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First-principles investigations on the structural, electronic and magnetic properties of Cr-doped $(ZnTe)_{12}$ clusters

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Abstract. We have studied the structural, electronic and magnetic properties of $(ZnTe)_{12}$ clusters doped with one (monodoped) and two (bidoped) Cr atoms in terms of a first-principles method. Substitutional, exohedral, and endohedral doping are considered. The exohedral isomer is found to be most favorable in energy for monodoped clusters, while the endohedral isomer is found to be most favorable for bidoped ones. The magnetic coupling between the Cr atoms is mainly governed by the competition between direct Cr-Cr antiferromagnetic (AFM) interaction and the ferromagnetic (FM) interaction between two Cr atoms via Te atom due to strong p-d hybridization. Calculations indicate that the substitutional bidoped $(ZnTe)_{12}$ clusters favor the FM state, which has potential applications in nanoscale quantum devices.

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Key words: diluted magnetic semiconductor, clusters, density functional theory

1 Introduction

The discovery of ferromagnetism in Mn-doped GaAs with a Curie temperature of 110K has created an intense interest in the study of dilute magnetic semiconductors (DMS) [1]. Studies of these systems are driven not only by the academic interest in understanding the origin of ferromagnetism but also by the potential applications. ZnTe is a direct wide band-gap (2.26 eV) II-VI semiconductor. Among other II-VI DMS, Cr-doped ZnTe has also been studied both experimentally and theoretically. For instance, Saito *et al.* [2] reported the occurrence of high Curie temperature ferromagnetism in epitaxially grown thin films of Cr-doped ZnTe. Pekarek *et al.* [3] have reported room temperature ferromagnetism in bulk Cr-doped ZnTe

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crystal. Theoretical calculations have also revealed the possibilities of achieving strong FM order in Cr-doped bulk ZnTe. Sato *et al.* [4] reported from KKR-CPA studies that ferromagnetism in Cr-doped bulk ZnTe is more stable than other TM (Mn, Fe, and Co) doped cases.

Compared with bulk and film, cluster usually displays some unique properties due to its special geometry and the quantum confinement effect, which hold promise for advanced nanodevice applications [5–7]. With the recent emergence of nanoscience and nanotechnology, doping of clusters and nanoparticles has also attracted a great deal of attention because of their prospects in technological applications [8–11]. The pristine ZnTe clusters have been studied theoretically [12, 13]. Among these cage-like ZnTe structures, the $(ZnTe)_{12}$ is the smallest cage structure with the highest possible symmetry (octahedral), which can be taken as a good candidate for the investigation of Cr-doped ZnTe clusters. Previous works have been performed on the $(ZnO)_{12}$, $(GaAs)_{12}$, and $(CdS)_{12}$ clusters doped with TM atoms [14–16]. Recently, Yadav *et al.* [17] have reported that both the short-ranged FM and AFM coupling could exist in the Cr-doped $(ZnTe)_{12}$ clusters, depending on the Cr-Cr distance and the local environment of Cr atoms. But they only considered the substitutional doing. As we know, Cr atom can interact with the host cluster in three possible ways, (a) replace the atom from the host cluster (substitutional); (b) occupy the center of the cage formed by the host cluster (endohedral); (c) absorbed on the surface of the host cluster (exohedral). In this paper, we present a systematical theoretical investigation on the geometry, electronic and magnetic properties of $(ZnTe)_{12}$ clusters doped with one or two Cr atoms. The exohedral isomer is found to be most favorable in energy for monodoped clusters, while the endohedral isomer is found to be most favorable for bidoped ones. The magnetic coupling between the Cr atoms is mainly governed by the competition between direct Cr-Cr AFM interaction and the FM interaction between two Cr atoms via Te atom due to strong *p*-*d* hybridization.

2 Theoretical method and computational details

The calculations are performed using spin-polarized density functional theory (DFT). All electrons treatment and double numerical basis set including *d*-polarization functions (DND) are chosen. The Direct Inversion in an Iterative Subspace (DIIS) approach is used to speed up Self-consistent field (SCF) convergence. We also apply thermal smearing to the orbital occupation to speed it up. For the accurate calculations, we have chosen an octupole scheme for the multipolar expansion of the charge density and Coulomb potential. The exchange-correlation interaction is treated by generalized gradient approximation (GGA) with the functional parameterized by Perdew-Burke-Ernzerhof correction (PBE) [18]. SCF calculations are done with a convergence criterion of 10^{-6} hartree on the total energy. All structures are fully optimized without any symmetry constraint with a convergence criterion of 0.002 hartee/Å for the forces and 0.005 Å for the displacement. Mulliken population analysis [19] is performed to determine the charge transfer and magnetic moment on each atomic site.

As is well known in the cluster, the orbital magnetic moment is quenched and the magnetic moment comes exclusively from the spin of the electrons [20]. Throughout this work we do