The effect of Cr impurity on electronic structure of the Al_2O_3 by first principles

S. J. MOUSAVI
Department of Physics, Rasht Branch, Islamic Azad University, Rasht, Iran

The electronic properties of a single Cr impurity in $\alpha - Al_2O_3$ are studied by means of supercell total-energy calculations using a first-principles method based on density-functional theory. The calculations were performed using the full potential–linearized augmented plane wave (FP-LAPW) with the GGA, LSDA and LSDA+U methods. The calculated value of the first excitation from the occupied impurity state to the conduction band was reproduced well by LSDA+U method, while GGA and LSDA yielded values that were less than the experimental value.

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1. Introduction

Ruby, or Cr-doped alumina is a material of central importance to high pressures science. Dielectrics, such as $\alpha - Al_2O_3$; SiO_2 and Mgo , are materials of primary importance when one considers their numerous applications in science [1–3] and technology [4]. Physical properties of these materials are closely related to properties of the electronic structure. Therefore, Cr-doped alumina is of interest for researchers concerned with electronic materials because a consistent description of the electronic structure is lacking [5-7].

Xia et al. [5] calculated the eigenvalue spectrum and the density of states of different clusters in $\alpha - Al_2O_3 : Cr$ using the embedded-cluster linear combination of atomic orbital–molecular orbital (LCAO–MO) discrete variational method. By this method they estimated the local geometry of the relaxed system.

Duan et al. [6] were calculated the multiplet structure under pressure and electronic and structural properties of the chromium impurity for a fully relaxed supercell containing one chromium impurity per 80 atoms. It was found that the atomic environment of the impurityin ruby was intermediate between chromium in Cr_2O_3 and aluminum in $\alpha - Al_2O_3$.

Ogasawara et al. [7] were calculated the multiplet structure of Cr^{+3} in $\alpha - Al_2O_3$ by using a hybrid method of the density-functional theory (DFT) and the configuration interaction (DFT-CI) calculation.To take into account the effect of electron correlations they concluded that it was important to introduce the correlation correction (CC) factor.

Most studies that have been carried about electronic structure are experimental.The aim of this study is to calculate the electronic structure and density of state of ruby with Cr additive on it. For this purpose, we used not only the GGA and LSDA approach, but also the LSDA+U calculation scheme, which is widely used in studies of compounds with strong electron–electron correlations. The GGA, LSDA and LSDA+U calculation results were compared with known experimental data.

2. The calculation method

The calculations were carried out with a self-consistent scheme by solving the Kohn–Sham equations using FPLAPW method in the framework of DFT along with the generalized gradient approximation (GGA) [8], local spin density approximation (LSDA) [9] and LSDA+U [13], using Wien2k codes [10]. The calculations were performed with Rkmax = 7 (R is the smallest muffin-tin radius and kmax is the cut off for the plane wave) for the convergence parameter for which the calculations stabilize and convergence, in terms of the energy, is achieved. The values of other parameters are Gmax = 14 (magnitude of largest vector in charge density Fourier expansion or the plane wave cut off), RMT(Al) = 2.4 a.u., RMT(Cr) = 1.84 a.u. and RMT(O) = 1.6 a.u. (muffin-tin radius). The iteration halted when the charge difference was less than 0.0001e between steps as convergence criterion. The cut off energy, which defines the separation of the valence and core states, was chosen -8 Ry. The number of k-points in the first Brillouin zone (BZ) was selected 1000 k-points. In order to calculate the electronic properties of $\alpha - Al_2O_3 : Cr$ using LSDA + U, we assumed that the density matrix is diagonal, U is the same for all Coulomb interactions $U_{ij} \equiv U$ and J is the same for all exchange interactions $J_{ij} \equiv J$. There are several methods to incorporate the U-term [11,12], but here we have used the self-interaction correction (SIC) introduced by

Anisimov et al. [13]. In $LSDA+U^{SIC}$ method the total energy may be written as

$$E = E_0 + E_{LSDA+U^{SIC}}$$

$$E_{LSDA+U} = \frac{U-J}{2}\left(N - \sum_{m,\sigma} n_{m,\sigma}^2\right)$$

Where N is the total number of electrons and $n_{m,\sigma}$ is the orbital occupancy of the ι-orbital in question (i.e. s, p, or d orbital) with spin σ. With an approximated correction value of $U-J$ for the self-interaction correction, this is probably best for a strong correlated system and for a fullpotential method.

3. Results and discussion

Total density of state (DOS) of pure $\alpha - Al_2O_3$ is shown in Fig. 1 which is calculated with GGA method. A band gap of 6.4 eV separated the upper part of valence band and lower part of conduction band. This value is the same as in other calculation [14,15] and is less than experimental values which are reported about 7.5-8.5 eV. [16,17].

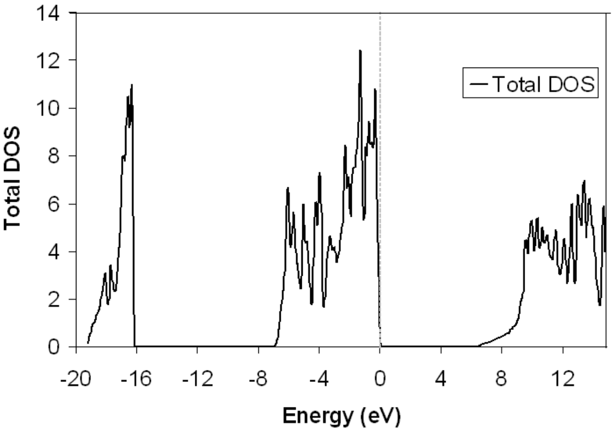

Fig. 1. Total Density of state of $\alpha - Al_2O_3$ *by GGA method.*

Total density of state of Cr doped $\alpha - Al_2O_3$ is shown in Fig. 2 which is calculated with GGA method. Cr impurity introduces two narrow peaks in $\alpha - Al_2O_3$ density of state. These peaks are related to T_{2g} and E_g of d band of Cr impurity atoms. The energy splitting between T_{2g} and E_g is about 3.66eV. This value is not far from its experimental value of 2.23 eV.

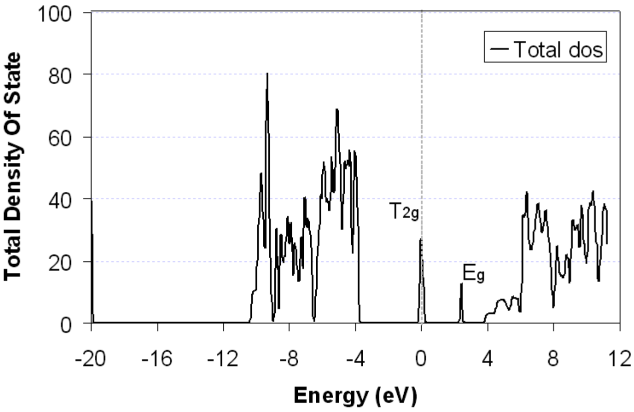

Fig. 2. Total Density of state of $\alpha - Al_2O_3 : Cr$ *by GGA method.*

Cr is a magnetic material, then we are calculated its electron properties with LSDA method. Fig. 3 shows the total density of state of $\alpha - Al_2O_3 : Cr$ with LSDA method. The d bands are splitting into four peaks in the gap region. The minimum energy for transition from $d - T_{2g} \uparrow$ in to conduction band is 3.83 eV. Transition energy from $d - T_{2g} \uparrow$ state to $d - T_{2g} \downarrow$ state (R line of ruby), and $d - T_{2g} \uparrow$ to $d - E_g \uparrow$ (U line of ruby) are 1.49 eV and 1.99 eV respectively.

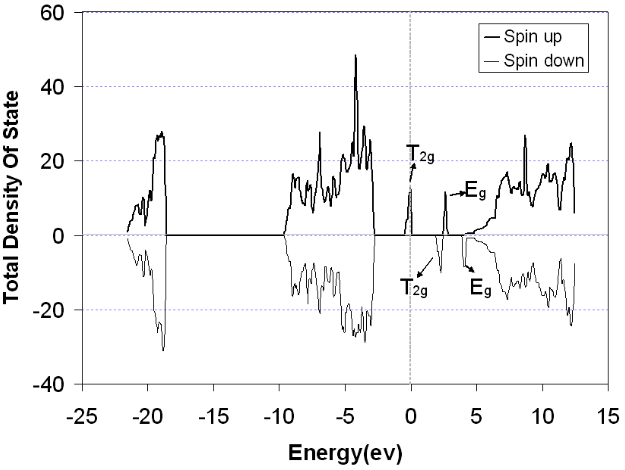

Fig. 3. Total Density of state of $\alpha - Al_2O_3 : Cr$ *by LSDA method.*

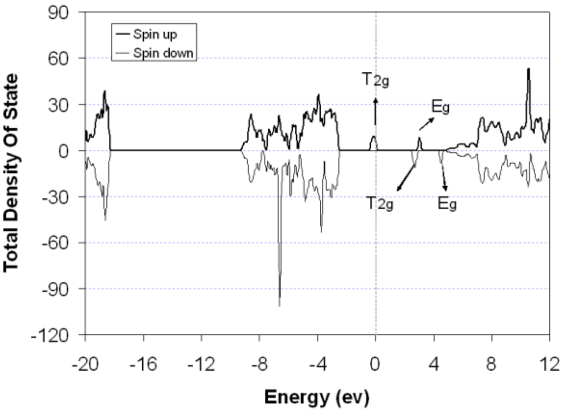

Fig.4.Total Density of state of $\alpha - Al_2O_3 : Cr$ *by LSDA+U method.*

To take in to account the coulomb correlation of localized state, which are disregarded in GGA and LSDA method we are calculated the electronic properties of $\alpha - Al_2O_3 : Cr$ with LSDA+U method. The coulomb interaction parameter U and the interatomic exchange J have been estimated to be 0.952 eV and 0.0 eV respectively. Calculated total density of state of $\alpha - Al_2O_3 : Cr$ with LSDA+U method is shown in Fig. 4. Transition energy of $d - T_{2g} \uparrow$ to conduction band is 4.73 eV which is close to its experimental value and is better than values of GGA and LSDA method. Transition energy from $d - T_{2g} \uparrow$ state to $d - T_{2g} \downarrow$ and $d - T_{2g} \uparrow$ to $d - E_g \uparrow$ are 2.13 eV and 2.61 eV respectively.

Table 1 shows the calculated and experimental values of transition energy of $\alpha - Al_2O_3 : Cr$.

Table 1. The calculated and experimental values of transition energy of $\alpha - Al_2O_3 : Cr$ *.*

	$T_{2g\uparrow} \rightarrow CB$ (eV)	$T_{2g\uparrow} \rightarrow T_{2g\downarrow}$ R (eV)	$T_{2g\uparrow} \rightarrow E_{g\uparrow}$ U (eV)
GGA	2.80	-	2.45
LSDA	3.43	1.49	1.99
LSDA+U	4.62	2.04	2.39
Exp.[18]	5.25	1.79	2.23

4. Conclusion

The details of the density of states of the chromium impurity in $\alpha - Al_2O_3$ have been studied in the framework of density functional theory using GGA, LSDA and LSDA+U methods. The calculated transition energy by LSDA+U method from $d - T_{2g} \uparrow$ to $d - T_{2g} \downarrow$ of Cr d orbital state is 1.66 eV, for $d - T_{2g} \uparrow$ to $d - E_g \uparrow$ state is 2.23 eV and from $d - T_{2g} \uparrow$ to conduction band is 4.7 eV. These results agreed well with the optical spectroscopic data.

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Corresponding author: J_Mousavi@iaurasht.ac.ir