Structural and electronic properties of Er_{0.5}Lu_{0.5}B_2 and LuB_2 compounds by using the PBE0 hybrid functional

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Abstract. We report first-principles calculations to determine the structural and electronic properties of Er_{0.5}Lu_{0.5}B_2 and LuB_2 compounds, by using Density Functional Theory (DFT) and Full Potential Linearized Augmented Plane-Waves (FP-LAPW) method. For the description of the electron-electron interaction was used the Local Density Approximation (LDA), Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) and PBE0 hybrid functional. From the density of states (DOS), it is found that the addition of a fraction of the exact Hartree-Fock exchange energy in PBE approximation, evidence the localization of the 4f-Er and 4f-Lu orbitals, which favours the polarization of the electronic spins of these orbitals in LuB_2 and Er_{0.5}Lu_{0.5}B_2 compounds. The PBE0 scheme is justified because it describes more appropriate manner the electronic and magnetic properties of strongly correlated systems than the LDA and PBE approaches.

1. Introduction

The rare earth diborides, REB_2, i.e. compounds with the presence of rare-earth metals in the boride lattice leads to a wide diversity of thermodynamic, structural, electronic and magnetic properties. These rare-earth borides such as diborides (XB_2), tetraborides (XB_4), hexaborides (XB_6), and dodecaborides (XB_12) have attracted great attention over the last years as a rich class of materials that exhibit various phenomena related with electronic spins of f-type orbitals. Within this family of materials, XB_2 diborides constitute a group of compounds with AlB_2-type crystal structure, integrated by hexagonal layers composed of rare earth element atoms alternating with layers of hexagonal boron atoms [1-3]. From the theoretical point of view, as pointed Fan et al. [4] in their work, it should be noted that in this type of compounds, the presence of f orbitals of rare earth element implies strong electronic correlation that theoretically, is not adequately described with the local density approximation (LDA) or generalized gradient (GGA). In this case, it becomes necessary to employ exchange-correlation functionals, such as LDA + U or GGA-PBE0 [5], taking into account this feature of the f orbitals.

In this work, we present a study of the electronic properties of the LuB_2 and Er_{0.5}Lu_{0.5}B_2 compounds, using the FP-LAPW method employing exchange-correlation functionals with the GGA-PBE and GGA-PBE0 parameterizations, within the formalism of DFT.

2. Computational details

Calculations are performed within the framework of DFT, using the FP-LAPW method. Exchange-correlation effects are treated using the LDA and GGA-PBE approximations [6-7], and PBE0 hybrid functional [8-10].
The charge density and potential are expanded in spherical harmonics up to \( l_{\text{max}} = 10 \) and the wave function is expanded in plane waves with cutoff parameter \( K_{\text{max}} = 8.00/R_{\text{mt-min}} \); where \( R_{\text{mt-min}} \) is the smallest radius of the atomic sphere in the unit cell and \( K_{\text{max}} \) limits the kinetic energy. To ensure convergence in the integration of the first Brillouin zone, are used 95 k-points in the irreducible part of the first Brillouin zone. The integrals over the Brillouin zone are solved using the k-point special approximation of Monkhorst-Pack [11]. The self-consistency is achieved by requiring that the convergence of the total energy is less than 10^{-4} \( \text{Ry} \). For expanding the potential in the interstitial region is considered \( G_{\text{max}} = 12.00 \). Muffin-tin radius used for Er, Lu, and B were \( R_{\text{mt-Er}} = 2.20 \), \( R_{\text{mt-Lu}} = 2.10 \) and \( R_{\text{mt-B}} = 1.60 \), respectively. The hybrid functional PBE0 is applied to the 4f electrons of the rare earth elements Er and Lu, similar to what was done in a previous work of Casiano et al [10].

3. Results and discussion

The crystalline structures of the compounds were optimized in AlB\(_2\)-type hexagonal structure with space group P6/\( \overline{mmm} \) (#191). The total energies are computed for different values of cell volume. The lattice parameters are obtained by minimizing the energy as a function of volume. To perform this, we fit the obtained energy by the equation of state of Murnaghan [12]. The calculated values in this work, the theoretical values reported by other authors and some available experimental values are shown in Table 1. Our results are in good agreement with the experimental values reported.

| Reference | Method       | \( a_0 \) (Å) | \( c/a \) | \( V_0 \) (Å\(^3\)) | \( B_0 \) (GPa) | \( E_0 \) (eV) | \( \mu \) (\( \mu_0 \)/cell) |
|-----------|--------------|---------------|-----------|---------------------|----------------|--------------|--------------------------|
| Er\(_{0.5}\)Lu\(_{0.5}\)B\(_2\) | [10] FP-LAPW:LDA | 3.168 | 1.191 | 32.78 | 168.81 | -11.085 | 2.659 |
|           | [10] FP-LAPW:GGA-PBE | 3.247 | 1.182 | 35.02 | 148.71 | -14.896 | 2.697 |
|           | [10] FP-LAPW:GGA-PBE0 | 3.260 | 1.166 | 34.98 | 168.33 | -13.713 | 3.072 |
|           | [4] FP-LAPW:LDA | 3.280 | 1.155 | - | - | - | - |
|           | [13] LDA | 3.171 | 1.192 | - | 169.47 | - | - |
|           | [14] PP-PW:GGA | 3.275 | 1.161 | - | 172.9 | - | - |
|           | [15] Experimental | 3.268 | 1.157 | - | - | - | - |
| Er\(_{0.5}\)Lu\(_{0.5}\)B\(_2\) | Our work FP-LAPW:LDA | 3.175 | 2.325 | 32.29 | 193.09 | -37.519 | 2.642 |
|           | Our work FP-LAPW:GGA-PBE | 3.241 | 2.323 | 34.26 | 163.03 | -32.991 | 2.644 |
|           | Our work FP-LAPW:GGA-PBE0 | 3.251 | 2.308 | 34.33 | 169.62 | -22.617 | 3.067 |
| Lu\(_2\) | Our work FP-LAPW:LDA | 3.181 | 1.137 | 31.69 | 277.52 | -18.721 | 0.000 |
|           | Our work FP-LAPW:GGA-PBE | 3.236 | 1.143 | 33.52 | 217.88 | -16.141 | 0.000 |
|           | Our work FP-LAPW:GGA-PBE0 | 3.237 | 1.141 | 33.56 | 189.27 | -16.064 | 0.000 |
|           | [4] PP-PW:LDA | 3.241 | 1.141 | - | - | - | - |
|           | [13] LDA | 3.181 | 1.144 | - | 204.35 | - | - |
|           | [16] PP-PW:GGA | 3.242 | 1.146 | - | 180.7 | - | - |
|           | [3] Experimental | 3.244 | 1.142 | - | - | - | - |

From the \( B_0 \) values shown in Table 1, is concluded that the compounds are rigid. This property, due to the strong bonds that exist between boron atoms present in the AlB\(_2\)-type hexagonal structure, makes it attractive for potential applications as coatings on cutting tools.
For the analysis of the electronic properties only is our interest to compare the results of ErB$_2$ [10] and Er$_{0.5}$Lu$_{0.5}$B$_2$ compounds.

The total (DOS) and partial (PDOS) density of states calculated for ErB$_2$ and Er$_{0.5}$Lu$_{0.5}$B$_2$ are shown in Figure 1. The calculations were carried out considering spin polarizations. In Figure 1 we consider only the orbitals that have the greatest contribution to the Fermi level. For our purpose we only analyze the DOS results for the ErB$_2$ and Er$_{0.5}$Lu$_{0.5}$B$_2$ compounds (LuB$_2$ not presents interesting properties: metallic, non-magnetic) in the PBE and PBE0 approximations (PBE is a refinement of the PBE).

In the case of ErB$_2$ [10], the GGA-PBE result indicates that for spin up polarization, the largest contribution at the Fermi level is mainly due to p-B and d-Er states, while f-Er states are located between energy $\sim$-3.5eV and $\sim$-1.0eV. For spin down polarization, the largest contribution at the Fermi level is due to f-Er states in the energy region $\sim$-1.5eV and $\sim$0eV. For Er$_{0.5}$Lu$_{0.5}$B$_2$ is observed that, in the GGA-PBE case with polarization of spin up, the largest contributions due to p-B, d-Er and d-Lu and f-Er states are located in the region of energies $\sim$-3.5eV and $\sim$-1.0eV. For polarization with spin down, the majority contribution is due to f-Er states. It also notes that GGA-PBE result, f-Lu states are located within the range $\sim$-5.0eV and $\sim$-2.5eV with spin up and down polarizations almost symmetric. This characteristic behaviour of f-Er and...
f-Lu states is the reason because the difference between the values of the magnetic moment of ErB₂ and Er₀.₅Lu₀.₅B₂ are relatively small (0.005µ₀/cell). Is not observed a significant mixing with other states of the valence band outside this region. Thus, f-Er and f-Lu states, particularly the 4f are highly localized and can only interact via a RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction as noted by Mori et al. [3] on a theoretical and experimental study of ferromagnetism and electronic structure of TmB₂. In the region -4eV<E<E_Fermi, for ErB₂, there are contributions from 2p states of B and 5d of Er. The latter, crossing the Fermi level and are responsible for the metallic character of the material. For Er₀.₅Lu₀.₅B₂ in addition to 2p-B and 5d-Er states are observed the presence of 5d-Lu states, which also contribute to metallic behaviour of this compound. This feature distinguishes the calculated DOS with GGA-PBE0 those obtained from GGA-PBE in which f-Er states also cross the Fermi level. For the energy values of ~1.0eV and ~2.0eV two peaks are observed that are characteristic of the diboride compounds based on rare-earth elements. This behaviour is consistent with the results of Mori et al. [3] for TmB₂ and YbB₂. It can be noted, moreover, that the differences between the derived DOS from the GGA-PBE and GGA-PBE0 parameterizations, must be, as explained Nourmohammadi et al. [17], in which the exchange splitting using PBE0 increases, causing that the localization of magnetic electrons (mainly the 4f of Er) is greater, and that the values of the lattice constant at equilibrium, and magnetic moment predicted by GGA-PBE0 be slightly greater than the result of GGA-PBE as shown in Table 1.

4. Conclusions
It was found that the effect of adding a fraction of the exact exchange energy of Hartree-Fock in PBE approximation, evidence the localization of 4f-Er and 4f-Lu orbitals, which favors electronic spin polarization of these orbitals in the ErB₂ and Er₀.₅Lu₀.₅B₂ compounds. This explains the increase in the total magnetic moment PBE0 (3.072µ₀/cell in ErB₂ and 3.067µ₀/cell in Er₀.₅Lu₀.₅B₂) compared to the total magnetic moment in PBE (2.697µ₀/cell in ErB₂ and 2.664µ₀/cell in Er₀.₅Lu₀.₅B₂).

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