Effect of different Mn doping and point vacancy ratios on the magnetic properties of ZnO

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Abstract. The magnetic source of Mn doping and Zn vacancy coexisting in ZnO is controversial. To solve this problem, this work used the generalized gradient approximation first-principles plane-wave ultrasoft pseudo potential + U method based on density functional theory to calculate the effect of different Mn doping to point vacancy ratios on the magnetic properties of ZnO. The formation energy of ZnO with different Mn-substituted Zn (MnZn) to oxygen/zinc vacancy (VO/VZn) ratios can be smaller and more stable in zinc (Zn)-rich conditions than in oxygen (O)-rich conditions. The ZnO system exhibits p-type half-metallic ferromagnetism when the MnZn to VZn ratio is 2:1 or 2:2. When the Mn doping amount is constant, the Zn vacancies increase and the total magnetic moment of the doped system decreases. For the ZnO system in which Mn doping and oxygen vacancies coexist, when the amount of oxygen vacancies is constant, with Mn doping increase, the magnetic moment becomes larger. Both Zn22Mn2O22 and Zn20Mn2O24 can achieve ferromagnetic characteristics above room temperature.

1 Introduction

II–VI semiconductor compound material, such as zinc oxide (ZnO), has a wide band gap (i.e., 3.370 eV) and high exciton binding energy (i.e., 60 meV) [1]. ZnO is rich in reserves and is non-toxic and harmless. On the one hand, improving the magnetic moment of ZnO can help improve ZnO-based spintronic device. On the other hand, scholars focus on the magnetic source of ZnO-based semiconductor materials. Manganese (Mn) is opted to be used as a doping element to improve the magnetic properties of ZnO and avoid controversy over its magnetic source. The radius of Mn2+ (0.083 nm) [2] is similar than that of Zn2+ (0.074 nm) [2], and substituting Zn with Mn can reduce lattice distortion and improve crystal quality [3]. Experimental literature [4] reported that Mn and its oxides are non-magnetic [4], and their precipitating capabilities did not affect their magnetic properties, thereby making the use of Mn beneficial in the study of magnetic sources.

In recent years, researchers have conducted extensive experimental and theoretical studies on the magneto-optical properties of ZnO doped with Mn. Senol et al. [5] investigated the magnetic properties of ZnO doped with Mn by using hydrothermal method. The results showed that the doped system did not demonstrate any second magnetic phase at 600°C, and the system was ferromagnetic (FM). Thamaraiselvan et al. [6] examined the effect of the magneto-optical properties of ZnO doped with Mn by using dip coating method. The results show that the doped system has a red-shift into the ultraviolet-visible region, FM properties are reduced, and oxygen vacancy (VO) is observed when Mn is annealed at 500 °C, and its doping amount is increased. Pazhanivelu et al. [7] investigated the effects of ZnO co-doped with Mn and cobalt (Co) on the magneto-optical properties of ZnO by using co-precipitation method. The results show that the FM Curie temperature of the doped system can reach above room temperature. Raman spectroscopy analysis and photoluminescence spectroscopy results show that VO exists in the doped system. Cao et al. [8] investigated the magnetic properties of ZnO co-doped with Mn and Co by using O plasma-assisted molecular beam epitaxy. The results show that the magnetic moment of the doped system increases with the amount of Mn doping, and VO/VZn are observed in the doped system when the amount of Co doping is constant. In theoretical calculations, Park et al. [9] used first-principles method to examine the effects of Mn and VO on the magnetic properties of ZnO. The results show that when the Mn doping amount is 4%, and VO is found between two Mn atoms. Aimouch et al. [10] investigated the magnetic properties of ZnO co-doped with Mn and chromium (Cr) by using the first-principles method. The results show that ZnO systems co-doped with Mn and Cr rare half-metallic and have improved ferromagnetism. Liu et al. [11] examined the magnetic properties of ZnO co-doped with Mn and Co by using first-principles method. The results show that the Co and Mn co-doped system can achieve room temperature ferromagnetism. Moulai et al. [12] investigated the magnetic sources...
properties of Mn-doped ZnO by using first-principles method. The results show that the magnetic moment of the doped system increases with the amount of Mn doping. Yan et al. [13] used the first-principles method to investigate the room temperature ferromagnetism of ZnO, in which Mn doping co-exists with VZn. The results show that the doped system is FM, and the Curie temperature can reach above room temperature. Ponnusamy et al. [14] used first-principles to study the magnetic effect mediated by Zn vacancies in Mn-doped ZnO. The results show that the ferromagnetism in undoped ZnO originates from VZn, VZn defects and Mn ions coexist in ZnO, and Mn ions also have obvious magnetization effects. Wang et al. [15] used first-principles to study the influence of point vacancies and Mn co-existing on the magnetoelectric properties of ZnO. The results show that the ZnO: Mn-VZn system has p-type conductivity, and the greater the distance between VZn and Mn, the better the electrical conductivity of the system. In contrast to VZn, the ZnO: Mn-V2O system is n-type conductivity. The longer the distance between V2O and Mn, the worse the conductivity of the system. In addition, the ZnO: Mn system containing neutral single VZn or single V2O may be in the antiferromagnetic phase. Although there are certain studies on the magnetic moment produced by the coexistence of Mn doping and oxygen vacancy in ZnO at home and abroad, the source and mechanism of the magnetic moment of ZnO doped with Mn double doping and Zn vacancy is still controversial. The calculation in literature [16] pointed out that the origin of ferromagnetic order in the ZnO system in which Mn double doping and Zn vacancy coexist is caused by the d-d hybrid coupling of Mn-Mn. That is, the source of the magnetic moment of the ZnO system in which Mn double doping and Zn vacancy coexist still adopts the traditional magnetic theory of double exchange interaction with oxygen atoms as an intermediate medium [17] to explain unscientifically. This is contrary to the magnetic theory of carrier as media proposed by Sato and Yoshida [18] and the organic combination of dual exchange mechanism proposed by Dietl et al. [19]. So far, a reasonable theoretical explanation is unavailable. The control of the amount of VO/VZn is experimentally reasonable theoretical explanation is unavailable. The mechanism proposed by Dietl et al. [19]. So far, a

2 Theoretical models and calculation methods

2.1 Theoretical model

This work was selected 2 × 2 × 3 supercells to perform all the calculations to study the magnetic properties of ZnO with MnZn and VO/VZn. First, pure 2 × 2 × 3 supercell of Zn23Mn2O24 and one/two Mn atom/s-doped supercell of Zn23Mn1O24/Zn22Mn2O24 were created. Second, literature [14,20] showed that the doped system was relatively stable when MnZn was close to VO/VZn. Therefore, the model with the closest MnZn to VZn was selected in subsequent studies. The ratio (MnZn:VO) of the four kinds of models were 2:2, 2:1, 1:2, and 1:1 with chemical formulas of Zn22Mn2O24, Zn23Mn2O25, Zn23Mn1O22, and Zn23Mn1O23, respectively. The ratio (MnZn:VZn) of the four kinds of models were 2:2, 2:1, 1:2 and 1:1 with chemical formulas of Zn23Mn1O24, Zn23Mn2O24, Zn23Mn1O24 and Zn23Mn1O24, respectively. Figure 1 shows 10 different ratios. Positions 1 and 2, 3 and 4, and 5 and 6 correspond to Mn Zn, VO and VZn, respectively. The results in literature [21] showed that the phase transition of the crystal structure did not occur when Mn was substituted into Zn and the Mn doping amount reached 10 mol%. The maximum doping amount of Mn herein is approximately 8.33 mol%. Thus, the phase transition will not occur.

2.2 Calculation method

All calculations were performed using the CASTEP [22] (Material studio 8.0) software package, which used the generalized gradient approximation (GGA) + U plane wave pseudo potential method and Perdew–Burke–Ernzer of [23] exchange correlation function to improve structure and calculate energy, respectively. Traditional density functional theory cannot accurately describe systems that contain d and f electrons, especially transition metal oxides and nitrides. Meanwhile, GGA + U can accurately describe electronic structures that contain doped transition metal oxides. For localized electrons, GGA + U introduce a Hubbard parameter U (i.e., repulsive energy) that describes the strong correlation among atoms in the model. Computing via test and referring to literature, U_d value of Zn-3d electrons, U_p value of O-2p electrons, U_d value of
3 Results and discussion

3.1 Formation energy and total magnetic moment

The formation energies of different models were calculated to analyze the relative stability of doping and defect systems as follows [30,31]:

\[
E_f(D) = E_{Tot}(D) - E_{Tot}(\text{ZnO}) + \sum n_i \mu_i + q(E_f + Ev)
\]

where \( E_{Tot}(D) \) is the total energy of the defect system, \( E_{Tot}(\text{ZnO}) \) is the total energy of the pure ZnO system that is as big as the defect system, and \( q \) is the charge of the system. \( \mu \) represents the energy value of the valence top band; \( n_i \) is the number of atoms \( i \) added or removed; \( n_i \) is positive when removed, otherwise, it is negative; and \( \mu_i \) is the chemical potential of the \( i \) atom. The formation energy affects the experimental conditions and is divided into O-enriched (O-rich) and Zn-enriched (Zn-rich or O-poor) conditions. Considering the model with the closest Mn to V was selected in subsequent studies. The thermal stability of O and Zn atoms in ZnO, their chemical potentials must satisfy the following condition: \( \mu_O + \mu_{Zn} = \mu_{ZnO} \). In O-rich conditions, the chemical potential of the O atom is represented by half the energy of the O molecule, that is, \( \mu_O = \mu_{O/2} \). Moreover, the chemical potential of the Zn atom is obtained by \( \mu_{Zn} = \mu_{ZnO} - \mu_O \). In O-poor conditions, \( \mu_{Zn} \) and \( \mu_{Mn} \) are calculated by Zn and Mn bulk materials, which are \( \mu_{Zn} = \mu_{Mn}^{metal} \) and \( \mu_{Mn} = \mu_{Mn}^{metal} \), respectively. The chemical potential of O is determined by using \( \mu_O = \mu_{ZnO} - \mu_{Zn} \). The calculated formation energies are listed in Table 1. The smaller the formation energy is, the easier the doping and defects are formed [32], and the stronger the stability is.

It is calculated that the total magnetic moment \( M \), the total anti-ferromagnetic and ferromagnetic energy, the total antiferromagnetic and ferromagnetic settings, and the energy difference between the magnetic states of \( \text{Zn}_{23}\text{Mn}_{1}\text{O}_{2} \), \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{24} \), \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{23} \), \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{22} \), \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{23} \), \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{22} \), \( \text{Zn}_{23}\text{Mn}_{1}\text{O}_{23} \), \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{24} \), and \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{24} \) systems are listed in Table 1.

In order to visually observe the formation energy and total magnetic moment of all doped systems in Table 1, the graphs of statistical bars of all doped systems are drawn, as shown in Figure 2.

It can be seen from the organic combination of Table 1 and Figure 2, the formation energy of \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{24} \) and \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{23} \) are the same in O-rich and Zn-rich conditions, in which ZnO with different proportions of MnZn and VO co-exists. The formation energy of \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{23} \) and \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{22} \) can be smaller and more stable in Zn-rich conditions than in O-rich conditions. In O-rich or Zn-rich conditions, the formation energy sequence of the four doped systems with different ratios is \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{23} < \text{Zn}_{22}\text{Mn}_{2}\text{O}_{22} < \text{Zn}_{22}\text{Mn}_{1}\text{O}_{23} < \text{Zn}_{22}\text{Mn}_{1}\text{O}_{22} \). The formation energies of \( \text{Zn}_{22}\text{Mn}_{2}\text{O}_{24} \), \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{24} \), \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{24} \), and \( \text{Zn}_{22}\text{Mn}_{1}\text{O}_{24} \) systems in Zn-rich conditions, in which ZnO with different proportions of MnZn and VO co-exists, are larger than those in O-rich conditions.
Table 1. Formation energy of all systems, total energy of antiferromagnetic and ferromagnetic settings, total magnetic moment, and energy difference between antiferromagnetic state and ferromagnetism state.

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Model</th>
<th>$E_f$ (eV)</th>
<th>O-rich</th>
<th>Zn-rich</th>
<th>$M$ ($\mu_B$)</th>
<th>$E_{AFM}$ (eV)</th>
<th>$E_{FM}$ (eV)</th>
<th>$\Delta E$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn$_{22}$Mn$<em>2$O$</em>{22}$</td>
<td>$-18.752$</td>
<td>$-18.752$</td>
<td></td>
<td>10</td>
<td>48515.083</td>
<td>48515.123</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Zn$<em>{22}$Mn$</em>{23}$O$_{23}$</td>
<td>$-22.792$</td>
<td>$-26.792$</td>
<td></td>
<td>10</td>
<td>$-48951.73$</td>
<td>48951.280</td>
<td>$-0.45$</td>
</tr>
<tr>
<td>3</td>
<td>Zn$_{23}$Mn$<em>2$O$</em>{22}$</td>
<td>$-7.507$</td>
<td>$-11.506$</td>
<td></td>
<td>5</td>
<td>49601.092</td>
<td>49600.582</td>
<td>$-0.51$</td>
</tr>
<tr>
<td>4</td>
<td>Zn$_{23}$Mn$<em>1$O$</em>{23}$</td>
<td>$-11.526$</td>
<td>$-11.526$</td>
<td></td>
<td>5</td>
<td>50012.810</td>
<td>50012.510</td>
<td>$-0.3$</td>
</tr>
<tr>
<td>5</td>
<td>Zn$_{20}$Mn$<em>2$O$</em>{24}$</td>
<td>$-29.352$</td>
<td>$-13.352$</td>
<td></td>
<td>7.06</td>
<td>45951.560</td>
<td>45951.598</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>Zn$_{21}$Mn$<em>2$O$</em>{24}$</td>
<td>$-27.652$</td>
<td>$-15.652$</td>
<td></td>
<td>8.49</td>
<td>47671.540</td>
<td>47671.140</td>
<td>$-0.4$</td>
</tr>
<tr>
<td>7</td>
<td>Zn$_{21}$Mn$<em>1$O$</em>{24}$</td>
<td>$-16.276$</td>
<td>$-4.276$</td>
<td></td>
<td>2.75</td>
<td>47010.528</td>
<td>47010.428</td>
<td>$-0.1$</td>
</tr>
<tr>
<td>8</td>
<td>Zn$_{22}$Mn$<em>1$O$</em>{24}$</td>
<td>$-17.176$</td>
<td>$-9.176$</td>
<td></td>
<td>4.98</td>
<td>48753.382</td>
<td>48732.782</td>
<td>$-20.6$</td>
</tr>
<tr>
<td>9</td>
<td>Zn$_{23}$Mn$<em>1$O$</em>{24}$</td>
<td>$-15.966$</td>
<td>$-11.966$</td>
<td></td>
<td>5</td>
<td>50450.990</td>
<td>50450.390</td>
<td>$-0.6$</td>
</tr>
<tr>
<td>10</td>
<td>Zn$_{22}$Mn$<em>2$O$</em>{24}$</td>
<td>1.2</td>
<td>0.6</td>
<td></td>
<td>10</td>
<td>49391.331</td>
<td>49391.258</td>
<td>$-73$</td>
</tr>
</tbody>
</table>

Fig. 2. Formation energy and total magnetic moment of all systems.

In O-rich or Zn-rich condition, the formation energy sequence of the four doped systems with different ratios is Zn$_{20}$Mn$_2$O$_{24}$ > Zn$_{21}$Mn$_1$O$_{24}$ > Zn$_{22}$Mn$_1$O$_{24}$ > Zn$_{23}$Mn$_1$O$_{24}$. The calculation results show that no matter under oxygen-rich conditions (O-rich) or zinc-rich conditions (Zn-rich), the formation energies of all doped systems are negative and compounds are easily formed.

It can be seen from the organic combination of Table 1 and Figure 2, the total magnetic moments of the Zn$_{23}$Mn$_1$O$_{24}$ and Zn$_{22}$Mn$_2$O$_{24}$ systems are 5 $\mu_B$ and 0 $\mu_B$, respectively; such findings are the same as the results in the previous study [33]. In contrast with the magnetic moment of ZnO doped with Mn, the total magnetic moment of ZnO, $\Delta E$, Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{20}$Mn$_2$O$_{24}$, and Zn$_{23}$Mn$_1$O$_{24}$ systems are related to the formation energy differences of all doped systems. The total magnetic moment of both doped systems is 10 $\mu_B$, which is larger than that of ZnO doped with Mn. The results show that compared with Zn$_{23}$Mn$_1$O$_{24}$ system, the total magnetic moments of Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{23}$Mn$_1$O$_{22}$, Zn$_{23}$Mn$_1$O$_{23}$, and Zn$_{23}$Mn$_1$O$_{24}$ systems are related to the Mn doping to V$_{O}$ ratios. This phenomenon is consistent with the reported experimental and theoretical results in the previous study [17,34,35]. The calculation results show that the conclusions of the experimental literature [16] are not contradictory to that of the experimental literature [17]. The magnetic size of ZnO with Mn$_{23}$ and V$_O$ is related to the relative Mn$_{23}$ to V$_O$ ratio. Also, the total magnetic moments of doped systems with Mn$_{23}$ and V$_{Zn}$ are 4.98, 2.75, 8.49, and 7.06 $\mu_B$ when V$_{Zn}$: Mn$_2$O$_{24}$ ratios are 1:1, 2:1, 1:2, respectively. When the Mn ratio is constant, the total magnetic moment of the doped system with Mn$_{23}$ and V$_{Zn}$ decreases with the increase in V$_{Zn}$ ratio. Due to controlling the ratio of Mn in the experiment is difficult, no experiment supports the aforementioned results.

It can be seen from Table 1 that, except for the ferromagnetic properties of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_1$O$_{24}$, all other doped systems exhibit antiferromagnetic properties.

3.2 Analysis of magnetic and half-metallic properties of doped system

It is calculated that the total density of states distribution of the Mn-doped non-vacancy system, the Mn-doped O-containing vacancy system and the Mn-doped Zn-containing system are shown in Figures 3a–3i.

Figures 3a–3i show that the total state density distributions of the electron spin up and spin down are asymmetric, thereby exhibit a net magnetic moment. This result is consistent with the results of the total magnetic moment analysis in Section 3.1.

Spin polarizability ($P$) refers to the ratio of the density of states of major carriers near the Fermi level less the density of states of minor carriers near the Fermi level, thereby exhibit a net magnetic moment. This result is consistent with the results of the total magnetic moment analysis in Section 3.1.

Spin polarizability ($P$) refers to the ratio of the density of states of major carriers near the Fermi level less the density of states of minor carriers near the Fermi level. Therefore, the magnetic moment is determined by the ratio of the density of states of major carriers near the Fermi level to the total density of states near the Fermi level, which is calculated by the following equation:

$$P = N^+ - N^- / N^+ + N^-$$  \(\text{(2)}\)

Figures 3f and 3g show that Zn$_{20}$Mn$_2$O$_{24}$ and Zn$_{23}$Mn$_1$O$_{24}$ have a band tail effect, respectively. Both Fermi levels enter the upper spin valence band, and the energy levels of the electron spin up $N^+$ and spin down $N^-$ are asymmetric, thereby exhibit a net magnetic moment. This result is consistent with the results of the total magnetic moment analysis in Section 3.1.

Spin polarizability ($P$) refers to the ratio of the density of states of major carriers near the Fermi level less the density of states of minor carriers near the Fermi level. Therefore, the magnetic moment is determined by the ratio of the density of states of major carriers near the Fermi level to the total density of states near the Fermi level, which is calculated by the following equation:

$$P = N^+ - N^- / N^+ + N^-$$  \(\text{(2)}\)
is, both of them have conduction hole Ps of up to 100%, and they can be used as hole injection source for the promising new type of half-metallized DMS.

3.3 Analysis of magnetic sources in doped system

According to the results in Section 3.1, the total magnetic moments of Zn$_{23}$Mn$_1$O$_{22}$, Zn$_{23}$Mn$_1$O$_{2}$, Zn$_{21}$Mn$_1$O$_{24}$, and Zn$_{22}$Mn$_1$O$_{24}$ systems do not increase, and their relative research values are insignificant compared with those of the Zn$_{23}$Mn$_1$O$_{24}$ system. However, the total magnetic moments of Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, and Zn$_{21}$Mn$_2$O$_{24}$ systems greatly increased. Therefore, the research of the next paragraph mainly focuses on the magnetic sources of Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, and Zn$_{21}$Mn$_2$O$_{24}$ systems.

The calculated partial density of state (PDOS) distributions of Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, and Zn$_{21}$Mn$_2$O$_{24}$ are shown in Figures 4a–4d.

Results show that the total magnetic moment of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{22}$Mn$_2$O$_{23}$ is 10$\mu_B$, and $\mu_B$ is Bohr magneton. For example, the magnetic moments of two Mn atoms in Zn$_{22}$Mn$_2$O$_{22}$ system are 5.13$\mu_B$ and 5.09$\mu_B$, and the magnetic moments of the main O atoms near V$_O$ are 0.02$\mu_B$ or 0.01$\mu_B$. The magnetic moments of Mn and O atoms are arranged in the same direction. The magnetic moments of the main Zn atoms near the V$_O$ are $-0.07$, $-0.06$, $-0.04$, and $-0.02\mu_B$, and they are arranged in the opposite direction. Therefore, the total magnetic moment of Zn$_{22}$Mn$_2$O$_{22}$ system is 10$\mu_B$. Since the magnetic moment source of the Zn$_{22}$Mn$_2$O$_{23}$ system is similar to that of the Zn$_{22}$Mn$_2$O$_{22}$ system, it will not be repeated.
From Figures 4a and 4b, it can be seen that the magnetic source of \( \text{Zn}_2\text{Mn}_2\text{O}_{22} \) and \( \text{Zn}_2\text{Mn}_2\text{O}_{23} \) system is \( \text{O}-2p \) orbital, there is a strong coupling electron exchange between \( \text{Zn}-4s \) orbital and \( \text{Mn}-3d \) orbital, \( \text{sp}-d \) caused by this strong interaction. That is, the \( \text{O}-2p \) partial density of state upper-spin orbit and the lower-spin orbit are asymmetric; the \( \text{Zn}-4s \) orbital partial density of state is asymmetric; the \( \text{Mn}-3d \) orbital partial density of state is asymmetric.

Results show that the total magnetic moments of \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) and \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) are 7.06\( \text{mB} \) and 8.49\( \text{mB} \), respectively. For example, the magnetic moments of the two Mn atoms in the \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) system are 4.35\( \text{mB} \) and 4.33\( \text{mB} \), and the magnetic moments of the main O atoms near the \( \text{V}_{\text{Zn}} \) are /C0\,0.40, /C0\,0.29, /C0\,0.27, and /C0\,0.26\( \text{mB} \).

Therefore, the total magnetic moment of \( \text{Zn}_2\text{Mn}_2\text{O}_{22} \) system is 7.06\( \text{mB} \). In the same way, the magnetic moment source of \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) is similar to that of \( \text{Zn}_2\text{Mn}_2\text{O}_{22} \), it will not be repeated.

Figures 4c and 4d show that a strong coupled-electron exchange exist among the \( \text{O}-2p, \text{Zn}-4s, \text{and Mn}-3d \) orbits of \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) and \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) systems. The PDOS of \( \text{O}-2p, \text{Zn}-4s, \) and \( \text{Mn}-3d \) orbits are asymmetric in spin-up and spin-down orbits because of the strong \( \text{sp}-d \) interaction. This can also be explained from the theory of defect chemistry. For example, due to 2 Mn substitutions for \( \text{Zn} \) doping and 2 \( \text{Zn} \) vacancies in \( \text{ZnO} \), the reaction formula is as follows.

\[
2\text{Mn}^{2+}_{\text{Zn}} + 2\text{V}^{2-}_{\text{Zn}} \rightarrow 2(\text{Mn}_{\text{Zn}} - \text{V}_{\text{Zn}})^\times.
\]  

It can be seen from the formula (3) that the \( 2\text{Mn}_{\text{Zn}} - 2\text{V}_{\text{Zn}} \) complex is formed in the doped system.

In the equilibrium state, the defect chemical reaction of \( \text{ZnO} \) is

\[
\frac{1}{2} \text{O}_2(g) = \text{V}^\times_{\text{Zn}} + \text{O}^\times_0 \tag{4}
\]

\[
\text{V}^\times_{\text{Zn}} = \text{V}'_{\text{Zn}} + h^* \tag{5}
\]

\[
\text{V}'_{\text{Zn}} = \text{V}''_{\text{Zn}} + h^*. \tag{6}
\]

From equations (4)–(6), we know that after \( \text{Zn} \) vacancies are formed, hole carriers appear in the doped system. This is because in \( \text{ZnO} \), \( \text{Zn} \) ions are usually positive divalent. Once there is excess oxygen, in order to maintain the neutral condition, the divalent \( \text{Zn} \) ions trap a hole. According to the density of states Figures 4c and 4d, it can be seen that the Fermi level enters the valence band, the doped system is a \( p \)-type degenerate semiconductor, and the ionization energy is 0. Therefore, free hole carriers appear in the doped system to conduct electricity. It can be concluded that the magnetic sources of \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) and \( \text{Zn}_2\text{Mn}_2\text{O}_{24} \) systems are consistent with the magnetic theory of carrier as media proposed by Sato and Yoshida [18] and the organic combination of dual exchange mechanism proposed by Dietl et al. [19]. However, the literature [16] not only neglected the magnetic source of \( \text{O}-2p \) orbital and \( \text{Zn}-4s \) orbital electron spin polarization, but also neglected the mechanism of magnetic source mediated by carriers. It is worth further study.
Figures 5a–5d show the calculation of the net spin density distributions of Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, and Zn$_{21}$Mn$_2$O$_{24}$ to intuitively analyze the magnetism sources of doped systems from the electron’s structure.

It can be seen from Figures 5a and 5b that the total magnetic moment of the Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{22}$Mn$_2$O$_{23}$ systems is contributed by the difference between the up-spin density and the down-spin density of the spin-polarized O atom, contributed by the difference between the up-spin density and the down-spin density of spin-polarized Mn atoms, the opposite is true for Zn atoms, which is contributed by the difference between the down-spin density and the up-spin density. The results are in good agreement with the findings in PDOS. It can be seen from Figures 5c and 5d that the total magnetic moment of the Zn$_{20}$Mn$_2$O$_{24}$ and Zn$_{21}$Mn$_2$O$_{24}$ systems is contributed by the difference between the up-spin density and the down-spin density of the spin-polarized O atom, contributed by the difference between the up-spin density and the down-spin density of spin-polarized Mn atoms, contributed by the difference between the up-spin density and the down-spin density of the spin-polarized Zn atom. This is consistent with the analysis results of the PDOS distribution.

In order to visually observe the difference in charge transfer before and after doping, we calculated that the differential charge density distribution in the (0,0,1) plane of Zn$_{24}$O$_{24}$, Zn$_{23}$Mn$_1$O$_{24}$, Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, Zn$_{21}$Mn$_2$O$_{24}$ systems are shown in Figures 6a–6f. As can be seen from Figures 6a–6f, compared with the pure system Zn$_{24}$O$_{24}$, the charge density around O and Mn in the system Zn$_{23}$Mn$_1$O$_{24}$, Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, Zn$_{21}$Mn$_2$O$_{24}$ is relatively denser. The calculation results show that the covalent bonds of Zn$_{23}$Mn$_1$O$_{24}$, Zn$_{22}$Mn$_2$O$_{22}$, Zn$_{22}$Mn$_2$O$_{23}$, Zn$_{20}$Mn$_2$O$_{24}$, Zn$_{21}$Mn$_2$O$_{24}$ are enhanced after doping.

### 3.4 Curie temperature analysis of doped system

As can be seen from Table 1, because the energy difference between the antiferromagnetic state and the ferromagnetic state of the Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems is relatively large, the Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems are used as the object to study the Curie temperature. That is, the Curie temperatures of the Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems were studied separately. The Curie temperature of DMS can be estimated from the energy difference ($\Delta E$) between the AFM and FM states according to the Heisenberg model in mean field approximation, which is illustrated by the following formula [36].

$$k_BT_c = \frac{2\Delta E}{3C}.$$  \hfill (7)
Where $k_B$ is the Boltzmann’s constant, $C$ is the magneticon concentration, and $T_C$ is the estimated Curie temperature of DMS. Formula (7) shows that the increase in $\Delta E$ results in high $T_C$ value. As can be seen from Table 1, the total energies of the AFM settings of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems correspond to $-48515.083$ and $-45951.560$ eV, respectively. The total energies of the FM settings of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems correspond to $-48515.123$ and $-45951.598$ eV, respectively. The $\Delta E$ between the AFM and FM states of the Zn$_{22}$Mn$_2$O$_{22}$ system has a value of 48 meV. Moreover, the $\Delta E$ between the AFM and FM states of the Zn$_{20}$Mn$_2$O$_{24}$ system has a value of 38 meV. The known data were substituted into formula (7), and the Curie temperatures of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ were calculated to be 400 and 380 k, respectively. The calculated results are in agreement with the experimental results [13,37]. The results show that Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems can meet the requirements of Curie temperature, which is above room temperature.

4 Conclusion

The effect of different Mn doping to point vacancy ratios on the magnetic properties of ZnO has been investigated using the first principle method. In the formation energy of doped systems, ZnO with different ratios of Mn$_{Zn}$ and V$_{Zn}$/V$_{O}$ can be smaller and more stable in Zn-rich conditions than in O-rich conditions. The doped system exhibits p-type half-metallic ferromagnetism when the Mn$_{Zn}$:V$_{Zn}$ is 2:1 or 2:2 in ZnO. The increase in V$_{Zn}$ results in small total magnetic moments when the doping amount of Mn is constant. For the ZnO system in which Mn doping and oxygen vacancies coexist, when the amount of oxygen vacancies is concentration, and $\Delta E$ results in high $T_C$ value. As can be seen from Table 1, the total energies of the AFM settings of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems correspond to $-48515.083$ and $-45951.560$ eV, respectively. The total energies of the FM settings of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems correspond to $-48515.123$ and $-45951.598$ eV, respectively. The $\Delta E$ between the AFM and FM states of the Zn$_{22}$Mn$_2$O$_{22}$ system has a value of 48 meV. Moreover, the $\Delta E$ between the AFM and FM states of the Zn$_{20}$Mn$_2$O$_{24}$ system has a value of 38 meV. The known data were substituted into formula (7), and the Curie temperatures of Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ were calculated to be 400 and 380 k, respectively. The calculated results are in agreement with the experimental results [13,37]. The results show that Zn$_{22}$Mn$_2$O$_{22}$ and Zn$_{20}$Mn$_2$O$_{24}$ systems can meet the requirements of Curie temperature, which is above room temperature.

Conflict of interest: the authors declare that they have no conflict of interest.

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Author contribution statement

Qingyu Hou: writing – original draft, project administration, funding acquisition.
Yuqin Guan: conceptualization, methodology, writing – review & editing, data curation.
Zhichao Wang: conceptualization, methodology, writing – review & editing, data curation.

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