First-principles Study of Electronic Structure in Mn-doped γ-Ga_2O_3

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Diluted magnetic semiconductors are of fundamental as well as practical interest in spintronics. Recently, we have fabricated room-temperature ferromagnetic Mn-doped γ-Ga_2O_3 thin films with a defective spinel structure on α-Al_2O_3 (0001) substrates [1,2] and analyzed the structure of γ-Ga_2O_3 thin films epitaxially grown on $MgAl_2O_4$ (001) substrates [3,4]. In this study, we report the electronic structure of Mn-doped γ-Ga_2O_3 investigated by density-functional theory (DFT) calculations.

The calculations were performed with the GGA+U approach [5,6] as implemented in the VASP code [7] to correct on-site Coulomb interactions of spatially localized Mn-3d electrons in Mn-doped Ga_2O_3. The value of U_{eff} was set at 5 eV. 54-atom spinel unit cells with two Mn ions and two vacant cation sites were used, considering 698 atomic configurations. Spin polarization was taken into account for all calculations. Additionally, we considered ferromagnetic and antiferromagnetic orderings of the Mn magnetic moments. A direct observation of the atomic arrangements in an Mn-doped Ga_2O_3 thin film, prepared on the $MgAl_2O_4$ (001) substrate by a pulsed laser deposition, was attempted by using a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) to compare the cationic site occupancy with the calculated results.

The DFT total-energy calculations indicate that the vacant site prefers the octahedral site. A consistent result on the site location of the vacant sites was obtained from a systematic analysis of intensity line-profiles on a cross-sectional HAADF-STEM image. The cell volume is smaller when the vacant sites are located on the octahedral site as shown in Fig. 1. This suggests that the vacant sites on the octahedral site lead to relatively large structural relaxation. The total density of states (DOS) and site-projected density of states (PDOS) in the structures with the octahedral vacant sites in the ferromagnetic state are presented in Fig. 2. The valence-band top is mainly composed of Mn-3d orbital both in the PDOS of the Mn ions located at tetrahedral and octahedral sites. A discrete state is found there in the PDOS of the octahedral Mn ions.

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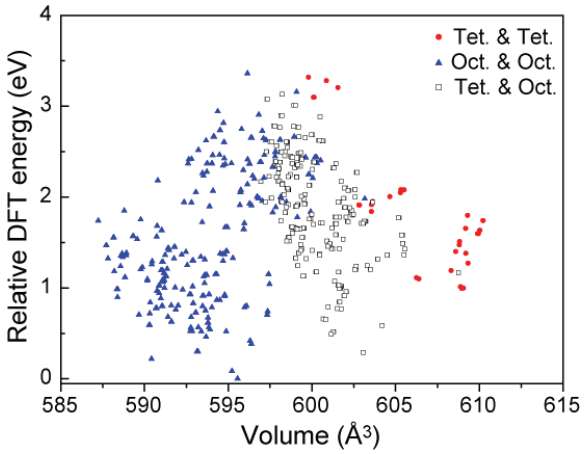

FIG. 1. Relative DFT energies against cell volume for 54-atom spinel unit cells with two Mn ions and two vacant sites.

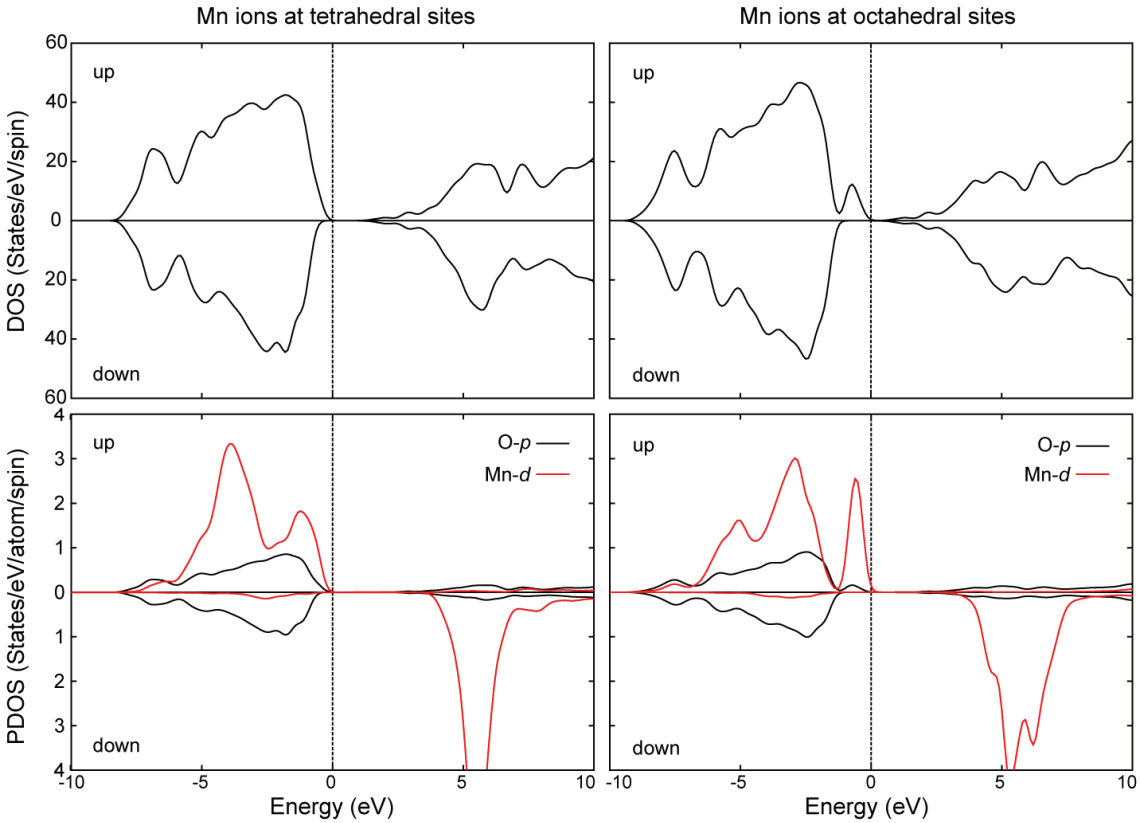

FIG. 2. DOS and PDOS in the structures with the octahedral vacant sites in the ferromagnetic state. The valence-band tops are set at 0 eV. The Mn ions are located at the (left) tetrahedral and (right) octahedral sites.