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Investigation on structure, electronic and magnetic properties of Cr doped $(ZnO)_{12}$ clusters: First-principles calculations

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ABSTRACT

The structural, electronic, and magnetic properties of $(ZnO)_{12}$ clusters doped with Cr atoms have been investigated by using spin-polarized first-principles calculations. The exohedral a3 isomer is favorable than endohedral a2 isomer. The isomer a1 and a5 respectively have the narrowest and biggest gap between highest unoccupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) of 0.473 and 1.291 eV among these five monodoped isomers. The magnetic moment may be related to the local environment around the Cr atom that the a2 isomer whose total magnetic moment is 6 μ_B while the other monodoped isomers which all isomers have nearly total magnetic moments 4 μ_B. For Cr-doped $(ZnO)_{12}$ on a1 or a3 isomer, the DOS of spin-up channel cross the Fermi level E_F showing a finite magnitude near the Fermi level which might be useful for half metallic character. For the bidoped cases, the exohedral isomers are found to be most favorable. Including all bipoed isomers of substitutional, exohedral and endohedral bidoped clusters, the total magnetic moment of the ferromagnetic (antiferromagnetic) state is 8 (0) μ_B and the HOMO-LUMO gap of antiferromagnetic state is slightly larger than that of ferromagnetic state. The magnetic coupling between the Cr atoms in bidoped configurations is mainly governed by the competition between direct Cr and Cr atoms antiferromagnetic interaction and the ferromagnetic interaction between two Cr atoms via O atom due to strong p-d hybridization. Most importantly, we show that the exohedral bidoped $(ZnO)_{12}$ clusters favor the ferromagnetic state, which may have the future applications in spin-dependent magneto-optical and magneto-electrical devices.

1. Introduction

Compared with conventional charging infrastructure, diluted magnetic semiconductors (DMSs) materials as the potential candidates of future spintronics and spintronic devices have advantages in the data-processing speed, non-volatile storage, density of magnetic recording and integration densities, etc. [1–5]. The doping can effectively tailor the material properties and is always an interesting issue in fabrication and application of the DMSs. Interests of both fundamental research and device applications stimulate the synthesis of novel ZnO structures with special properties. Transition metal (TM) doped ZnO DMSs have been considered to be potential candidates for room-temperature spintronic applicants [6,7]. This target is confirmed by an amount of theoretical and experimental researches of TM doped bulk ZnO [8–13].

Contrary to theoretical prediction that Cr-doped bulk ZnO is ferromagnetic (FM) coupling among Cr atoms which is driven by Cr-3d and O-2p exchange interactions as in Cr_2O cluster the Cr atoms prefer to cluster around O atoms, recent experiments on Cr-doped ZnO thin film reveal the coupling to be antiferromagnetic (AFM) due to bonds expand preventing Cr atoms from clustering around O atoms, showing that a possible origin of this disagreement may be associated with the different bonding environment [14]. Recently, ZnO nanosized systems have been widely studied both in pure atomic assembly and as magnetically doped semiconducting host [15–24]. In addition, the ZnO clusters are also synthesized and exhibited some unique properties than bulk or film ZnO due to their special geometry and quantum confinement effect [16–19].

Previous works have been performed on the $(ZnO)_{12}$, $(ZnS)_{12}$, $(ZnTe)_{12}$, $(CdS)_{12}$, $(GaAs)_{12}$, $(GaN)_{12}$ clusters doped with TM atoms [24–29]. In detail, Liu et al. [24] and Kaur et al. [25] investigate the structure, electronic, and magnetic properties of Mn-doped $(ZnO)_{12}$ and $(ZnS)_{12}$ clusters and conclude that Mn impurities have a clustering tendency and the coupling is dominated by short-range AFM ordering. Also, Yadav et al. [26] and Ghost et al. [27] find that both the short-ranged FM and AFM coupling could exist in the Cr-doped $(ZnTe)_{12}$ and $(CdS)_{12}$ clusters, depending on the Cr-Cr distance and the local environment of Cr atoms. Wang et al. [28] investigate the electronic and magnetic

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properties of Mn- and Fe-doped Ga_nAs_n nanocages (n = 7–12). Lu et al. [29] find that the substitutional doping is the most favorable for Mn monodoped $(GaN)_{12}$ clusters, while the Mn bidoped $(GaN)_{12}$ clusters prefer the exohedral isomers.

According to previous theoretical studies [30–32], the $(ZnO)_{12}$ cluster is a particularly stable cage structure, which can be taken as a good candidate for the investigation of doped ZnO clusters. The Cr dopant is considered because it has five 3*d* electrons and thus large magnetic moment as well as a comparable ionic radius to that of Zn atom. Furthermore, there are no theoretical and experimental reports for Cr-doped ZnO cluster. Therefore, in this paper, we present a systematical investigation on the structural, electronic and magnetic properties of the substitutional, endohedral and exohedral monodoped or bidoped $(ZnO)_{12}$ clusters with one or two Cr atoms.

2. Computation method and model

The calculations are performed within the density functional theory (DFT) by using the Vienna *ab initio* simulation package (VASP) [33–35]. The projector augmented wave (PAW) method is used to describe the electron-ion interaction and Perdew-Burke-Ernzerhof (PBE) formulation of generalized gradient approximation (GGA) is used to describe the exchange and correlation interactions of the electrons [36,37]. The energy cutoff is set to 400 eV and only one k-point (i.e., Γ point) was used for these calculations [38]. All the atoms are fully relaxed to their equilibrium positions using a standard *ab-initio* molecular dynamics (MD) simulation with a time step of 0.5 femtosecond (fs) when the successive energy change is less than 10^{-4} eV and the force applied on each atom is less than 0.02 eV/Å. The valence electron configurations of the Cr, Zn and O atoms are taken as $3d^5 4s^1$, $3d^{10} 4s^2$ and $2s^2 2p^4$, respectively. Considering the importance of Coulomb interaction, we have implemented a GGA + U method with U = 8.0 and 2.6 eV for Zn-3d and Cr-3d states [39], respectively, and J = 1 eV for both of them.

It is helpfulness to firstly investigate the pristine $(ZnO)_{12}$ cluster for the understanding of Cr-doped cases. Although $(ZnO)_{12}$ cluster has considerable kinds of allotropes, it is found that the $(ZnO)_{12}$ cluster is highly stable at a fullerene like structure (T_h symmetry) with each atom of the cluster is coordinated with three neighbors and the atoms are

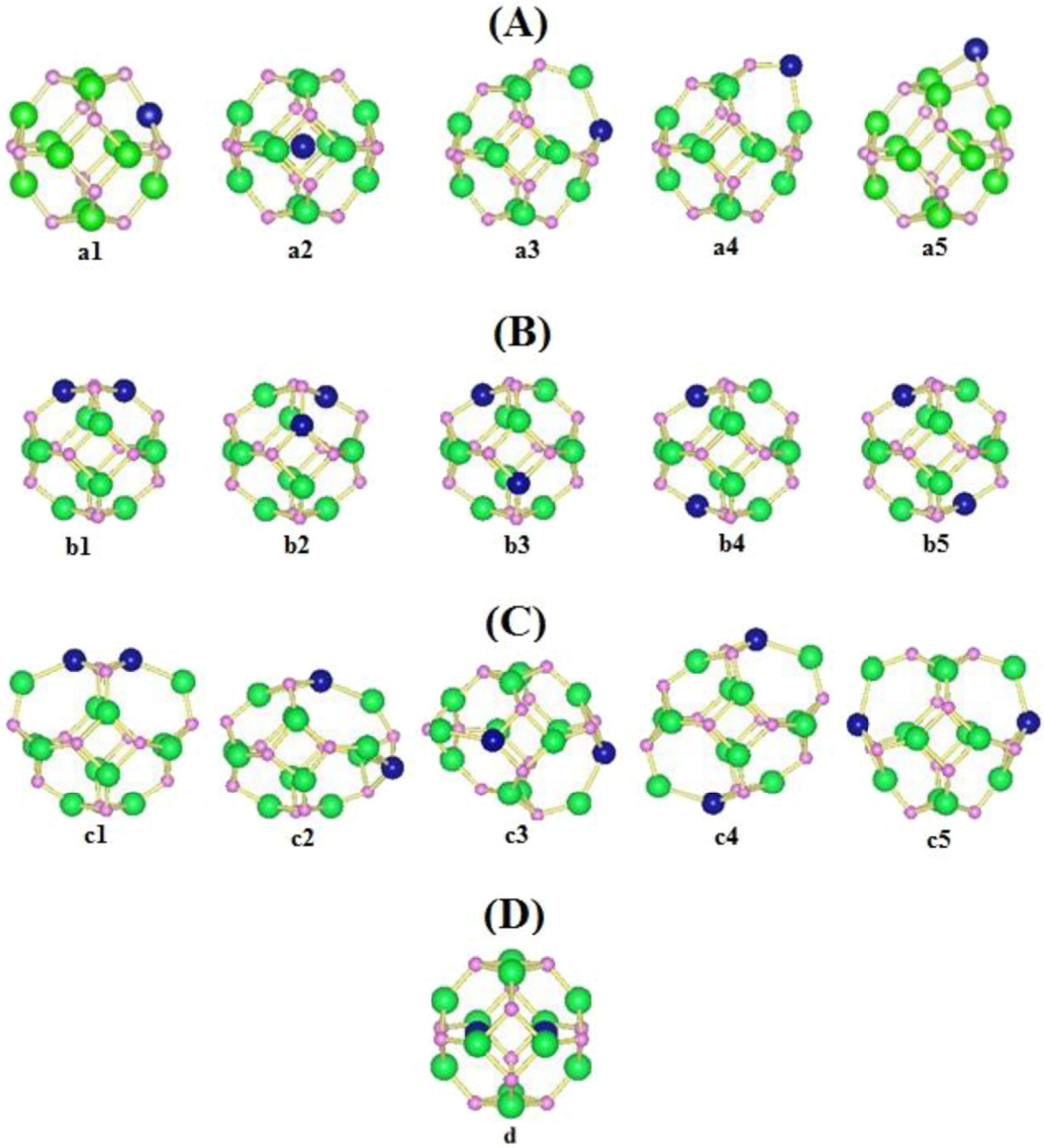

Fig. 1. The optimized structures of various isomers of Cr-doped $(ZnO)_{12}$ clusters. The pink, green and blue balls represent O, Zn and Cr atoms, respectively. (A) Monodoped configurations. (B) Substitutional bidoped configurations. (C) Exohedral bidoped configurations. (D) Endohedral bidoped configuration. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)