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## Magnetic properties of C-doped $Zn_{12}O_{12}$ clusters: First-principles study

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**Abstract** – First-principles calculations have been performed to study the magnetic properties of  $Zn_{12}O_{12}$  clusters doped with one or two C atoms at the O site. The results show that one C introduces a total moment of  $2\mu_B$ , which mainly comes from the spin-polarized C-2p states in the band gap. The ferromagnetic coupling occurs only at the (0, 1) doping configuration, in which the C…C distance is 5.42 Å, and other doping configurations are nonmagnetic or antiferromagnetic. The ferromagnetism is mediated by holes through the *p*-*d* hybridization-like *p*-*p* coupling interaction between the C dopants and the neighboring O atoms.

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Introduction. - Transition metals (TM) doped ZnO diluted magnetic semiconductors (DMS) have been widely researched for their potential applications in spintronic devices [1,2]. Even though a lot of intensive research effort has been devoted to synthesize ZnO-based DMS and ferromagnetism has been observed in some systems at or above room temperature (RT) [3–10]. However, the mechanism of ferromagnetism still remains unclear. It is speculated that TM dopants in ZnO form clusters and secondary phases [11,12], which are detrimental to the applications of DMS. Recently, since 2007, when Pan et al. [13] observed RT-ferromagnetism of C-doped ZnO experimentally by pulsed-laser deposition and confirmed it through firstprinciples study, the magnetic property of ZnO doped with 2p light elements, such as B, C and N nonmagnetic elements, has begun to draw people's attention [14–21]. Feng et al. [19] reported that the magnetism of the semiconductors doped with 2p light elements is determined by the electronegativities of dopants and anions in the host materials. They also reported that, to have a stable magnetic ground state, the electronegativity of the dopant must be smaller than that of the host anion so that the 2porbitals of the dopant remain localized and atomic like. In C- and N-doped ZnO, Shen *et al.* [13,17] proposed that the ferromagnetism is attributed to the *p-d* exchangelike *p-p* coupling interaction through the electronic structure calculations. However, Wu *et al.* [22] demonstrated by using the Heyd-Scuseria-Ernzerhof hybrid functional that a resonance of the spin-polarized  $C_2 pp\pi^*$  states with the host conduction band is responsible for the long-range ferromagnetism. Therefore, much more effort is highly desired for completely understanding the mechanism of ferromagnetic (FM) coupling in 2*p*-light-elements-doped ZnO.

So far, the theoretical studies of the C-doped ZnO system was mainly focussed on bulks and thin films, and only few refer to clusters. In comparison with bulks and thin films, a cluster usually exhibits some unique properties due to its special geometry and the quantum confinement effect. Consequently, it is useful to study C-doped ZnO clusters, which may bring a new insight into the mechanism of FM coupling in DMS. According to previous theoretical studies [23–26], the Zn<sub>12</sub>O<sub>12</sub> cluster is a particularly stable cage structure, which can be taken as a good candidate for the investigation of doped ZnO clusters. Recently, Sharma *et al.* [27] investigated the magnetic properties of C-doped (ZnO)<sub>n</sub> clusters (n = 1-12, 16). However, they mainly researched the variation in magnetic moment in these C-doped (ZnO)<sub>n</sub> clusters

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Fig. 1: (Color online) (a) The crystal structure of the  $Zn_{12}O_{12}$  cluster. The numbers denote the atom that will be substituted. (b) The spin-density distribution of one-C-doped  $Zn_{12}O_{12}$  cluster. Most of the spin-density localized on the doped C atom. The big (pink) and small (gray) balls represent the Zn and O atoms, the C atoms cannot be seen because they are wrapped by the yellow spin-density region. ( $\rho = 0.0038 \, e/a.u.^3$ )

and did not systematically investigate the relationship between the distribution of C dopants and the magnetic ordering.

In this letter, we carry out a systematic theoretical investigation on the geometry, electronic structure and magnetic properties of  $Zn_{12}O_{12}$  clusters doped with one or two C atoms. We found that each doped C atom at an O site produces a total moment of  $2\mu_B$ . The ferromagnetic coupling occurs only at the (0, 1) doping configuration, in which the C…C distance is 5.42 Å, and other doping configurations are nonmagnetic or antiferromagnetic (AFM).

Method and computational details. – Our calculations have been carried out with plane-wave basis set and ultrasoft pseudopotentials as implemented in the Quantum-Espresso package [28]. The generalized gradient approximation (GGA) functional in the form of Perdew-Burke-Ernzherof (PBE) [29] was employed. The wave functions were expanded by plane waves up to a cutoff energy of 30 Ry (the charge-density cutoff is 300 Ry). Brillouin Zone intergrations were performed with the Gaussian-smearing [30] special-point technique [31], using a smearing parameter of 0.005 Ry. All atoms were allowed to relax until the atomic forces were smaller than  $10^{-3}$  Ry/bohr.

**Results and discussion.** – The pristine  $Zn_{12}O_{12}$  cluster, as shown in fig. 1(a), is a  $T_h$  symmetry cage with six isolated squares and eight hexagons, and is similar to the first Brillouin Zone of a face-centered cubic lattice. The diameter of the cluster is about 6.35 Å. The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital for this cluster is found to be 2.37 eV still indicating its semiconductor nature, which is in good agreement with the results of previous DFT calculations [32,33].

We firstly researched samples where one O atom was substituted by a C atom in the cluster. Based on the calculated total energy, we found that the system favors the spin-polarized state and its energy is 319 meV lower than that of the non–spin-polarized state. Comparing with our result calculated in the C-doped ZnO bulk consisting of 72 ions (the spin-polarized state is 285 meV lower than the non–spin-polarized in energy), it is found that the C-doped ZnO cluster is more easily spin-polarized. Each C dopant introduces a total magnetic moment of  $2 \mu_B/$ cluster, which is mainly contributed by the  $C(\sim 1.67 \mu_B)$  and the residual by its second-neighboring O ( $\sim 0.26 \mu_B$ ) and the nearest-neighboring Zn ( $\sim 0.05 \mu_B$ ), the corresponding spin-density distribution is shown in fig. 1(b).

The electronic structure analysis is desirable for researching the origin of magnetism in the C-ZnO cluster. For the sake of comparison, the total density of state (DOS) of the pristine  $Zn_{12}O_{12}$  cluster is also presented. As shown in fig. 2(a), the spin-up and spin-down states are identical for the pristine  $Zn_{12}O_{12}$  cluster, which indicates the cluster is nonmagnetic. Figures 2(b)-(d) show the calculated total DOS of one-C-atom-doped  $Zn_{12}O_{12}$ cluster and the partial DOS of the 2p states of carbon and the second-nearest-neighboring oxygen, respectively. Comparing fig. 2(b) with fig. 2(a), it can be seen that new impurity states occur in the band gap and the total DOS is not identical in the C-doped  $Zn_{12}O_{12}$  cluster. As can be seen in fig. 2(c), the localized C-2p states overlap well with the O-2p states near the Fermi level, suggesting a strong coupling between them. The strong interaction leads the energy levels to split at the Fermi level. The spin-up triplet states (*i.e.*, C- $2p_x$ ,  $2p_y$  and  $2p_z$ ) are nearly fully occupied ( $\sim 2.54 e$  occupied), however, for spin-down triplet states, only the  $C-2p_{y}$  is nearly fully occupied, as shown in fig. 2(d). As a consequence, the observed magnetism is  $2\mu_B$ , which is primarily from the C-2p orbitals instead of the Zn-3d orbitals. Besides, the strong coupling between the C-2p and the O-2p also induces their moments to align parallelly.

We investigate the change of bond length in a C-doped  $Zn_{12}O_{12}$  cluster. It is known that the electronegativity of C (2.55) is smaller than that of O (3.44). Consequently, the C atom will outward relaxation when one C atom substitutes an O atom, leading to a longer Zn-C bond compared to the Zn-O bond in the C-doped (ZnO)<sub>12</sub> cluster, as shown in fig. 3. The Zn-C bond is relatively weaker than the native Zn-O bond, which leads to localized atomic-like C-2p states and a stable magnetic ground state. This is in good agreement with the calculated results of Yang *et al.* [19] in C-doped bulk ZnO.

To investigate the magnetic coupling between C impurities, a pair of O atoms was substituted by C atoms in the clusters. There are five independent doping configurations for the bidoped  $Zn_{12}C_2O_{10}$  clusters. The five independent configurations are obtained by substituting two C atoms for two O atoms at the positions (0, 1), (0, 2), (0, 3), (0, 4),



Fig. 2: (Color online) Total DOS of the pristine  $Zn_{12}O_{12}$  cluster (a), one-C-doped  $Zn_{12}O_{12}$  cluster (b), the partial DOS of C-2p (red line) and O-2p (black line) (c), the partial DOS of C-2p<sub>x</sub> (blue line),  $2p_y$  (red line) and  $2p_z$  (green line) states (d). The vertical dashed line denotes the Fermi level.



Table 1: The calculated results of the C-doped Zn<sub>12</sub>O<sub>12</sub> cluster: C···C distance  $(d_{C...C})$ , relative energy  $(\Delta E)$ , energy difference  $(E_{mag} = E_{FM} - E_{AFM})$ , total magnetic moment (M) under the lower-energy state of each configuration. The relative energy  $\Delta E$  is got by the energy of the lower-energy state of each configuration minus that of configuration (0, 1).

(i, j)	$d_{\mathrm{C}\cdots\mathrm{C}}(\mathrm{\AA})$	$\Delta E$ (eV)	$E_{mag} \ (\mathrm{meV})$	$M \ (\mu_B/\text{cell})$
(0, 1)	1.27	0.000	0	0
(0, 2)	1.35	0.532	0	0
(0, 3)	5.42	4.824	-20	4
(0, 4)	5.74	4.860	36	0
(0, 5)	6.47	4.850	12	0

optimized C…C distance and the total magnetic moment in the lower-energy state of each configuration (either FM or AFM). Besides, table 1 also lists the energy difference  $\Delta E$  between the lower-energy state of each configuration and the ground state of the system, *i.e.*, the nonmagnetic state of the (0, 1) configuration, and the energy difference  $E_{mag}$  between the FM and AFM states of each configuration.

Fig. 3: (Color online) The optimized crystal structure of one-C–doped  $Zn_{12}O_{12}$  cluster. Numbers of the same color correspond to bond lengths of the same type.

(0, 5) (see fig. 1(a)), and we named these configurations (i, j) for convenience. For each configuration, both the FM and AFM orderings have been calculated. Table 1 lists the

As can be seen from table 1, the C…C distances of the configurations (0, 1) and (0, 2) 1.27 Å and 1.35 Å, respectively, which are close to those of a typical C-C



Fig. 4: (Color online) Fully optimized structures of configurations (0, 1) (a) and (0, 2) (b). The pink, gray and yellow balls represent the Zn, O and C atoms, respectively.

triple bond (i.e., 1.2 Å) [19] and a C-C double bond (i.e.,1.34 Å [34]. The fully optimized structures are shown in fig. 4. Obviously, some bonds are broken down and the C-C bonds are formed in the two configurations. The two configurations are both nonmagnetic and considerably more stable than other configurations due to the formation of the C-C bond. This indicates that the C atoms would form carbon clusters through the direct C-C bonding interaction under favorable condition. This is in agreement with the calculated result in the C-doped bulk ZnO [19], which has been confirmed experimentally by Pan et al. [13] through X-ray photoelectron spectroscopy (XPS) measurements. A similar phenomenon was also found in the C-doped anatase  $TiO_2$  [34]. The very close C-C distance induces the wave functions of the two C atoms to overlap, which results in the delocalization of the C-2pstates, and the disappearance of the localized magnetic moment [19].

In configuration (0, 3), in which the C…C distance is 5.42 Å, the system shows ferromagnetism. This indicates that the ferromagnetism is possible in C-doped ZnO clusters. However, the configurations (0, 4) and (0, 5), in which the C…C distances are larger than that of configuration (0, 3), are antiferromagnetic. Consequently, we proposed that the magnetic state is very sensitive to the distance between the two C atoms. Pan *et al.* [13]proposed hole mediation as the mechanism of FM coupling in C-doped ZnO. Each C substitution for O introduces two holes in C-2p states. The C-2p states wave function spatially extends to neighboring O-2p states, hybridizing with them. By the p-d hybridization-like p-p coupling interaction, holes mediate the spin alignment of the two C atoms, resulting in an indirect FM coupling of C atoms. Figure 5 shows the spin-density distribution of the configuration (0, 3) in the FM state. The ferromagnetism is mediated by holes through the strong p-p coupling between the two C atoms and their mutual neighboring O atoms. The spin alignment can be shown as  $C(\uparrow)-O(\uparrow) C(\uparrow)$ , which is different from the Mn-doped GaAs system (shown as  $Mn(\uparrow)$ -As( $\downarrow$ )-Mn( $\uparrow$ )) [35]. For the configuration (0, 4), though the two C atoms have mutual neighboring O atoms, the distance between the two C atoms is, however,



Fig. 5: (Color online) The spin-density distribution of the (0, 3) configuration in the lower-energy state. The pink, gray and yellow balls represent the Zn, O and C atoms, respectively. ( $\rho = 0.004 \text{ e/a.u.}^3$ )

too large, which leads to the fact that the FM coupling is unfavorable in energy compared to the AFM coupling. Similarly, for the configuration (0, 5), the FM coupling is also unfavorable in energy because the two C atoms are too far apart. Consequently, the configuration (0, 4) and the configuration (0, 5) are both antiferromagnetic.

Conclusion. – The magnetic properties of C-doped  $Zn_{12}O_{12}$  clusters were studied by first-principles calculations. The results show that substitution of one C atom at one O site generates a total magnetic moment of  $2\mu_B$ , which is attributed to the orbital coupling between C-2pand O-2p states. The magnetic state is sensitive to the distance between the two doped C atoms. When the two C dopants are placed at the two O sites connecting the same Zn atom, typical C-C double and C-C triple bonds, which are both nonmagnetic, are more easily formed. At appropriate C…C distance, ferromagnetism will occur and it is mediated by holes through the p-d hybridization-like p-p coupling interaction between the two C dopants and their mutual neighboring O atoms. However, if the C…C distance is too large, the doped clusters will show antiferromagnetism .

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