Many-Body electronic structure calculations of Eu doped ZnO

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The formation energies and electronic structure of europium doped zinc oxide has been determined using DFT and many-body GW methods. In the absence of intrinsic defects we find that the europium-\(f\) states are located in the ZnO band gap with europium possessing a formal charge of \(2^+\). On the other hand, the presence of intrinsic defects in ZnO allows intraband \(f-f\) transitions otherwise forbidden in atomic europium. This result coororobates with recently observed photoluminescence in the visible red region \[1\].

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\section{I. INTRODUCTION}

Doping has been widely used to tailor the electronic, magnetic and optical properties of semiconductors. Wide band-gap semiconductors such as ZnO are attractive for ultraviolet light-emitting diodes, lasers and high-power photonic applications. In ZnO, rare-earth elements can be incorporated in the material and the long life times of the excited states allow for an easy realization of population inversion with promising applications in optoelectronic applications \[11,12\]. ZnO has a large band gap of 3.4 eV and a high thermal conductivity, enabling new electroluminescent devices.

Channeling experiments \[6,7\] indicate, that rare-earth elements in ZnO are preferentially incorporated at cation sites. More recent photoluminescence (PL) and photoluminescence excitation (PLE) investigations on ZnO nanoparticles confirmed this finding, where Eu occupies Zn sites \[8,9\]. PL investigations of Eu-doped ZnO nanoneedles showed sharp emission lines from Eu\(^{3+}\), suggesting the emission arises from intra-\(f\) transitions, in addition to the ZnO interband emission \[10\]. Besides optical emission from rare-earth orbitals has been achieved in ZnO nanowires implanted with erbium and ytterbium \[8\] and thin ZnO films doped with erbium, samarium and europium \[11\]. The above experimental investigations have suggested explanations for the optical activation of rare-earths in ZnO by means of substitutional hydrogen incorporation \[15\] or formation of defect complexes \[8,16,17\].

Theoretical investigations using density functional theory (DFT) in the generalized-gradient approximation (GGA) have performed for Eu doped ZnO \[18,19\], but were unable to ascertain the origin of the experimentally observed emission in ZnO. The main challenge here is the correct description of both ZnO band edges and defect states. It is common understanding that the use of local exchange-correlation functionals wrongly described the ZnO band gap, which could lead to misleading conclusions on the location of the impurity rare-earth \(f\)-states. It has been shown that the correct description of the band gap is of paramount importance for the understanding of impurity and defect states in semiconductors \[20–24\]. Besides, intrinsic defects may also play an important role, since during ion implantation they are often introduced in ZnO. Using DFT calculations and the \(GW\) technique, we have previously shown that a complex containing a single oxygen interstitial defect and an europium atom substituting a zinc atom is a probable candidate to explain the observed emission in the red region of the spectrum in europium doped ZnO nanowires \[1\]. Note that \(GW\) calculations do not include excitonic electron-hole interactions.

In this work we show further \(GW_0\) calculations for Eu-doped ZnO. Besides the work reported in Ref. \[1\] we have considered the presence of the most common defects in ZnO, such as oxygen and zinc vacancies and interstitials. The wave functions are kept fixed to the GGA level, whereas the eigenvalues are updated in the Green’s function only. Here we show that this kind of defect has a relatively low formation energy and suggest possible mechanisms for the formation of such defect. Besides, we investigate other defects and calculate their formation energies and electronic structure.

\section{II. THEORETICAL DETAILS}

In this work we have employed density functional theory (DFT) \[25,26\] and many-body \(GW\) techniques \[27\] to investigate the formation energies and electronic structure of Eu doped ZnO. The projected augmented wave method (PAW) \[28\] has been used as implemented in the Vienna Ab-initio Package (VASP) \[29\].
supercell containing 72 atoms with a (2×2×1) k-point sampling and a cutoff of 500 eV is used to calculate all isolated intrinsic defects and complexes. For Eu₂O₃ we have used (2×2×2) k-points. For Eu metal we adopted a bcc structure with a (6×6×6) k-point mesh.

### A. Thermodynamic properties

To verify the thermodynamic stability of the investigated defect complexes, we follow the approach derived by van de Walle and Neugebauer \[30\]. The formation energy of a neutral defect or impurity is defined as:

\[
E_{\text{f}} = E_{\text{tot}}^{\text{ZnO-defect}} - E_{\text{tot}}^{\text{ZnO-bulk}} - \sum_{i} n_i \mu_i
\]

where \(E_{\text{tot}}^{\text{ZnO-defect}}\) is the total energy of a defective supercell and \(E_{\text{tot}}^{\text{ZnO-bulk}}\) is the total energy for the supercell of pure ZnO. \(n_i\) is the number of atoms of type \(i\) (defects or impurities) that have been added or removed from the supercell and \(\mu_i\) is the corresponding chemical potential of each species. We should point out that the presence of charged complexes is also possible. Here we present calculations for the neutral defects only. Calculations for charged systems are currently being performed and will be published in the future.

The lower bound of the chemical potential corresponds to the total absence of impurities/defects in the nanowire. An upper bound on the chemical potential is given by the oxygen and zinc chemical potential are not independent, but related by \(\mu_{\text{ZnO}} = \mu_{\text{Zn}} + \mu_{\text{O}}\), where \(\mu_{\text{Zn}}, \mu_{\text{O}}\) and \(\mu_{\text{ZnO}}\) are the zinc, oxygen and zinc oxide chemical potentials, respectively. \(\Delta H_{\text{ZnO}}\) is the formation enthalpy of ZnO. Combining Eqs. 2 and 3 and these conditions, we obtain the following relations:

\[
\mu_{\text{O}} = \mu_{\text{O}_2} - \lambda \Delta H_{\text{ZnO}}
\]

\[
\mu_{\text{Eu}} - \mu_{\text{Eu}_2\text{O}_3} \leq \frac{1}{2} \Delta H_{\text{Eu}_2\text{O}_3} - \frac{3}{2} \lambda \Delta H_{\text{ZnO}}
\]

where for \(\lambda = 0\) one has O-rich conditions and for \(\lambda = 1\) one has O-poor conditions.

### B. Electronic structure

The many-body methodology that is underlying the GW approximation goes back to pioneering work by Kadanoff and Baym \[31, 32\] and Hedin \[33\]. We will briefly overview the GW framework used in this paper and motivate our choice of the partially self-consistent GW₀ scheme. For detailed implementation we refer the reader to Ref. \[27\] and references therein.

In many-body methods based on DFT, the quasiparticle energy for the \(n\)th band with Bloch vector \(\mathbf{k}\) is given iteratively by:

\[
\varepsilon_{\mathbf{k}n} = \text{Re}\left[\langle \psi_{\mathbf{k}n} | T + V_{\text{ion}} + V_{\text{H}} + \Sigma(\varepsilon_{\mathbf{k}n}) | \psi_{\mathbf{k}n} \rangle\right].
\]

The non-local self-energy operator is given in the GW approximation by:

\[
\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon) = \frac{i}{4\pi} \int_{-\infty}^{\infty} d\omega' e^{i\omega'\eta}G(\mathbf{r}, \mathbf{r}', \varepsilon + \omega')W(\mathbf{r}, \mathbf{r}', \omega').
\]

Here, \(G\) is the Green’s function (GF), \(W\) the screened Coulomb interaction and \(\eta\) is an infinitesimal to achieve the correct time-ordering of \(\Sigma\).

The self-energy term can be evaluated in reciprocal space as

\[
\Sigma(\varepsilon)_{nk,nk} = \frac{1}{\Omega} \sum_{qG} \sum_{n'} W(G + q, G' + q, \omega') \times \langle \psi_{nk} | e^{i(q+G)r} | \psi_{nk} \rangle \langle \psi_{nk} | e^{-i(q+G')r'} | \psi_{nk} \rangle \times \frac{1}{\varepsilon + \omega' - \varepsilon_{nk} - q + i\eta \text{sgn}(\varepsilon_{nk} - \mu)},
\]

where \(\Omega\) is the cell volume, \(q\) and \(G\) are Bloch and reciprocal lattice vectors, and \(\mu\) is the Fermi energy.

The screened Coulomb interaction can be evaluated from the bare Coulomb kernel and the inverse dielectric function as

\[
W(G + q, G' + q, \omega) = 4\pi e^2 \frac{1}{|q + G|} \times \varepsilon_{-1}(G, G', \omega) \frac{1}{|q + G'|}.
\]

In the random phase approximation (RPA), used throughout this work \[34\], the dielectric function is given as

\[
\varepsilon_{-1}(G, G', \omega) = \delta_{GG'} - \frac{4\pi e^2}{|q + G||q + G'|} \sigma_0(G, G', \omega).
\]
with the independent-particle polarizability given by
\[ \chi_q^0(G, G', \omega) = \frac{2}{\Omega} \sum_k \sum_{n' n} \langle \psi_{n' k} | e^{i(q+G) \cdot r} | \psi_{n k} \rangle \]
\[ \times \langle \psi_{n k} | e^{-i(q+G') \cdot r} | \psi_{n' k-q} \rangle \times ( \omega + \varepsilon_{n' k-q} - \varepsilon_{n k} + i \eta \gamma \text{sgn}(\varepsilon_{n' k-q} - \varepsilon_{n k}) ) \quad \text{(11)} \]

In this (Lindhardt-like) formula \( f_{n' k} \) represent the occupancies of the given one-electron state. The RPA stems from the choice of \( L = GG \) for the density-density correlation function \( L(1, 2; 1' 2') = G_2(1, 2; 1' 2') - G(1, 1')G(2, 2') \) with the two-particle GF \( G_2(1, 2; 1' 2') \) \[31\]. In literature there exist a variety of different GW schemes, depending on whether energies in \( G \) and \( W \) are iterated (GW), iterations are performed only the energies in \( G \) (GW0) or not at all (single shot \( G_0W_0 \)). Moreover, in QP-GW or QP-GW0 schemes the wave function can also be updated via a Hermitian approximation to \( \Sigma \) \[27\].

In this work we have chosen to employ the partially self-consistent GW0 scheme for reasons we will elaborate briefly as follows. The "fully self-consistent" GW approximation using \( \Sigma = GW \) and \( L = GG \), with the full GF \( G \) entering the density-density correlation function \( L \), suffers from several shortcomings. In practice, this approximation typically underestimates the screening, leading to too large quasi-particle band gaps in converged calculations.

The underlying problem lies in the choice of the screened interaction in Hedin's equations \[33\], i.e. in the choice of the vertex function for the density-density correlation function \( L \). The choice of the same vertex for the single-particle property \( \Sigma \) which determined \( G \) and the two-particle density-density correlation function \( L \) which determines the screened potential \( W \) is inconsistent in approximate schemes \[31\] \[32\] \[33\]. Rather, for the \( \Sigma = GW \) approximation, the vertex for the determination of \( W \) has to be chosen from the Bethe-Salpeter type equation
\[ \Gamma(1, 2, 3) = i\hbar \delta(1 - 2)\delta(1 - 3) + \]
\[ \int d\alpha d\beta d\gamma X(1, 2, 4, 5)G(4, 6)\Gamma(6, 7, 3)G(7, 5) \quad \text{(12)} \]

of Hedin's equations \[33\], with the effective two-particle interaction \( X \) resulting from the functional derivative \( X(1, 2, 4, 5) = \frac{\delta^2}{\delta G(4, 5)} \) to conserve all Ward identities of the underlying theory \[32\]. This procedure would result in a dynamically screened ladder approximation for \( W \) in the GW approximation. The inconsistency in using only the RPA density-density correlation function \( L \) is especially apparent, when considering for the sake of argument not the time-ordered GF \( G \) in equilibrium, as it is typically dealt with in band structure calculations, but the kinetic problem, contained in the \( G^\infty \) component of the full Keldysh non-equilibrium GF \[35\].

As it has been shown in Ref. \[33\], the choice of \( \Sigma = GW \) in conjunction with \( L = GG \) leads to (infrared) divergencies for the \( \Sigma^\infty \) component of the self-energy, yielding the approximation scheme ill-defined. An improved scheme, fulfilling all Ward identities by construction has been proposed \[37\]. However this scheme is not computationally feasible at present for larger systems. Practically speaking, the GW0 approximation gives a good description of the band gap for many materials \[24\], as it appears that GW0 \( \approx \) GWT. This approximation consists in essentially calculating \( W_0 \) from \( L = G_0DFTGDT \), which amounts to using \( \psi = \psi^{DFT} \) and \( \varepsilon = \varepsilon^{DFT} \) in Eq. (11). The reason lies in the fact that the DFT energies and wavefunctions are closer to those calculated in the Hartree approximation for which the scheme \( \Sigma = GW \) and \( L = G_{\text{Hartree}}G_{\text{Hartree}} \) would be fully consistent \[32\] \[37\]. We will show the rather good description of ZnO in the GW0 approximation in what follows. We will keep the wavefunctions at the GGA level, that also has been used to optimize the geometry.

III. RESULTS

A. Thermodynamic properties

As the calculation of the total energy from the Green’s function of GW-based calculations is computationally exceedingly demanding, due to the occurring frequency integrations, the calculation of formation energies on the GW level is not readily possible. Therefore, we have decided to calculate the formation energies at GGA level. This can be justified taking into account that the GGA calculations are used as starting point for more accurate calculations using the GW method.

For europium oxide, the formation enthalpy is calculated to be \( \Delta H_f(\text{Eu}_2\text{O}_3) = -14.43 \) eV, in fair agreement with the experimental value of \(-16.51 \) eV \[38\]. For zinc oxide the formation enthalpy is \( \Delta H_f(\text{ZnO}) = -2.90 \) eV, which is also in good agreement with other GGA values \[39\] and even GGA+U calculations \[22\]. Using these values, we can obtain the binding energy of the defect complexes, which are defined as

\[ E_{\text{binding}} = E_{i \text{complex}} - \sum_i E_{i \text{isolated}} \quad \text{(13)} \]

where \( E_{i \text{complex}} \) is the formation energy of the defects and \( E_{i \text{isolated}} \) is the formation energy of isolated defects calculated according to Eq. (11). The calculated values are shown in Table IIIA. Calculations for intrinsic defects can reproduce well previous calculations reported using local functionals \[39\] \[41\]. Neutral oxygen vacancies have a low formation energy under oxygen poor-conditions. On the other hand, zinc vacancies can be formed under Zn-poor preparation conditions. Oxygen and zinc interstitials, as expected, have high formation energies, which
is due to the size [41]. For Eu doped ZnO at cation site we obtain a formation energy of 2.42 eV under O-rich conditions. Incorporation of Eu at interstitial positions is highly unfavorable, due to the strain Eu causes in the ZnO, leading to a strongly distorted lattice. Similar results have been reported in Ref. [42]. Complex formation with zinc and oxygen vacancies and zinc interstitials have a much higher formation energy. This can be understood by considering size effects, which causes a large strain in the lattice.

As we can see the most stable defect is under O-rich conditions is the Eu-O$_i$(s) complex. It is interesting to point out that the formation of neutral oxygen defects at interstitial sites in pure ZnO has a high formation energy under thermodynamic equilibrium. However, as has been shown in Ref. [41] the diffusion barrier for this kind of defect is relatively low (around 0.2 eV). Therefore, once this defect is formed under ion implantation (non-equilibrium conditions), it can rapidly diffuse in the material and form complexes with europium atoms. This may explain why the complex Eu-O$_i$(s) is so stable in ZnO.

### Table I: Formation energies $E_f$ and binding energies $E_b$ for intrinsic defects and defect complexes in ZnO.

| Defect       | $E_f$ (eV)   | $E_b$ (eV)   |
|--------------|-------------|-------------|
| Zn$_{int}$   |             |             |
| Eu$_{Zn}$    | 2.42        | 7.44        |
| O$_i$(split) | 2.58        | 5.48        |
| O$_i$(oct)   | 3.39        | 6.28        |
| V$_0$        | 3.20        | 0.30        |
| V$_{Zn}$     | 1.37        | 4.27        |
| Zn$_{int}$   | 6.68        | 3.78        |
| Eu$_{Zn}$    | -0.48       | 1.75        |
| Eu$_{Zn}$    | -1.40       | 0.83        |
| Eu$_{Zn}$ + V$_0$ | 0.48 | 2.70        |
| Eu$_{Zn}$ + V$_{Zn}$ | 7.11 | 2.09        |
| Eu$_{Zn}$ + Zn$_{int}$ | 0.79 | 1.56        |

### B. Electronic properties

Because $GW$ calculations can be performed using different approximations, the results for the theoretical band gap of ZnO has been under debate. Parameters controlling the calculations include the number of bands [43–45], the exchange-correlation potential for the starting wave function [22] as well as the use of approximate models for the screening, like plasmon pole approximations [43].

Shishkin and Kresse [27] suggested that the single shot $G_0W_0$ approximation always yields too small band gaps. To improve agreement with experiment, they suggested the eigenvalues in the Green’s function $G$ ($GW_0$) and in the Green’s function and the dielectric matrix ($GW$) are updated until self-consistency is reached (see Sec. II for further details).

Depending on the starting functional and the details of the calculation (like number of bands and model dielectric function), values between 2.1 and 3.6 eV are obtained for $G_0W_0$ [21, 27, 43, 49], between 2.54-3.6 for $GW_0$ [21, 46, 47, 49] and between 3.2-4.3 for $GW_0$ [24, 50].

We start by validating the $GW_0$ method for bulk ZnO. For this purpose we consider a four-atom wurzite ZnO unit cell and employ a $8 \times 8 \times 8$ $k$ point sampling with an energy cutoff of 500 eV. The resulting band gaps and energetic positions of the Zn-3$d$ states (with respect to the valence band maximum set at zero) for several levels of $GW$ calculations are a) PBE: 0.8 and -5.1 eV, b) PBE0: 3.2 and -7.3 eV, c) HSE06: 2.5 and -7.1 eV, d) $PBE+GW$: 4.3 and -7.2 eV, e) $PBE+GW_0$: 3.3 and -7.0 eV. For the $GW_0$ calculation, a cutoff of 200 eV for the response functions $\chi$, as well as 1024 bands have been employed. It has been shown that a large number of bands is necessary to obtain properly converged results in earlier one-shot $G_0W_0$ calculations [43, 45]. We speculate that the deviations to Ref. [46] are due to the rather low number of bands in that publication. The results are shown in Fig. 1. We find a band gap of 3.3 eV in reasonable agreement with the experimental value of 3.44 eV [51], as well as with other all-electron $GW_0$ calculations [45, 49]. The center of the Zn-3$d$ orbitals is localized at -7 eV, in agreement with previous $GW_0$-calculations for ZnO [27, 49, 52]. We want to point out, that a fully-selfconsistent $GW$ calculation results in a much too high quasi-particle gap of 4.2 eV, due to the reasons explained in detail in section II. Again this agrees well with recent all-electron calculations that find a quasi-particle gap of 4.3 [49].

It has been shown that the position of defect states is not strongly influenced by the number of empty bands and the response function cutoff [24]. The relaxed geom-
etry of Eu at a zinc lattice position without the presence of intrinsic defects is shown in Fig. 2. The europium distance to nearest oxygen atoms are 2.23 Å and 2.27 Å for in-plane and c-direction, respectively. These values are slightly larger than the Zn-O bond lengths in pure ZnO. This means that if Eu is incorporated at a Zn lattice position, it should not disturb the lattice significantly.

In Fig. 3 the electronic density-of-states of substitutionally this geometry is shown. The Eu-\( f \) states lie within the band gap, around 2 eV above the VBM (valence band maximum), hybridize weakly with the Zn-s and O-p states. As expected for substitutional Eu at a Zn lattice position, Eu has a formal charge closer to 2+. The \( f \) spin-up orbitals are fully occupied, giving a total magnetic moment of 7\( \mu_B \). Furthermore, the Eu \( d \) states lie deep in the conduction band of ZnO, \( \approx \) 2.5 eV above the CBM, leading to an energetic difference to the Eu \( f \) states of over 3 eV. These results explain why the 4\( f^7 - 4f^6/5d^1 \) optical transition at 530 nm (\( \approx \) 2.3 eV) cannot be due to a single Eu dopant in the ZnO lattice.

Therefore to a possible way to modify the oxidation state of Eu in the ZnO lattice is therefore by changing its environment. It is known that during ion implantation intrinsic defects are likely to form \[17\]. We therefore investigated Eu doped ZnO in the presence of nearby oxygen and zinc vacancies as well as zinc and oxygen interstitials. In the presence of a neutral oxygen vacancy the Eu-O distances for neighboring oxygen atoms remain almost unchanged, compared to the case without vacancy, and increase slightly to 2.24 Å. The geometry is shown in Fig. 4. The Eu-Zn distance is 3.27 Å and relaxation of farther neighbors is insignificant.

The electronic structure for this system is shown in Fig. 5. The states due to the oxygen vacancy lie 1 eV above the VBM. This is in good agreement with calculations for pure ZnO (see e.g. Refs. \[23, 39, 40\]). The Eu \( f \) states are located now at 2.5 eV above the VBM. Moreover, we observe a small splitting of the Eu-\( f \) states as well as a small hybridization with the Eu-\( d \) and O-\( p \) states. The splitting is caused by a shift of one of the seven Eu-\( f \) states that we assume to be induced by changes in the environment and the screening. These results are in strong contrast to the findings of Ref. \[18\], where the Eu-\( f \) states are energetically located directly above the \( V_O \) states. We attribute this discrepancy to the choice of the GGA functional in Ref. \[18\], predicting a much too narrow band gap. On the other hand, the presence of the \( V_O \) does not significantly change the formal charge around the Eu atom. Moreover, the positions of the Eu-\( f \) spin down and Eu \( d \) states remain practically unchanged. Again this defects cannot explain the experimental observed \( f - f \) transition in ZnO.

The relaxed geometry of the Eu+Zn\(_i\) defect is shown in Fig. 6. The bond lengths between the Eu atom and the nearest oxygen atoms are 2.19 Å, 2.19 Å and 2.24 Å in the in-plane direction, and 2.41 Å in the c-direction. This is because Eu atom relaxes away from the Zn atom. The Eu-Zn distance is 2.72 Å, while the distances to Zn

**FIG. 2:** (color online) Atomic structure around the europium impurity calculated within GGA for substitutional europium in ZnO. Blue, red and grey spheres are Eu, O and Zn atoms, respectively.

**FIG. 3:** (color online) Total and projected density of states for Eu at Zn site in ZnO. The vertical dashed line denotes the Fermi level. Positive (negative) values of the DOS denote spin up (down).

**FIG. 4:** (color online) Atomic structure around the Eu – \( V_O \) complex calculated within GGA. Blue, red and gray spheres are Eu, O and Zn atoms, respectively.
FIG. 5: (color online) Total and projected density of states for Eu incorporated at Zn position in ZnO next to a oxygen vacancy. The vertical line denotes the Fermi level. Positive (negative) values of the DOS denote spin up (down).

FIG. 6: (color online) Atomic structure around the Eu – Zn complex calculated within GGA. Blue, red and gray spheres are Eu, O and Zn atoms, respectively.

second neighbors are 3.29Å.

The electronic structure of this system is shown in Fig. 7. The location of the Eu f-states lies close to the conduction band minimum (CBM), around 2.9 eV above the VBM. We can infer a weak hybridization with both Zn-s and Zn-d states of the Zn interstitial atom. Similarly, a very small hybridization with the O-p states is found. Here, the formal charge of the Eu atom remains close to 2+ and all spin-up f-states are occupied. However, as all mentioned defects behave as donors, it is not surprising, that they cannot corroborate the Eu³⁺ state, connected with the observed photon emitted in the red spectral region.

For the oxygen interstitial plus Eu defect, we have considered two geometries. The first consists of an Eu atom at substitutional Zn site next to an oxygen interstitial in dumbbell configuration. This configuration is shown in Fig. 8. In this case the lattice relaxations are more pronounced. The Eu atom is shifted away from the interstitial complex, decreasing the Eu-O bond lengths to 2.21Å. The Eu-Zn distance is also slightly increased to 3.29Å and the distances to the oxygen atoms of the interstitial are 2.31Å and 2.33Å, respectively.

The electronic structure is presented in Fig. 9. We observe a splitting of the Eu-f states that we attribute to a combination of the changed symmetry in the local environment and the changes in the screening. While 6 of the Eu-f are located closer to the VBM, the remaining occupied Eu-f state lies about 1 eV higher in energy. We find contributions to the localized states from both O_int-p and O_host states. However, also in this case, the Eu atom possesses a formal charge of 2+ with all Eu-f spin-up states fully occupied. The oxygen interstitial atom possesses a magnetic moment of 0μB, a further confirmation, that no electron is transferred from the Eu atom.
FIG. 9: (color online) Density of states of Eu doped ZnO in the presence of a nearby split oxygen interstitial. The vertical line denotes the Fermi level. Positive (negative) values are the spin up (down) components.

to the oxygen site.

The geometry of Eu doped ZnO in the presence of a neutral Zn vacancy (V\textsubscript{Zn}) is shown in Fig. 10. The Eu atom shifts towards the vacancy, increasing the in-plane Zn-Eu distance to 3.49Å and 3.40Å in comparison to 3.3Å that would correspond to Eu exactly on Zn lattice position. Consequently, the in-plane Eu-O distances also change, asymmetrically, to 2.09Å, 2.19Å and 2.24Å, respectively. Along the c-direction the Eu-O distance is 2.22Å. The corresponding electronic structure is shown in Fig. 11. We find no occupied Eu-f states in the band gap. These states lie within the VB, close to the O-p states and hybridize both with with O-p and Zn-d states. The local projected moment on the V\textsubscript{Zn} site is 1\(\mu_B\), which is aligned anti-parallel to the magnetic moment on the Eu which is 6\(\mu_B\). However the fact that the Eu-f states are energetically located inside the VB and the unoccupied Eu-f state is energetically located at 2 eV above the VBM, does not fit with experimentally observed transition.

The other defect complex including an oxygen interstitial consists of an oxygen at a octahedral interstitial site next to an Eu at Zn lattice position. The corresponding atomic structure is shown in Fig. 12. We find much more pronounced lattice relaxations in this case, also involving second nearest neighbors. The Eu-Zn distance is 3.2Å, while the Eu-O bond lengths are 2.2Å to the oxygen atoms in the basal plane and 2.25Å to the oxygen along the c-direction. The distance between the Eu atom and the oxygen interstitial is 2.24Å. This can be explained by looking at the coordination Eu adopts. The Eu-O distance to the nearest neighbors is very similar to Eu\textsubscript{2}O\textsubscript{3}, which possess a coordination number of 6±1 and a radial distance of 2.33±0.015 Å according to Ref\[54\].

FIG. 10: (color online) Atomic structure around the Eu – V\textsubscript{Zn} complex within GGA. Blue, red and gray spheres are Eu, O and Zn atoms, respectively.

FIG. 11: (color online) Density of states of Eu doped ZnO in the presence of a nearby zinc vacancy. The vertical line denotes the Fermi level. Positive (negative) values are the spin up (down) components.

FIG. 12: (color online) Atomic structure around the Eu+O\textsubscript{int}\textsuperscript{oct} complex within GGA. Blue, red and gray spheres are Eu, O and Zn atoms, respectively.

The corresponding electronic structure is shown in Fig. 13. We find the occupied Eu f-states are located...
in the band gap, with the Eu-\textit{f} orbitals being occupied with six electrons. The occupied and unoccupied states are located at -0.7 eV and 1.3 eV, respectively. We find a small hybridization with O-\textit{p}(\text{host}) and O-\textit{p}(\text{oct})-\textit{O}. The total magnetic moment of the complex is 5\(\mu_B\), determined by a magnetic moment of 6\(\mu_B\) spin up at the europium aligned anti-parallel to the magnetic moment of 1\(\mu_B\) at the oxygen interstitialal interstitial. Therefore, we suggest that the intra-\textit{f} luminescence of the ZnO:Eu samples is most likely due to Eu\textsubscript{Zn}+O\textsubscript{oct}\textsuperscript{\text{\small{\text{\textit{}}}}}} complexes. We have also explored the mechanism for optical activation of Eu in ZnO reported in Ref. [13], where substitutional hydrogen at Zn lattice position next to an europium atom is suggested. However, this configuration does not change the formal charge of Eu.

IV. CONCLUSIONS

In conclusion, we have investigated Eu-doped ZnO using DFT and many-body GW technique within the GW\textsubscript{\text{\small{}}} approximation. We find that the position and formal charge of the Eu-\textit{f} states is strongly dependent on the environment around the Eu atom. We conclude that the optical activity of Eu in ZnO is due to Eu+O\textsubscript{\text{\small{}}} oct defect complexes. We would like to mention that we do not exclude other possible mechanisms (at the moment we are carrying on calculations on charged systems to further clarify the incorporation of Eu in ZnO). Finally, we believe our results can open the pathway for a better understanding of these complex dopants in zinc oxide.

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FIG. 13: (color online) Density of states of Eu doped ZnO in the presence of a nearby octahedral oxygen interstitial. The vertical dashed line denotes the Fermi energy. Positive (negative) values are the spin up (down) components.
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