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Electronic structure of cubic $Er_xGa_{1-x}N$ using the LSDA + U approach

A. Lazreg[a,*], Z. Dridi[a], F. Benkabou[b], B. Bouhafs[a]

[a] *Modelling and Simulation in Materials Science Laboratory, Physics Department, University of Sidi Bel-Abbes, 22000 Sidi Bel-Abbes, Algeria*
[b] *Département de Physique et d'Astronomie, Faculté des Sciences, Université de Moncton, Moncton, Canada NB E1A 3E9*

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Abstract

Electronic structure calculations were performed for substitutional erbium rare-earth impurity in cubic GaN using density-functional theory calculations within the LSDA + U approach (local spin-density approximation with Hubbard-U corrections). The LSDA + U method is applied to the rare-earth 4f states. The $Er_xGa_{1-x}N$ is found to be a semiconductor, where the filled f-states are located in the valence bands and the empty ones above the conduction band edge. The filled and empty f-states are also shown to shift downwards and upwards in the valence and conduction bands, respectively, with increase in the U potentials.

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Keywords: Rare-earth; GaN; LSDA + U

1. Introduction

The diluted ferromagnetic semiconductors are considered as promising materials for spintronic applications due to their unique combination of magnetic, semiconducting, and optical properties. Most of the materials that have been studied are III–V and II–VI semiconductors doped with Mn and other 3d transition metals (TMs), which have been predicted and, in some cases, observed to show hole-mediated ferromagnetic behavior above room temperature [1–3]. However, ferromagnetism has been also observed in $Gd_xGa_{1-x}N$, with Curie temperature larger than 400 K [4–6], meaning that rare-earth (RE) ions can become an interesting alternative to TMs for spintronic applications. In optoelectronics, it has been reported that in contrast to Er-doped Si, the intra-f luminescence in Er-doped GaN is not drastically quenched at room temperature [7], and both electroluminescence as well as photoluminescence (PL) in the visible have been observed [8]. RE-doped GaN leads to red, green, infrared, and blue light emission for use as primary colors in screen displays for optoelectronic applications [9–11].

An accurate description of the electronic structure of solid containing REs is a challenging problem because of the correlated nature of the f-electrons in the filled 4f shell [12]. Calculations based on the local spin density approximation (LSDA) invoked in the framework of density-functional theory, place the f-derived states which appear as a set of narrow bands at the Fermi level, while experiments reveal their localized nature as atomic multiplets over a broad energy range [13]. To overcome these failures, a variety of strategies to extend the LSDA have been developed, among them the self-interaction correction (SIC) [14] and the LSDA + U [15,16].

A number of calculations of the electronic and magnetic properties have been reported on RE-doped GaN [17–20]. Concerning erbium, the number of investigations on Er-doped GaN is still small; Filhol et al. [17] have reported first-principles calculations on Er-, Eu-, Tm-doped GaN including the f-electrons in the core and assuming trivalent configuration. They have studied the different defects resulting from doping GaN with RE; substitutional RE_{Ga}, RE-N and Ga vacancies, RE-interstitial, and RE-oxygen defects; they concluded that RE_{Ga} was the simplest stable defect [17].

*Corresponding author. Tel./fax: +213 48569546.
E-mail address: aeklazreg@yahoo.fr (A. Lazreg).

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Hourahine et al. [18], using the LSDA + U, have studied the Er-doped GaN in the wurtzite structure, and have also focussed on substitutional Er_{Ga} and complexes with nitrogen vacancies ($Er_{Ga} + V_N$). They have reported that the substitutional Er_{Ga} neither produces an important distortion of the GaN host lattice nor introduces levels in the band gap, in opposite to the $Er_{Ga} + V_N$ complex [18].

Svane et al. [19], using SIC-LSDA, have studied the electronic structure of substitutional RE defects in cubic GaAs and GaN. The latter have reported a relatively weak magnetic interaction of the RE ions with the host states at the valence and conduction band edges, and concluded that the RE dopants may not, by themselves, induce room-temperature ferromagnetism [19]. For $Er_xGa_{1-x}N$, they have located the unoccupied f-bands below the conduction band minimum (CBM), and have reported a weaker effect of the exchange interaction of the erbium ion with the host states at the valence band maximum (VBM) in comparison to that at the CBM [19].

In this work, we have studied the Er-doped GaN to obtain a deep understanding of the nature of magnetic coupling. The strong correlation of the Er f-electrons was taken into account using an LSDA + U-like potential. The SIC approach can describe the essential localization aspects of the 4f-electrons but it has certain fundamental problems, as described in a discussion by Jones and Gunnarsson [21], and lacks some of the flexibility to describe different configurations of the 4f states that may be important. The LSDA + U approach [15,16] is an alternative approach, which adds a screened Hartree–Fock-type treatment for the f orbitals to the LSDA formalism. One advantage of this approach is that it can be formally justified as an approximation to the quasiparticle GW approach [22].

Our calculations were performed in the zinc-blend structure at the concentration $x = 0.25$, where the erbium is substituted with gallium. We have reported the spin-polarized band structures, the density of states and have calculated the exchange splitting and the exchange interaction parameters. We show that the magnetic properties are different from Mn-doped GaN [23]. Further, we have studied the effect of the $+U$ potentials on the f-electrons.

The present paper is organized as follows: Section 2 presents details of our calculations, results and discussion are presented in Section 3, and Section 4 summarizes our conclusion.

2. Calculation

Our electronic structure calculations are based on the density-functional theory in the LSDA, with additional Hubbard correlation terms describing on-site electron–electron repulsion associated with the 4f narrow bands (LSDA + U approach) [15,16]. The first-principles band structure approach applied in this work is the scalar relativistic full-potential linear-augmented-plane-wave plus local orbital (FPLAPW + lo) method [24,25] (Wien2k implementation [26]). Basis functions were expanded as combinations of spherical harmonic functions inside non-overlapping spheres around the atomic sites (muffin-tin (MT) spheres) and in Fourier series in the interstitial region. In the MT spheres, the l-expansion of the non-spherical potential and charge density was carried out up to $l_{max} = 10$. In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region were expanded in plane waves with a cutoff of $k_{max} = 7/R_{mt}$ (where R_{mt} is the average radius of the MT spheres). In the calculations, the Er 5p and Ga 3d are treated at the same footing as the other valence orbitals.

The cubic $Er_xGa_{1-x}N$ alloy was studied in the ferromagnetic phase and modeled using supercells of 16 atoms generated using the fcc (zinc-blend) unit cell. The erbium is substituted with gallium. We have taken the isoelectronic trivalent configuration of the RE $4f^{11}5d^16s^2$, which is seen to be the preferred valency as reported by previous calculation [17,19] and experiment [9] (the atomic configuration of the free atom is $4f^{12}5d^06s^2$ hence divalent from the f occupation). We have chosen MT radii of 2.35, 1.8, and 1.4 bohr for Er, Ga, and N, respectively. The Brillouin-zone integration were performed using $2 \times 2 \times 2$ Mokhorst–Pack special k-points [27]. Following Ref. [28], we have used $U = 8.6$ eV and $J = 0.75$ eV in the LSDA + U scheme where these parameters are used for Er in zinc-blend ErN.

3. Results and discussion

For $Er_{0.25}Ga_{0.75}N$ alloy, we have calculated the spin-polarized band structures, total and partial density of states (DOS) at the equilibrium lattice constant estimated to 4.698 Å. The spin direction (↑ and ↓) is taken as the direction of the RE spin (majority ↑ and minority spin ↓ direction). The band structures are given in Fig. 1 for majority and minority spin, and the total and partial spin-polarized density of states in Fig. 2. For both majority and minority spin (Fig. 1), the bottom of the valence bands (from −14.5 to −11 eV) is dominated by N-2s states and Ga-3d states with a less contribution of Er-5p states. From −6 eV, the two band structures differ. For majority spin, from ∼−6 to −4.5 eV, the corresponding bands originate essentially from the Er-4f states, which exhibit narrow bands with a weak contribution of N-2p and Ga-4s states. From ∼−4 to −1 eV, the bands are dominated by the N-2p states with a weak contribution of Er-5d, Ga-4p and Er-5p states. The VBM is located at X. For minority spin, the bottom of the valence band is followed by bands, from ∼−6 to −4 eV, which are dominated by the N-2p and Ga-4s states. These latter are followed, from ∼−4 to −2 eV, by the Er-4f states. From ∼−2 to −1 eV, the bands come mainly from N-2p states with a weak contribution of Er-5d, Ga-4p and Er-5p states. The VBM occurs at X as observed for majority spin. The CBM occurs at Γ and exhibits an s character for the majority and minority spins.

The partial densities of states shown in Fig. 2 are given for Er-4f, Er-5d, and N-2p states. For majority spin, the