Electronic structure of gadolinium complexes in ZnO in the GW approximation

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The role of intrinsic defects has been investigated to determine binding energies and the electronic structure of Gd complexes in ZnO. We use density-functional theory and the GW method to show that the presence of vacancies and interstitials affect the electronic structure of Gd doped ZnO. However, the strong localization of the Gd-\(f\) and \(d\) states suggest that carrier mediated ferromagnetism in this material may be difficult to achieve.
I. INTRODUCTION

Doping ZnO with rare-earth elements has been widely used to tailor its electronic, magnetic and optical properties. In particular, the long life times of the excited states allow for an easy realization of population inversion with promising applications in optoelectronics [1], as well as spintronics [2]. Channeling experiments as well as photoluminescence studies [1, 3–10] indicate, that rare-earth elements in ZnO are preferentially incorporated at cation sites. The incorporation of Gd in the presence of intrinsic defects in ZnO could lead to the formation of stable compounds inside the crystal [11–16]. In particular, the formation of such complexes involving gadolinium and oxygen vacancies or zinc interstitials could promote ferromagnetism in ZnO as suggested in Refs. [13, 16]. This idea has been reinforced by investigations of Gd doped ZnO thin films grown by pulsed laser deposition which suggested that the formation of Gd-O vacancies complexes may be formed under oxygen deficient conditions [15, 16]. However, magnetic properties of ZnO doped with Gd have been investigated using ion implantation [17] and pulsed-laser deposition (PLD) [18] and the samples were found to be paramagnetic. X-ray spectroscopy (XPS) and Fourier Transform Infra Red (FT-IR) spectroscopy suggested that nearest Gd ions do not take part in carrier mediated ferromagnetism [19]. On the theoretical side, DFT calculations using the generalized-gradient approximation (GGA) and GGA plus Hubbard U [11] show no coupling between Gd atoms rendering Gd doped ZnO to be paramagnetic in the absence of defects. Under O-deficient conditions Roqan et al. [16] used GGA plus U and hybrid functionals to show that either oxygen vacancies or zinc interstitials could stabilized ferromagnetism in Gd doped ZnO. Therefore, a more clear understanding of formation energies and electronic structure of Gd complexes in ZnO is needed to clarify these aspects.

In this letter, we investigate the role of oxygen and zinc vacancies and interstitials using DFT and the GW method in order to determine changes in the magnetic properties and electronic structure of Gd doped ZnO. We show that although there is a strong localization of the Gd states with no significant change in its magnetic moment, other than in the presence of oxygen interstitial defects. Furthermore, the electronic structure shows negligible overlap of Gd states with the ZnO matrix, suggesting that carrier mediated ferromagnetism in this material may be difficult to achieve.
II. COMPUTATIONAL DETAILS

We have used density-functional theory (DFT) together with the projected augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) for the exchange-correlation potential was used to obtain geometries, formation energies and magnetic moments. To model Gd impurities and Gd complexes in ZnO we built up a 72 atom supercell using our calculated PBE lattice parameters of ZnO, \( a=3.25\,\text{Å} \) and \( c=5.25\,\text{Å} \). To ensure convergence of structural, electronic and magnetic properties, a cutoff of 400 eV was used for the plane-wave expansion of the wave function. The criteria on force convergence was 0.01 eV/Å. For Brillouin zone integrations, a \((3 \times 3 \times 3)\) Monkhorst-Pack k-point sampling was used. The Gd-5s, -5p, and -4f electrons are treated as a valence shell, as well as the Zn-3d electrons.

For the determination of the electronic structure we have used the GW method. The wave functions are kept fixed to the GGA level, whereas the eigenvalues are updated in the Green’s function only. A cutoff of 200 eV for the response functions, as well as 1024 bands have been employed. For ZnO in particular, we obtain a band gap of 3.3 eV and Zn-3d states at 7.0 eV which is in reasonable agreement with the experimental value of 3.44 eV, as well as with other all-electron GW0 calculations.

III. RESULTS

The geometry of the structures we have investigated is shown in Figs. From Fig. (a) we see that a single Gd occupying a substitutional Zn sites does not produce strong distortion in the ZnO lattice. The Gd-O bond lengths remain very close to the values in pure ZnO. We obtain 2.17-2.24 Å. If a second Gd atom is added at a near Zn site, as shown in Fig. (f) a negligible relaxation is seen. The Gd-O bond lengths are in the range 2.15-2.21 Å. This is due to the strong localization of the Gd-f states with negligible overlap with the ZnO lattice other than the oxygen nearest neighbors.

An oxygen interstitial atom at the octahedral position near a Gd atom as shown in Fig. (b) increases Gd coordination from four-fold to five fold. The bond Gd-O lengths are in the range 2.18-2.23 Å. The ZnO cage where the oxygen atom is inserted relaxes inwards.
to accomodate the Gd-O bonds. Adding again a Gd atom along the ZnO c axis to form a complex containing two Gd atoms and an O interstitial (2Gd\textsubscript{Zn} + O\textsubscript{i}), as shown in Fig. 1(g) the Gd-Gd distance is 4.41 Å. The Gd-O distances lies between 2.19 and 2.25 Å. As a matter of comparison in Gd\textsubscript{2}O\textsubscript{3} this distance is 2.39 Å. There is a distortion of the oxygen at a octahedral site, which now is bonded to two Gd atoms. Due to the strain around the Gd-O-Gd complex, some Zn atoms relax outwards the defect complex. We should point out that this is a different defect from the one with two gadolinium atoms stacked along the c direction separated by an oxygen atom described in Refs. [13].

A complex involving a Gd substitutional and a Zn interstitial atom (Gd\textsubscript{Zn} + Zn\textsubscript{i}), shown in Fig. 1(c), leads to a huge distortion of the Zn interstitial atoms and also other Zn atoms around the Gd substitutional, although Gd itself is not much displaced. Gd-O bond lengths are found to be 2.15-2.25 Å. A configuration where two Gd atoms sit close to a Zn interstitial atoms (2Gd\textsubscript{Zn} + Zn\textsubscript{i}), shown in Fig. 1(h), leads to a huge distortion in the lattice. The Zn atom moves away from the Gd atoms and from the defect. The Gd-Gd distance is 3.57 Å.

Next we consider the removal of an oxygen atom near a Gd atom as shown in Fig. 1(d) forming a Gd\textsubscript{Zn} + V\textsubscript{O} complex. There is a clear relaxation of the surrounding zinc atoms towards the oxygen vacancy, as expected. The Gd substitutional atom shows a very small relaxation. This configuration is not expected to be favorable, as we will discuss later, since it decreases the Gd coordination number. Gd-O bond lengths vary between 2.12 and 2.16 Å. By adding an extra Gd atom in order to have a 2Gd\textsubscript{Zn} + V\textsubscript{O} complex (Fig. 1(i)) allows the Gd atoms to move further apart and a slight relaxation of the oxygen atoms towards the Gd is seen. Gd-O bond lengths are 1.99 and 2.30 Å.

Finally we consider the formation of a complex with a Gd substitutional and a Zn vacancy Gd\textsubscript{Zn} + V\textsubscript{Zn} as has been suggested in Ref. [13]. The Gd-O distances lie between 2.10 and 2.30 Å. The structure is somewhat distorted because the Gd atom which is initially substitutional, moves towards the center of the cage to increase their coordination with nearby oxygen atoms, as shown in Fig. 1(e). Adding a Gd atom at a nearby Zn site leads to a distortion of the both oxygen and gadolinium atoms to better accomodate the bond angles. Gd-O atoms lie between 2.15-2.43 Å.

To verify the thermodynamic stability of the investigated defect complexes, we follow the approach derived by van de Walle and Neugebauer. The binding energy is calculated according to $E_b = E_{\text{complex}} - \sum_i E_{\text{defect}}^i$ where $E_{\text{complex}}^i$ is the formation energy of a defect...
complex and $E_f^{\text{defect}}$ is the formation energy of an isolated defect (Gd impurity or intrinsic defect).

![Relaxed geometries within PBE for Gd complexes in ZnO](image)

FIG. 1. Relaxed geometries within PBE for Gd complexes in ZnO. Gray are Zn, red are O and magenta are Gd. a) Gd\textsubscript{Zn}, b) Gd\textsubscript{Zn} + O\textsubscript{i}, c) Gd\textsubscript{Zn} + Zn\textsubscript{i}, d) Gd\textsubscript{Zn} + V\textsubscript{O} e) Gd\textsubscript{Zn} + V\textsubscript{Zn}, f)2Gd\textsubscript{Zn}, g) 2Gd\textsubscript{Zn} + O\textsubscript{i}, h)2Gd\textsubscript{Zn} + Zn\textsubscript{i}, i) 2Gd\textsubscript{Zn} + V\textsubscript{O}, j) 2Gd\textsubscript{Zn} + V\textsubscript{Zn}.

The incorporation of a Gd atom at a Zn site costs 2.61 (9.86) eV under O-rich (O-poor) conditions. The Gd magnetic moment remains almost unchanged and has a value of 6.92 $\mu_B$). The addition of another Gd atom at a Zn second nearest neighbor is 1.34 eV higher in energy. The total magnetic moment of 14 $\mu_B$) (7 $\mu_B$)/Gd) reflects the negligible interaction between Gd atoms in the cell. Table shows the binding energy of Gd in ZnO under the presence of intrinsic defects. One can identify some defect complexes with low formation energy under O-poor conditions, the Gd\textsubscript{Zn} + V\textsubscript{Zn} and under O-rich conditions the Gd\textsubscript{Zn} + O\textsubscript{i}. The Gd\textsubscript{Zn} + O\textsubscript{i} complex is the only defect able to change the Gd magnetic moment due to the overlap of Gd with its nearest neighbor oxygen atoms. The magnetic moment on Gd is 6.02 $\mu_B$ and 0.72 $\mu_B$ on the p orbitals of oxygens. Around 0.1 $\mu_B$ is distributed on the 5d orbitals of Gd. Murmu et al.,\cite{ref30} suggested that after annealing a reduction of Gd can be observed and attributed it to Gd clustering. Here we suggest that the formation of a Gd\textsubscript{Zn} + O\textsubscript{i} complex can be responsible for this reduction. We find a similar behavior for Eu doping in ZnO \cite{ref31, ref32}. Also, Roqan\cite{ref16} suggested that oxygen deficient defects may be responsible for mediating ferromagnetism in ZnO. Our results indeed show that this defect
has a low formation energy in ZnO. However, the there is no direct exchange interaction between Gd-\(f\) electrons, so they cannot be responsible for take part in carrier mediated ferromagnetism. We have further considered the complexes in the -1 and +1 and 2+ charge states (to be published). These defects are not energetically favorable neither under O-rich and nor Zn-rich conditions and have no influence on the Gd magnetic moment atoms, indicating strong localization of \(f\) orbitals.

### TABLE I. Total magnetic moments \(\mu_{\text{tot}}\) (in \(\mu_B\)) and binding energies \(E_b\) (in eV) of neutral Gd complexes in ZnO calculated at PBE level under O-rich and O-poor conditions, respectively.

| complex         | \(\mu_{\text{tot}}\) | \(E_b\)  |
|-----------------|----------------------|----------|
| Gd\(_{\text{Zn}}\) + O\(_i\) | 6.02                 | -1.65    |
| Gd\(_{\text{Zn}}\) + Zn\(_i\) | 6.86                 | 2.05     |
| Gd\(_{\text{Zn}}\) + V\(_O\) | 6.99                 | 1.13     |
| Gd\(_{\text{Zn}}\) + V\(_{\text{Zn}}\) | 6.98                 | -0.97    |
| 2 Gd\(_{\text{Zn}}\) + O\(_i\) | 14.00                | -4.43    |
| 2 Gd\(_{\text{Zn}}\) + Zn\(_i\) | 14.00                | 1.26     |
| 2 Gd\(_{\text{Zn}}\) + V\(_O\) | 14.00                | 1.04     |
| 2 Gd\(_{\text{Zn}}\) + V\(_{\text{Zn}}\) | 14.00                | -2.92    |

Next we discuss the electronic structure of the above mentioned neutral complexes. In Fig.2(a)-(j) the density of states (DOS) of Gd-doped ZnO calculated with GW@PBE for Gd concentrations of 3.7% and 5.6%. Due to the strong localization of the Gd-4\(f\) orbitals, the degree of mixing usually is small. Therefore, any perturbation to the crystal due to the presence of intrinsic defects should overlap with these states in order to delocalize the Gd-\(f\) states.

The presence of a single Gd atom at a zinc site, shown in Fig.2(a) leads to no change in the Gd-\(f\) states. The \(f\) spin-up states are fully occupied, giving a total magnetic moment of \(6.9\mu_B\). Furthermore, the Gd spin splitting is around 10 eV. The presence of two Gd atoms as shown in Fig.2(f) leads to completely filled Gd-\(f\) up states but partially filled \(f\)-down states. However, the magnetic moment of Gd does not change, because there is little overlap...
neither between the Gd atoms nor between the Gd and the ZnO crystal.

Next we show the electronic structure for the structure Gd$_{Zn} + O_i$. The band structure of this defect is shown in Fig. 2(b). We find the occupied Gd-$f$ spin up states are still located within the valence band of ZnO, while the Gd-$f$ down states lie well above the ZnO conduction band. The presence of an additional oxygen atom nearby a Gd can promote a change in the oxidation state of Gd by populating the O$_{int}$ $- p$ orbitals, which lie right above the top of the valence band. Similarly, we have recently show that the presence of a nearby oxygen atom can modify the europium spin magnetic moment in Eu doped ZnO [31]. As an additional Gd atom is added to this complex to form the 2Gd$_{Zn} + O_i$, the electronic structure changes. The O-$2p$ state present in the band gap moves towards the ZnO valence band below the Fermi level, as shown in Fig. 2(g).

For the Gd$_{Zn} + Zn_i$ complex new states are introduced in the band gap due to presence of the defect, as shown in Fig. 2(c). However, no overlap between Gd states in found. The incorporation of an extra Gd atoms to form the 2 Gd$_{Zn} + Zn_i$ complex produces little change in the band structure. This defect has been suggested in Ref. [16] to have overlap between Zn-$p$ and $-d$ states and Gd-$f$ states in the conduction band. Our GW@PBE results show that this overlap is negligible as it can be seen in Fig. 2(h). Although the splitting between the Gd-$f$ spin up and spin down is significantly reduced to about 3.6 eV, the Zn-$d$ states lie well below the Gd states deep in the valence band an does not overlap with the Gd-$f$ states, as found in Ref. [16]. A possible explanation for this discrepancy is that the description of Zn-$d$ states is well known to have a dependence on the choice of $U$ [33, 34], which may affect its relative position with respect to the valence band top.

Next we consider the Gd$_{Zn} + V_O$ complex. The electronic structure is similar to the one without the oxygen vacancy with a large Gd $f-f$ spin splitting of 10 eV (see Fig. 2(d)). The oxygen vacancy states appear 2.6 eV above the top of the valence band. The introduction of a second Gd atom to produce the 2Gd$_{Zn} + V_O$ complex nearby disturbs the ZnO lattice and shifts the Fermi level to within the conduction band, as it can be seen in Fig. 2(i).

Finally we consider a zinc vacancy near a Gd atom, the Gd$_{Zn} + V_{Zn}$ defect complex. Its band structure is shown in Fig. 2(e). Extra states appear close to the top of the valence band. The introduction of a second Gd atom to have a Gd$_{Zn} + V_{Zn}$ defect shifts the conduction band, as it can be seen in Fig. 2(i) but with no overlap of the Gd states with other atoms.
FIG. 2. Density of states for (a) substitutional Gd atom in ZnO, (b) substitutional Gd plus an oxygen interstitial atom, (c) substitutional Gd plus a zinc interstitial atom, (d) substitutional Gd plus an oxygen vacancy, (e) substitutional Gd plus a zinc vacancy, (f) two substitutional Gd atoms in ZnO, (g) 2 substitutional Gd atoms plus an oxygen interstitial atom, (h) two substitutional Gd atoms plus a zinc interstitial atom, (i) two substitutional Gd atoms plus an oxygen vacancy and (j) two substitutional Gd atoms plus a zinc vacancy. The vertical dashed line represents the Fermi level.

IV. CONCLUSIONS

We have investigated ZnO doped with Gd in the presence and absence of intrinsic defects using density-functional theory and the GW method. We show that even the presence of intrinsic defects can change the distance between the Gd $f$ spin-up and spin-down states. However, this energy difference is not enough to promote a significant overlap with defect
states, which would lead ferromagnetism in diluted ZnO samples.

V. ACKNOWLEDGEMENT

The authors are thankful to the Deutsche Forschungsgemeinschaft (DFG) for a Mercator Fellowship under the program FOR1616. A. L. Rosa would like to thanks Sebastien Lebégue for fruitful discussions.

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