Study of Electronic Properties of Dy₂O₃ using First Principles Calculations

G. Ahuja, Department of Physics, Faculty of Science, PAHER University, Udaipur (Raj.) 313022, India
G. Arora, Department of Physics, Geetanjali Institute of Technical Studies, Udaipur-313022, Rajasthan

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_2O_3.

The energy bands confirm a wide indirect band gap of Dy_2O_3. The large band gap semiconducting properties of Dy_2O_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 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, $J(p_z)$, is defined as [1]:

$$J(p_z) = \int \int n(p) \, dp_x \, dp_y \qquad (1)$$

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_2O_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_2O_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_2O_3 using the density functional theory within the GGA. Rammo [8] has studied Ln_xO_y rare-earth oxides (where Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy and Er, x=1, 2, 4, 6 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, REO_2, and sesquioxides, RE_2O_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_2O_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],

$$\hat{h}_{PP} = \hat{t} + \hat{c} + \hat{x}_{HF} + \hat{e}_{PP} \qquad (2)$$

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_2O_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_2O_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_2O_3. In Table 1, we have collated the computed band gaps along with the available data.
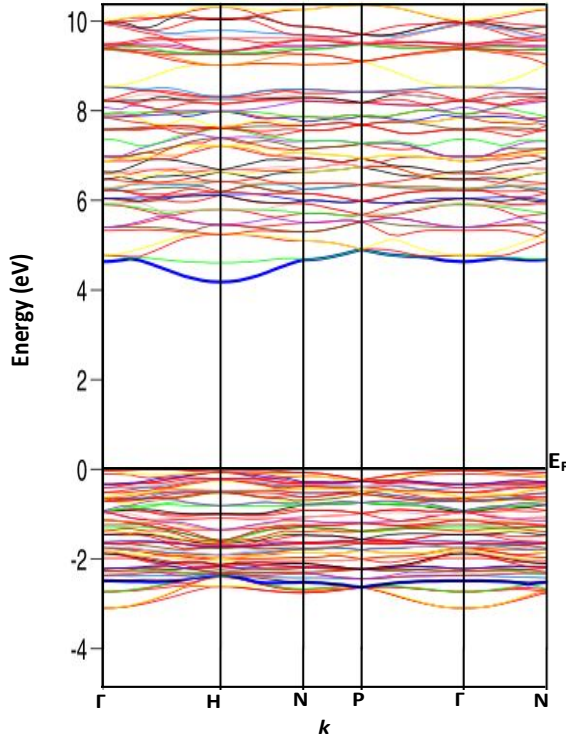
The DOS just below the E_F level i.e. in the range −2.9 eV to E_F are due the hybridization of $2sp$ states of O atoms and $5d$ states of the Dy atoms with dominancy of O atoms. The DOS in the energy range above 4.60 eV are due to the $5d$ states of Dy atoms. Therefore, we conclude that the large band gap semiconducting properties of Dy_2O_3 are formed due positioning of $2sp$ states of O and $5d$ states of Dy atoms. The band gap value is less than the previously reported data.
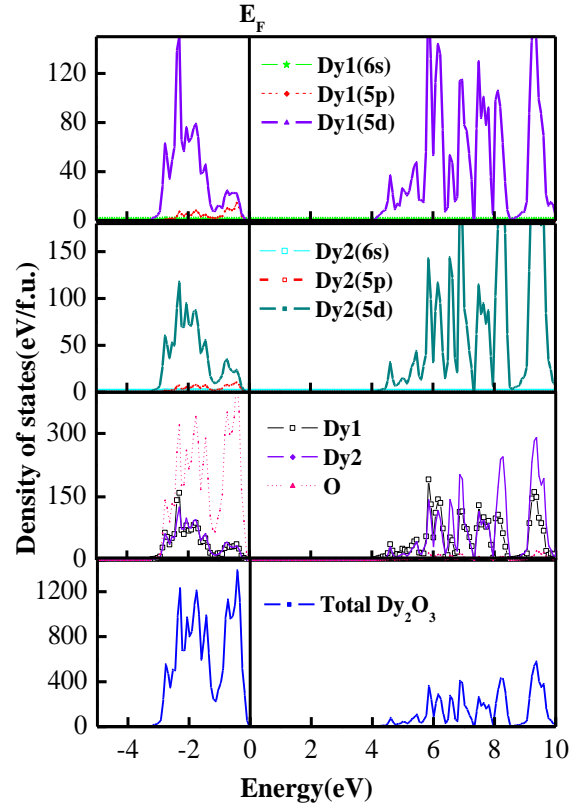

Fig. 1 Energy bands of cubic Dy_2O_3 along the high symmetry directions using DFT- PP-WCGGA scheme.

Fig. 2 Total and partial density of states of Dy_2O_3 along the high symmetry directions using DFT- PP-WCGGA scheme.

TABLE I
ENERGY BAND GAP (E_G IN EV) FOR Dy_2O_3 CALCULATED USING THE VARIOUS FIRST PRINCIPLE METHODS ALONG WITH THE AVAILABLE DATA

Approach	Band gap (E_g) (in eV)
(i) Present Work	
(a) PP-DFT-GGA	4.18
(b) PP-DFT-LDA	4.09
(c) PP-DFT-SOGGA	4.17
(ii) Available data	
Theoretical work	
(a) Gillen et al. [6]	4.7 (HSE03)
	4.9 (HSE06)
(b) Jiang et al. [18]	3.47 (LDA-U)
	4.41 (G_0W_0)
	4.24 (GW_0)
Experimental work	
Prokofiev et al.[19]	4.9

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_2O_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_2O_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 Γ point of BZ.
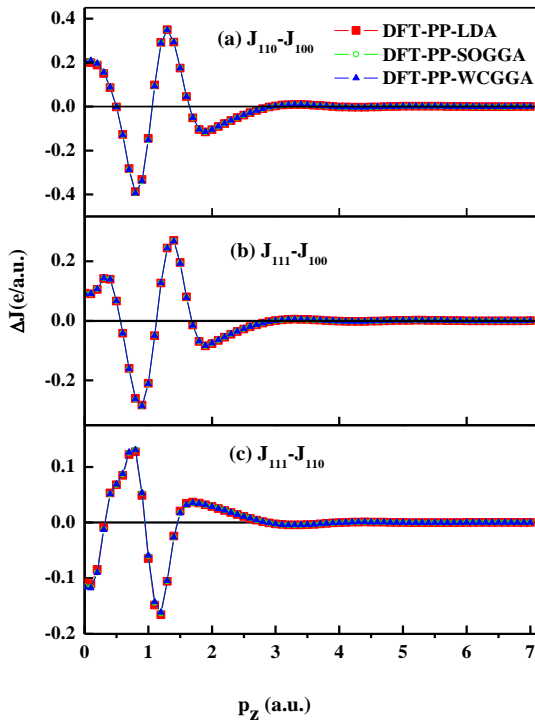
Fig. 3 Anisotropy in the convoluted theoretical Compton profiles of Dy_2O_3 calculated using different density functional schemes within the effective pseudo-core potential. Since the statistical error $\pm\sigma$ is within the size of symbols used, it is not clearly visible. The solid lines are drawn to guide the eyes.

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 Dy_2O_3 is 3.503 e$^-$ for PP-DFT-WCGGA scheme, while the values using PP-DFT-LDA-PZ, PP-DFT-SOGGGA and PP-DFT-PBEsol schemes are 3.536, 3.508 and 3.506e$^-$ respectively.

TABLE II
MULLIKEN'S POPULATION CHARGE TRANSFER DATA FROM DONOR ATOMS TO THE ACCEPTOR ATOMS

Method	Valence charge e$^-$		
	Dy (1)	Dy (1)	O
PP-DFT-GGA	1.776	1.760	-1.176
PP-DFT-LDA	1.762	1.746	-1.166
PP-DFT-SOGGA	1.759	1.744	-1.165
PP-DFT-PBEsol	1.761	1.745	-1.166

Almost similar amount of charge transfer by Dy1/Dy2 to oxygen atoms in Dy_2O_3 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 Dy_2O_3. 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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Mr. Gagan Ahuja was born in Banga city in 1976. He received the B.Sc. and M.Sc. degree in Maths and Physics from the Guru Nanak Dev and Anna Malai University.
He is currently pursuing the Ph.D. degree in Physics at Pacific University, Pacific Academy of Higher Education and Research, Udaipur.

Dr. Gunjan Arora was born in Udaipur, Rajasthan, India in 1978. She received the M.Sc. degree in Physics from the ML Sukhadia University, Udaipur, in 2001. She has completed Ph.D. on the topic of "Compton Spectroscopy of some Binary Alloys and Compounds" from ML Sukhadia University, Udaipur under the guidance of Prof. B. L. Ahuja.

She has published 36 research papers in international and national journals and conferences and written eight books for B. Tech. students. She is carrying out two major research projects with DST, New Delhi and BRNS, Mumbai. She is also guiding three research scholars for Ph.D. from various universities. She has teaching experience of 12 years in Geetanjali Institute of Technical Studies, Udaipur.
Dr. Arora is life member of "Indian Society for Radiation Physics (ISRP)" Udaipur Chapter. She has been awarded by University Gold Medal for standing first in the M.Sc. (Physics) Examination 2001, held by Mohan Lal Sukhadia University, Udaipur.