First Principle Study on Ferromagnetism from Oxygen Interstitials in ZnO Crystal

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ABSTRACT

Recently, ZnO thin films grown from the sol-gel technique have displayed ferromagnetism experimentally. Here, \textit{ab initio} energy calculations based on density functional theory was carried out to investigate a possible cause behind this observation – O interstitials. The octahedral O interstitials in ZnO was found to be spin polarized and are more stable in the ferromagnetic (FM) state. This observation is attributed to the strong p-p coupling between the interstitial O and the O anions of the crystal, which produces spin polarized holes that mediates ferromagnetic interaction between interstitial atoms. On the other hand, split interstitials are attributed to be electrically inactive and thus cause no ferromagnetism in ZnO. Because split interstitials were found to be more stable energetically in ZnO, it is predicted that they occur in greater concentrations during the growth of ZnO thin films.

INTRODUCTION

Dilute magnetic semiconductors (DMS) is a field that is subject to intense research to produce a suitable material for spintronics application that works above room temperature. Initially, much progress was made on transition metals (TM) doped semiconductors. Despite ferromagnetism being observed in TM-doped semiconductors, experiments have been plagued with inconsistencies and the inability to pinpoint the exact source of ferromagnetism within the material. It was in fact speculated that TM dopants precipitate easily to form small clusters of magnetic domains which are detrimental to its application. Furthermore, it was also speculated that ferromagnetism observed in semiconductors like ZnO thin films originates from their intrinsic defects, while TM elements have a minute role the observed results.

Much effort was focussed on O vacancies as a possible source of ferromagnetism in ZnO (Hsu, Huang et al. 2006; Banerjee, Mandal et al. 2007), despite contradicting results from other works (Hong, Sakai et al. 2007). Nonetheless, alternative intrinsic defects should be considered to better understand the role of intrinsic defects in producing ferromagnetic ZnO thin films. Thus, it is of interest to consider O interstitials in ZnO as a source of ferromagnetism, and to observe its stability within the ZnO thin films. In this report, we will present computational studies on $O_i$ in ZnO and show that $O_i$ could be a source of ferromagnetism in ZnO thin films.

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METHODOLOGIES AND RESULTS

*Ab initio* calculations based on density functional theory was carried out to investigate the role of O\(_i\) in ZnO. The projector augmented-wave method (PAW) was used with Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA) to describe its exchange-correlation functional. A 9.849 by 9.849 by 10.568 Å ZnO supercell was used as the model a ZnO thin film, which prevents O\(_i\) atoms from interacting with one another. Upon optimization, the energy cut-off was set at 450 eV, and a 3x3x2 k-point mesh generated by the Monkhorst-Pack scheme was applied to describe the plane wave basis sets. Good energy convergence was found with these parameters, and the lattice constants of the ZnO unit cell calculated (a=3.283 Å, c=5.284 Å) were comparable to experimental values. The O\(_i\) was positioned in two different possible sites: octahedral and tetrahedral positions, before a full relaxation was done on the initial atomic configurations. The tetrahedral O\(_i\) was found to be unstable and caused the formation of a split interstitial. Thus, the octahedral and split interstitial O\(_i\) were considered for ferromagnetism in the ZnO supercell.

![Figure 1](image-url)  
*Figure 1* Calculated partial density of state for the O\(_i\) defect, O anions and Zn cations in the ZnO crystal. The Fermi level is indicated by the dotted line.
Our calculations reveal that only octahedral O\textsubscript{i} produce magnetism from the two scenarios described previously. Figure 1 shows the calculated local density of states (LDOS) for the O\textsubscript{i} atom, indicating a split near the Fermi level for the O\textsubscript{i}-p orbitals, which results in a magnetic moment of 0.7 \(\mu_B\). This can be explained by the strong coupling observed between the O-p and O\textsubscript{i}-p orbitals, which caused the peaks near the Fermi level to split. Additionally, O anions contribute a small amount too to the total magnetic moment (0.2 \(\mu_B\)) due to this interaction. The estimated formation energy of the octahedral O\textsubscript{i} defect was determined to be around 3.41 eV, while the corresponding value for tetrahedral O\textsubscript{i} was determined to be lower by 0.5 eV. This thus indicates that split interstitial O\textsubscript{i} are more abundant in ZnO crystals under normal conditions.

To investigate the interaction between magnetic O\textsubscript{i} in ZnO, we consider two octahedral O\textsubscript{i} atoms in the same ZnO supercell. These two defects are then separated by a distance of 6.2 Å, and set into the ferromagnetic (FM) or the anti-ferromagnetic (AFM) states to compare their total energies. The atomic positions were fully relaxed before total energy was obtained. The FM state was found to have lower energy by 16 meV.

POSSIBLE MECHANISM

Similar to C-doped ZnO (H. Pan, Yi et al. 2007), hole mediated ferromagnetism is proposed as the possible mechanism behind ferromagnetic coupling between the octahedral O\textsubscript{i} atoms. Based on the band structure of the system with octahedral O\textsubscript{i}, there exist extra transition levels that correspond to holes in the O2p states. This will then couple with the O2p states through p-p interaction, which then causes the states of the minority spin to be pushed upwards, and the states with opposite spin downwards to achieve lower energy. Since the O2p states is spatially wide enough to couple with the O2p states, we can infer that this interaction will indirectly allow coupling between the spin states of O\textsubscript{i}. As for the split interstitial configuration, the existence of charge carriers can be inferred from calculations, which corresponds to the electrical inactivity deduced by other works (Erhart et al. 2006). Since we require hole mediation for ferromagnetism to occur, this thus explains the null result from our work on split interstitial O\textsubscript{i}.

Despite the fact that the formation energy of O\textsubscript{i} split interstitial is higher, it is still possible to observe ferromagnetism in ZnO as we do not require a high concentration of octahedral O\textsubscript{i} atoms to have a reasonable magnitude of ferromagnetism. The growth condition should be reasonably rich in oxygen as well in order to have greater concentrations of these defects.

CONCLUSION

In conclusion, we found ferromagnetic interactions between octahedral O\textsubscript{i} in ZnO, while split interstitial O\textsubscript{i} produced no ferromagnetic interaction. We propose hole mediated p-p interaction between O\textsubscript{i} and O atoms to be the cause behind ferromagnetism observed in ZnO with O\textsubscript{i} atoms.
REFERENCES


