Study of Electronic Properties of Dy$_2$O$_3$ using 
First Principles Calculations

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Abstract—In the present paper, we have studied the electronic properties of dysprosium sesquioxide by applying the linear combination of atomic orbitals method within the framework of density functional theory. We have computed the energy bands, density of states, Mulliken’s populations of Dy$_2$O$_3$.

The energy bands confirm a wide indirect band gap of Dy$_2$O$_3$. The large band gap semiconducting properties of Dy$_2$O$_3$ are formed due positioning of 2sp states of O and 5d states of Dy atoms. Also, the computed band gaps are in good agreement with the previously reported data. The data on Mulliken’s population and theoretical Compton profiles are discussed in terms of bonding, energy bands and density of states.

Index Terms—Band Structure Calculations; Rare Earth Oxides; First Principles Studies

I. INTRODUCTION

The study of electron momentum density distribution through the Compton scattering depends on the impulse approximation, which allows, if the target electrons to be treated as free electrons. Moreover, if the interaction is truly impulsive, the electron does not move appreciably during the interaction and therefore sees the same potential just before and after collision with the photon. If the target consists of electrons with a distribution of momenta $n(p)$, the Doppler broadening of the spectrum of the scattered radiation known as Compton profile, $J(p)$, is defined as [1]:

$$ J(p) = \int \int n(p) dp, dp $$

(1)

The Compton spectroscopy is a well recognized tool to study the electron momentum density of materials and hence their electronic properties [2].

Within last decade, rare earth oxides have been extensively investigated due to their high resistivities, high dielectric constants, and large band gap characteristics for wide range of technological applications including memory devices, switching mechanism for logic devices, and optoelectronic devices [3]. These oxides are also found as potential candidates for metal oxide semiconductor devices [4]. Specially, Dy$_2$O$_3$ is attractive to substitute SiO$_2$ in the CMOS devices because of its dielectric constant and high chemical and thermal stability with Si. The crystal structure of the trivalent sesquioxides (Ln$_2$O$_3$) fall into three distinct polymorphic forms cubic Ia3, hexagonal P-3m1 and monoclinic C2/m, while the tetravalent fall into cubic Fm3m [5]. Recently, Gillen et al. [6] have calculated the electronic structure of lanthanides (Ln2O3) and CeO2 using hybrid density functional HSE03, HSE06 and screened exchange (sX-LDA). Horoz et al. [7] have investigated the electronic and optical properties of Dy$_2$O$_3$ using the density functional theory within the GGA. Rammo [8] has studied Ln$_2$O$_7$ rare-earth oxides (where Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy and Er, x=1, 2, 4 and y=2, 3, 7, 11) by X-ray diffraction and pair potentials modeling using the GULP code. Zhao et al. [9] have studied the electronic polarizability and optical basicity of lanthanide oxides. The electronic structures of dioxides, RE$_2$O$_3$, and sesquioxides, RE$_2$O$_3$, of the rare earths, RE = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy and Ho, have been calculated by Petit et al. [10] with the self-interaction-corrected local-spin-density approximation.

II. COMPUTATIONAL DETAILS

We have computed the electronic properties of Dy$_2$O$_3$ by using the ab-initio linear combination of atomic orbitals (LCAO) method [11]. A variety of schemes of exchange and correlation within the density functional theory (DFT) namely local density approximation (LDA) [12] and generalized gradient approximation (GGA) with different exchange and correlation functions like Wu-Cohen (WC-GGA) [13], second-order GGA (SOGGA) [14]. In the present computations, we have employed the pseudopotential (PP) approach. In PP-HF scheme, the one electron Hamiltonian operator is given as [11],

$$ \hat{H}_{PP} = \hat{t} + \hat{c} + \hat{x}_{HF} + \hat{e}_{pp} $$

(2)

where $\hat{t}$, $\hat{c}$, $\hat{x}_{HF}$ and $\hat{e}_{pp}$ are kinetic, Coulomb, exchange and effective core pseudopotential (ECP) operators, respectively. The ECP was used to describe the core part of Dy [15] while the all electron basis sets were taken for O [16]. The lattice parameter for cubic Dy$_2$O$_3$ was taken as a=10.671 Å [8]. Following the default tolerances in the CRYSTAL09 code, the SCF calculations have been performed for 120 k points in the irreducible Brillouin zone using Monkhorst–Pack shrinking factor of 15. Also, BROYDEN [17] scheme was used to achieve fast convergence.
III. RESULTS AND DISCUSSION

A. Energy Bands and Density of States

In Figs. 1 and 2, we have plotted the E-k relations (with \( E_F \) shifted to zero reference level) along with the high-symmetry directions of BZ for C-phased Dy\(_2\)O\(_3\) using PP-DFT-WCGGA scheme. The trend of the energy bands computed using PP-DFT-LDA and PP-DFT-SOGGA is almost similar to those of PP-DFT-WCGGA scheme, hence we have shown the bands only for PP-DFT-WCGGA approximation. The energy bands confirm a wide indirect band gap of Dy\(_2\)O\(_3\). In Table 1, we have collated the computed band gaps along with the available data.

The DOS just below the \( E_F \) level i.e. in the range \(-2.9\) eV to \( E_F \) are due the hybridization of 2\( sp\) states of O atoms and 5\( d\) states of the Dy atoms with dominancy of O atoms. The DOS in the energy range above \( 4.60 \) eV are due to the 5\( d\) states of Dy atoms. Therefore, we conclude that the large band gap semiconducting properties of Dy\(_2\)O\(_3\) are formed due positioning of 2\( sp\) states of O and 5\( d\) states of Dy atoms. The band gap value is less than the previously reported data.

![Fig. 1](image1.png)

**Fig. 1** Energy bands of cubic Dy\(_2\)O\(_3\) along the high symmetry directions using DFT-PP-WCGGA scheme.

![Fig. 2](image2.png)

**Fig. 2** Total and partial density of states of Dy\(_2\)O\(_3\) along the high symmetry directions using DFT-PP-WCGGA scheme.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Band gap (( E_F )) (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(i) Present Work</strong></td>
<td></td>
</tr>
<tr>
<td>(a) PP-DFT-GGA</td>
<td>4.18</td>
</tr>
<tr>
<td>(b) PP-DFT-LDA</td>
<td>4.09</td>
</tr>
<tr>
<td>(c) PP-DFT-SOGGA</td>
<td>4.17</td>
</tr>
<tr>
<td><strong>(ii) Available data</strong></td>
<td></td>
</tr>
<tr>
<td>Theoretical work</td>
<td></td>
</tr>
<tr>
<td>(a) Gillen et al. [6]</td>
<td>4.7 (HSE03)</td>
</tr>
<tr>
<td>(b) Jiang et al. [18]</td>
<td>3.47 (LDA-U)</td>
</tr>
<tr>
<td></td>
<td>4.41 (G(_S)W(_0))</td>
</tr>
<tr>
<td></td>
<td>4.24 (G(_W)W(_0))</td>
</tr>
<tr>
<td>Experimental work</td>
<td></td>
</tr>
<tr>
<td>Prokofiev et al.[19]</td>
<td>4.9</td>
</tr>
</tbody>
</table>

**Table 1** Energy band gap \( (E_F \) in eV) for Dy\(_2\)O\(_3\) calculated using the various first principle methods along with the available data.

B. Compton Profile

In Fig. 3, the anisotropies in momentum densities \( (J_{110}-J_{100}; J_{111}-J_{100} \) and \( J_{111}-J_{110} \) for Dy\(_2\)O\(_3\) have been plotted PP-DFT-LDA and PP-DFT-SOGGA schemes, respectively. It is observed that the general trends of oscillations in the anisotropies from different schemes are almost identical. In high momentum region (above 3 a.u.) the anisotropy is almost zero as the high momentum region is dominated by core electrons whose isotropic contributions are cancelled while taking the directional differences. Further, in the low momentum region, small amplitudes of anisotropies \( \Delta J(p_z) \) depicts a small anisotropic nature of electron density in Dy\(_2\)O\(_3\). The value of anisotropies \( J_{111}-J_{100} \) at \( p_z = 0 \) is higher than \( J_{111}-J_{110} \) which shows the higher value of EMD along \([110]\) as compared to \([100]\) at \( \Gamma \) point of BZ.
The role of donor atoms while the charge transfer (total) from donor to acceptor in C. Mulliken’s Populations

Here Dy1 and Dy2 play the role of donor atoms while the oxygen atoms play the role of acceptor atoms. Table 2 depicts that charge transfer (total) from donor to acceptor in Dy2O3 is 3.503 e− for PP-DFT-WCGGA scheme, while the values using PP-DFT-LDA-PZ, PP-DFT-SOGGA and PP-DFT-PBEsol schemes are 3.536, 3.508 and 3.506 e− respectively.

<table>
<thead>
<tr>
<th>Method</th>
<th>Dy (1)</th>
<th>O (1)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-DFT-GGA</td>
<td>1.776</td>
<td>1.760</td>
<td>-1.176</td>
</tr>
<tr>
<td>PP-DFT-LDA</td>
<td>1.762</td>
<td>1.746</td>
<td>-1.166</td>
</tr>
<tr>
<td>PP-DFT-SOGGA</td>
<td>1.759</td>
<td>1.744</td>
<td>-1.165</td>
</tr>
<tr>
<td>PP-DFT-PBEsol</td>
<td>1.761</td>
<td>1.745</td>
<td>-1.166</td>
</tr>
</tbody>
</table>

Almost similar amount of charge transfer by Dy1/Dy2 to oxygen atoms in Dy2O3 is observed. It is seen that the charge transfer from the rare earth elements is equally distributed among the three oxygen atoms.

IV. CONCLUSIONS

We have presented the first theoretical (LCAO based) Compton profiles of Dy2O3. It is seen that the LCAO-DFT-GGA (WC) gives a marginally better agreement with the experiment than other LDA/GGA schemes. To compare the experiment in a more accurate way, relativistic Compton profiles with Lam-Platzman correlation corrections are required.

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REFERENCES

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