$ point sampling is checked. Spin–orbit coupling (SOC) term was included using the second-variation method employing the scalar-relativistic eigenfunctions of the valence states \cite{34}.

3. Results and discussion

We first optimize the lattice parameters of the nondefective and defective ZnO monolayer and the results are shown in table 1. The lattice constant of the nondefective ZnO monolayer is 3.29 Å, which agrees with experimental (-3.29–3.30 Å) \cite{10, 16, 18} and previous theoretical values (-3.20–3.28 Å) \cite{12, 13, 23}. While the lattice constant of the nondefective ZnO remains almost unchanged in the presence of a Zn-vacancy, it is reduced by -1% when an O-vacancy is introduced (in a $4 \times 4$ unit cell of ZnO monolayer). The former is due to the direct repulsive interaction between O–O anions without Zn mediation. As presented in table 1, the further calculations of formation energy $H_f$, defined as $H_f = E_{\text{Nondef}} - E_{\text{Def}} - E_{\text{Zn/O}}$, where $E_{\text{Nondef}}$, $E_{\text{Def}}$, and $E_{\text{Zn/O}}$ represent the total energies of the nondefective and defective ZnO with a Zn/O-vacancy, and a Zn/O atom in its bulk/O$_2$-molecule phase, indicate the favorable formation of a vacancy in ZnO, particularly for the Zn-site vacancy, as reported in experiments \cite{35–41}.

The significance of induced magnetism, as fairly addressed in experimental \cite{20, 22, 26} and previous theoretical studies \cite{19, 23, 24}, is then justified. Note that the magnetic moments
of the first-neighboring Zn and O atoms to the Zn-vacancy site are the most prominent beyond those (negligibly small) of the other sites away from the vacancy. We thus refer the results and discussion here and hereafter mainly to those corresponding to the first-neighbor Zn and O atoms. As seen in table 1, the nondefective and defective ZnO with an O-vacancy behave nonmagnetic nature as in bulk [42, 43], but the Zn and O atoms in the Zn-vacancy defected ZnO exhibit significant spin magnetic moments of 0.04 and 0.32 \( \mu_B \), respectively. The ferromagnetic state of the induced moments is more favored than the spin-nonpolarized and spin-antiparallel (i.e. antiferromagnetic arrangement between the first-nearest-neighbor Zn atoms) configurations by energy differences of ~0.17 and 0.12 eV/cell, respectively. This vacancy-induced ferromagnetic instability simply reproduces the results reported in previous \textit{ab initio} calculations [19, 23, 24], where the total magnetization in an unit cell is 2 \( \mu_B \). Moreover, our results (table 1) are more and less comparable with those (\( \mu_{\text{Zn}} = -0.04 \) and \( \mu^{O} = -0.14\)–0.48 \( \mu_B \)) found in ZnO thin films [19, 24]. The vacancy defect driven magnetism can be understood in terms of the spin-polarized charge excess or deficit, where the total magnetization is determined by the unpaired electron counts within the unit cell. Our additional calculations with an injected charge show that such a charge deficit is compensated by an extra charge of +2e\(^-\) per Zn-vacancy and thereby the induced magnetism disappears.

To better understand the Zn-vacancy induced magnetism, we show the projected density of states (PDOS) of the Zn \( d \) and O \( p \) orbital states in figures 2(e) and (f), respectively, in comparison to those of the nondefective (figures 2(a) and (b)) and O-vacancy defected ZnO (figures 2(c) and (d)). In hexagonal lattice, the five \( d \)-orbital states split into one singlet \( a_1 \) or \( m = 0 \) (\( dz^2 \)) and two doublets \( e' \) or \( m = \pm 2 \) (\( d_{xy}/x^2-y^2 \) and \( d_{yz/yz} \)). Both the nondefective and O-vacancy defected ZnO exhibit wide-bandgap insulating electronic features, where the Zn \( d \) orbital states are fully occupied while the conduction band is mainly the characteristics of the O \( p \) states. Furthermore, the spin subbands of the majority- and minority-spin states are essentially degenerate. On the other hand, for the Zn-vacancy defected ZnO the majority- and minority-spin states of Zn and O atoms reflect unequally (i.e. net exchange splitting); The minority-spin filled bands of Zn \( e' \) and O \( p_{xy} \) states move simultaneously upward across the Fermi level in energy relative to the corresponding majority-spin states, thus exhibits a half-metallic behavior. This is mainly due to the charge delocalization of the minority-spin
electrons of Zn and O atoms due to the broken charge quantization associated with the absence of a Zn atom, which are most likely distributed toward the Zn-vacancy site. From the charge analysis taken account within the Wigner–Seitz atomic radius (table 1), the charges of 0.02 and 0.21 $e^{-}$ are depleted from the Zn and O atoms, respectively.

As the stability of the layered ZnO can be enhanced by an epitaxial strain [14], we next explore the impact of strain on magnetism of the Zn-vacancy defected ZnO monolayer. Here we have considered three different types of strain, namely uniaxial strains along the zigzag and armchair directions of a hexagonal lattice and the biaxial strain [44–46], as shown in figures 3(a)–(c). For each type, the compressive and tensile strains ($\varepsilon$) up to ±3% have been applied, where $\varepsilon = (a - a_0)/a_0 \times 100\%$; $a_0$ is the equilibrium lattice (3.296 Å) of the Zn-vacancy defected ZnO and $a$ is a variable. Positive and negative values of $\varepsilon$ correspond to tensile and compressive strain, respectively. In zigzag (armchair) type, both the compressive and tensile strains are applied along the zigzag (armchair) direction while the lattice parameter along the armchair (zigzag) direction is kept fixed, where all the atoms are fully relaxed. Note that either the in-plane lattice expansion and compression up to ~3% of graphitic ZnO layers can be practically achieved by controlling the number of atomic layers [16].

The magnetic moments of Zn (blue) and O (black) atoms are shown in figures 4(a) and (b) for the uniaxial strains along the zigzag (filled) and armchair (unfilled symbol) direction and biaxial strain, respectively, ranging from a compressive strain of $\varepsilon = -3\%$ to a tensile strain of $\varepsilon = +3\%$. For both the uniaxial and biaxial strains, the Zn moment decreases as strain increases (compressive $\rightarrow$ tensile) whereas it increases for the O case, which is solely a reflection of Vergard’s law [47]. As expected, the biaxial type strain exhibits larger enhancement in the absolute values of the Zn and O moments than the uniaxial strains.

Figures 4(c) and (d) show the strain-dependent MAE of the Zn-vacancy defected ZnO for the uniaxial strains along the zigzag (filled) and armchair (unfilled symbol) directions and biaxial strain, respectively. The result of the negative MAE ($\mu$) at zero strain indicates that the induced magnetism prefers an in-plane spin orientation parallel to the lateral lattice. Two uniaxial strains exhibit almost the same MAE, where both the compressive and tensile strains reduce MAE in magnitude and the values of MAE almost reach zero at the largest compressive and tensile strains of $\pm 3\%$ considered in the

Table 2. The atomic contributions of Zn and O species to the total MAE (meV) of a single-layer ZnO with a Zn-vacancy for different strains $\varepsilon$ (%), where the corresponding in-plane lattice constants $a$ (Å) are also listed.

| Strain $\varepsilon$ (%) | $a$ | MAE (Zn) | MAE (O) | MAE (Total) |
|-------------------------|----|----------|---------|-------------|
| $-2$                    | 3.230 | +0.05 | -0.01 | +1.06 |
| 0                       | 3.296 | -0.05 | -0.01 | -0.50 |
| $+2$                    | 3.361 | -0.03 | -0.01 | -0.29 |

The magnetic moments of Zn (blue) and O (black) atoms are shown in figures 4(a) and (b) for the uniaxial strains along the zigzag (filled) and armchair (unfilled symbol) direction and biaxial strain, respectively. The insets in (d) show the schematics for magnetization switching from in-plane (bottom in negative MAE) to out-of-plane magnetization (top in positive MAE) at a compressive biaxial strain of ~1–2%.

Figure 4. Spin magnetic moments $\mu$ of Zn (blue) and O (black) atoms for a single-layer ZnO with a Zn-vacancy as a function of strain ($\varepsilon$) for the (a) uniaxial strain along the zigzag (filled) and armchair (unfilled directions and (b) biaxial strain. Magnetic anisotropy energy MAE for a single-layer ZnO with a Zn-vacancy as a function of strain ($\varepsilon$) for the (c) uniaxial strain along the zigzag (filled) and armchair (unfilled) directions and (d) biaxial strain. In all panels, the negative and positive values of $\varepsilon$ correspond to the compressive and tensile strain, respectively. The insets in (d) show the schematics for magnetization switching from in-plane (bottom in negative MAE) to out-of-plane magnetization (top in positive MAE) at a compressive biaxial strain of ~1–2%.

Table 2. The atomic contributions of Zn and O species to the total MAE (meV) of a single-layer ZnO with a Zn-vacancy for different strains $\varepsilon$ (%), where the corresponding in-plane lattice constants $a$ (Å) are also listed.
present study (figure 4(c)). One can thus expect that the application of a larger uniaxial strain beyond ±3% strain results in positive MAE, thereby the strain-induced magnetization switching. Remarkably, the sign of MAE under the biaxial compressive strain is reversed into the positive and reaches up to +1 meV at strain −2%, as shown in figure 4(d). This indicates that the magnetization direction can reorient from in-plane to perpendicular orientation (PMA) upon an application of biaxial compressive strain. While the PMA remains at the compressive biaxial strain up to −3%, the MAE tends to disappear (or reorient) at the larger tensile strain beyond +3% as the Zn moment reaches zero. Thus, we hereafter mainly focus on the origin of MAE and magnetization switching by the biaxial strain.

To elucidate the underlying mechanism of the strain-induced magnetization reversal, in table 2 we analyze the contributions of different atomic species (Zn and O) to the total MAE for the selected biaxial strains of ε = −2, 0, and +2%, from the difference of SOC energies between in- and out-of-plane magnetization, ∆ESOC = E∥SOC − E⊥SOC. Here, \( E_{soc} = \frac{\mathbf{L} \cdot \mathbf{S}}{2m_{e^2}^2} \), where \( V(r) \) is the spherical part of the effective potential within the PAW sphere, and \( \mathbf{L} \) and \( \mathbf{S} \) are orbital and spin operators, respectively. The expectation value of \( E_{soc} \) is twice the actual value of the total energy correction to the second-order in SOC, i.e. \( \text{MAE} \approx \frac{1}{2}\Delta E_{soc} \) [48, 49]. Our test calculations indicate that the second-order perturbation theory is a reasonable approximation as the total MAE overall agree within a few percent accuracy with those obtained from the atom and orbital projected calculations. The other 50% of the SOC energy translates into the crystal-field energy and the formation of the unquenched orbital moment [50].

As seen in table 2, the ∆ESOC of Zn atom exhibits a trend similar to the changes in sign of the total MAE under strain, whereas the contribution of O atom is rather small and insensitive against strain. One can thus note that the dominant contribution mainly comes from the Zn atom, where the larger SOC effect of \( d \) orbitals (\( l = 2 \)) than \( p \) orbitals (\( l = 1 \)) as a physics origin of anisotropic phenomena is well manifested. The validity of this argument is further demonstrated in connection with the Bruno theory \( \text{MAE} = \frac{\xi}{4\mu_B} \Delta \mu_o \) [51], where \( \Delta \mu_o = \mu_o^\perp - \mu_o^\parallel \) is the orbital magnetic anisotropy (OMA) and \( \xi \) is the SOC constant. The calculated OMA values of Zn and O atoms are −0.60 × and 1.04 × 10−2 µB at zero strain, respectively.

To get more insights on MAE, we further decompose the ∆ESOC into the \( d \)-orbital matrix of Zn atom for −2, 0, and +2% biaxial strains in figure 5. For comparison, we also plot the same for the \( p \)-orbital matrix of O atom.
right panels in figure 5). The O p-orbital contributions of MAE are relatively small and insensitive, compared with the Zn d-orbital contributions, to the sensitivity of MAE under strain effect. We thus focus on the d-orbital states of Zn atom for the discussion of the electronic origin for magnetization reversal.

In the second-order perturbation theory adopted extensively in our previous ab initio MAE calculations [52–56], the MAE is determined by the SOC between occupied and unoccupied d-orbital states [57]: MAE$^\sigma\sigma' = \xi^2 \sum_{n,k} \left| \langle \Psi_{n,k} | \hat{L}_{\sigma} \rangle \right|^2 \left( \langle \Psi_{n,k} | \hat{L}_{\sigma'} \rangle \right|^2 - \langle \Psi_{n,k} | \hat{L}_{\sigma} \rangle \left( \langle \Psi_{n,k} | \hat{L}_{\sigma'} \rangle \right|^2 \right)$, where $\Psi_{n,k}$ and $E_0$ ($E_0$) are the eigenstates and eigenvalues of occupied (unoccupied) states (band index $n$ and wave vector $k$ are omitted for simplicity) for each spin state, $\sigma, \sigma' = \uparrow, \downarrow$, respectively, and $\hat{L}_{\alpha}$ is the $x$ ($z$) component of the orbital angular momentum operator. For $\sigma \sigma' = \uparrow \uparrow$ or $\downarrow \downarrow$, the positive (negative) contribution to MAE is determined by the SOC interaction between the occupied and unoccupied states with the same (different by one) magnetic quantum number ($m$) through the $\hat{L}_z$ ($\hat{L}_x$) operator. Relative contributions of the nonzero $\hat{L}_z$ and $\hat{L}_x$ matrix elements are

$\langle xy | \hat{L}_x | yz \rangle = 1$, $\langle xy | \hat{L}_y | x^2 - y^2 \rangle = 2$, $\langle xz, yz | \hat{L}_z | z^2 \rangle = \sqrt{3}$, $\langle xz, yz | \hat{L}_z | xy \rangle = 1$ and $\langle xz, yz | \hat{L}_x | x^2 - y^2 \rangle = 1$ [49]. For $\sigma \sigma' = \uparrow \downarrow$, the MAE has the opposite sign, so the positive (negative) contribution comes from the $\hat{L}_z$ ($\hat{L}_x$) coupling.

In figures 6(a)–(f), we show the d-orbital PDOS of the Zn d-orbital and O p-orbital states for the biaxial strains of $-2$, $0$, and $+2\%$, respectively. For the Zn atom, while the minority-spin states are rather strain-insensitive, the majority-spin PDOS, particularly in-plane $e'$ states ($d_{xy}$ and $d_{x^2-y^2}$), around the Fermi level differs substantially under strain. The partially unoccupied majority-spin $e'$ states at $\varepsilon = -2\%$ shift downward in energy relative to the Fermi level as the lattice expands, and becomes fully occupied at the tensile strain $\varepsilon = +2\%$. The similar phenomenon appears for the majority-spin O $p_x$ and $p_y$ states. The peak coincidence feature of these Zn and O in-plane orbital states is a reflection of the hybridization effect within the in-plane lattice. The out-of-plane orbital states, i.e. $a_1$ and $e'$ ($p_z$) states for Zn (O) atom, remain almost unchanged under strain although there is a very small downward-shift with strain.

Figure 7 illustrates a simple energy level diagram for the changes of Zn $e'$ peak states near the Fermi level under strain. The electronic structure analyses along with the $d$-orbital decomposed MAE indicate that the underlying origin of the
negative MAE at zero strain is the spin–orbit coupling between the majority-spin occupied and the minority-spin unoccupied \(e'\) states through the in-plane orbital angular momentum operator, 
\[
\langle xy \mid \hat{L}_x \mid x^2 - y^2 \rangle \quad \text{or} \quad \langle x^2 - y^2 \mid \hat{L}_x \mid xy \rangle.
\]
This negative contribution must weaken at +2\% strain because of the downward shift of the majority-spin filled \(e'\) states away from the Fermi level (figure 6(e)). For the compressive strain, the positive MAE arises primarily from the same spin-channel \(\uparrow\uparrow\) matrix elements by 
\[
\langle xy \mid \hat{L}_z \mid x^2 - y^2 \rangle \quad \text{and} \quad \langle x^2 - y^2 \mid \hat{L}_z \mid xy \rangle,
\]
as the majority-spin degenerate \(e'\) states become partially unoccupied. Such a modification of the energy landscape of the Zn \(e'\) electronic state around the Fermi level is the result of the changes in the strength of orbital hybridization with the in-plane O \(p_{xy}\) states (figures 6(b), (d), and (f)) under strain.

The engineering of MAE by Fermi level shifts further suggests to explore crucial effects of the external gating and chemical doping on magnetization reversal. To anticipate this phenomenon, we have performed electrostatic doping calculations by changing the number of valence electrons \(n_e\) in the whole system (4 \times 4 unit cell of ZnO monolayer) from \(n_e = -1.5\) to +1.5\(e^-\). This approach reflects to the charge transitions

**Figure 7.** Simplified schematic diagram for the relative energy level changes of the occupancy of Zn \(e'\) orbital states under the biaxial compressive (\(\varepsilon = -2\%\)) and expansive (\(\varepsilon = +2\%\)) strain. The upward red and downward blue arrows denote the majority-spin and minority-spin states, respectively. The horizontal thin-line indicates the position of the Fermi level \((E_F)\) for reference. The minority-spin \(e'\) states are not much perturbed under strain. The spin–orbit coupling pairs near the Fermi level between the occupied and unoccupied states are emphasized; where the spin up-up and up-down couplings provide the positive (by \(L_z\)) and negative contribution (by \(L_x\)) to the MAE, respectively. The atomic and vacancy symbols at the top crystallographic images are the same as used in figure 1.

**Figure 8.** (a) Magnetic moments \(\mu\) of Zn (blue) and O (black) atoms and (b) MAE as a function of the number of extra valence electrons \(n_e\) \((e^-)\) in a \(4 \times 4\) unit cell of ZnO monolayer with a Zn-vacancy. The negative and positive values in \(n_e\) correspond to the charge deficit and addition, respectively. The insets in (b) show the schematics for magnetization switching from in-plane (bottom in negative MAE) to out-of-plane magnetization (top in positive MAE) at \(n_e = -0.5e^-\) and \(n_e = +1e^-\).
carrier density that is confined over the metallic surface rather than exceeding to a vacuum region, which is analogous to the electric field effect by the positive and negative gating as well as chemical doping with the neighboring elements (e.g. Cu or Ga for Zn, and N or F for O site) [49].

The calculated magnetic moments and MAE as a function of $n_e$ are shown in figures 8(a) and (b), respectively. It is expected that the charge deficit enhances the magnetic moments of both Zn and O atoms whereas the charge excess reduces because of the electron/hole doping. Nevertheless, both the deficit and excess valence charges promptly enhance MAE and change its sign from in-plane to perpendicular magnetization at $n_e = -0.5$ and $+1e^-$, respectively. These results are of considerable interest in the area of the voltage-controlled magnetic anisotropy (VCMA) and magnetoelectric phenomena. The VCMA is determined the slope of the curve of magnetic anisotropy versus an applied electric field or $n_e$ in the present study. The nonlinear parabola-like shape behavior of the VCMA within a small range of $n_e (−1 < n_e < +1)$ is quite typical in most magnetoelectric materials reported in previous studies [49, 58–61].

The electronic origin of MAE changes in sign under the valence charge modification is analyzed with the $d$-orbital PDOS of Zn (along with the O $p$-PDOS) in figures 9(a), (c), and (e) ((b), (d), and (f)) for $n_e = −1, 0$, and $+1e^-$. The entire band structures of both Zn and O atoms shift toward the low-energy region upon the presence of external electrons from $−1$ to $+1e^-$ due to the band filling effect. Since the majority-spin $e'$ peak of Zn exists at the Fermi level (figure 9(a)), the similar argument discussed for the $−2%$ strained ZnO (figure 6(a)) must apply to the origin of PMA at $n_e = −1e^-$. On the other hand, for $n_e = +1e^-$ the peak position of the minority-spin empty $e'$ bands appears just above the Fermi level while the majority-spin states are fully occupied, as shown in figure 9(e). Thus the SOC pair between the minority-spin filled and empty $e'$ states around the Fermi level leads to the positive MAE through $\langle x^2 − y^2 | L_z | xy \rangle$ and $\langle x^2 − y^2 | L_z | xy \rangle$.

4. Conclusion

In summary, we have performed the first-principles electronic structure calculations to reveal the critical effects of strain and external gating on magnetism and magnetic anisotropy of a single-layer ZnO with a Zn-vacancy. In contrast to the pristine and defective ZnO with an O-vacancy, the presence of a Zn-vacancy induces significant magnetic moments to its first
neighboring O and Zn atoms due to the charge deficit. More remarkably, we show that a compressive biaxial strain of only \(-1 \sim -2\%\) or either negative and positive gate voltages give rise to magnetization reorientation from in- to out-of-plane magnetization. The further analyses provide the underlying mechanism for magnetization reversal, which is the result of the strain- and electric field-induced changes in spin–orbit coupled Zn d-orbital states hybridized with O p states. These predictions may inspire further experimental and theoretical explorations of exploiting epitaxial biaxial strain and electric field to manipulate magnetism and magnetization direction for 2D spintronic applications.

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