A DFT Study of Electronic and Magnetic Properties of Cr₂O₃ using Spin-Polarized Approach

Abeer E. Aly¹ and D. P. Rai²

¹Department of basic science, higher institution for engineering and technology
²Department of Physics, Pachhunga University College, Aizawl, India-796001

Email: abeerresmat782000@yahoo.com

Abstract: The study of Cr₂O₃ magneto-electric material, particularly, the profound understanding of its antiferro-magnetic, is vital for its spintronics applications. In this paper, we present a study on electronic and magnetic properties of Cr₂O₃ crystal using the first-principles calculations based on the density functional theory. For more accurate results, additional Hubbard (U) parameter has been employed to GGA as well. Our calculated results are homogeneous with available experimental measurements. Results show the effects produced by GGA+U method upon the electronic and magnetic features of the material. We prove that, the spherically symmetric GGA+U approach for exchange correlation approximation portray is a superior depiction of electronic and magnetic properties of Cr₂O₃.

Keywords: Density functional theory; Full Potential Linearized Augmented Plane Waves (FPLAPW), Spin-polarized calculations, Density of states, Band structure, Generalized Gradient Approximation (GGA).

1 Introduction

The Cr₂O₃ is an important material among the corundum family crystals such as Al₂O₃, Fe₂O₃, Ti₂O₃, and V₂O₃ [1]. The significance of Cr₂O₃ is due to its applications such as fuel cell electrodes, heterogeneous catalysis, gas sensors, energy collectors, high-performance industrial alloys, the primary constituent of passive films protecting stainless steels coatings of high-temperature materials, black matrix film, ceramics and thermal barrier coatings etcetera [2-5]. Due to its important industrial applications, Cr₂O₃ is under extensive investigations for a long time, both experimentally and theoretically [6-8]. Cr₂O₃ favors anti-ferromagnetic coupling at ground state that may play an important role for it spintronic applications. However, it’s partially filled spin-polarized 3d shell that led Cr₂O₃ as a strongly correlated material, rather offer a challenge to electronic band theory. Hence, the role of strong electronic correlation in determining the physical properties of Cr₂O₃ is of common interest. On the other hand, density functional theory based computational investigations of transition-metal oxides, particularly the Cr₂O₃, correlation effects can’t be reasonably treated using with common exchange-correlation potentials at a local spin density approximation (LSDA) or generalized-gradient approximation (GGA) [9]. These exchange correlation potentials, as a known fact, are unable to reproduce the electronic and magnetic properties of bulk Cr₂O₃ [10-12]. However, several efforts have been made in the past years to overcome this shortcoming of standard DFT calculations. The most common and one of the effective approach adapted in this regard is the addition Hubbard (U) parameter to LDA or GGA. For instance, Rohrbach et al [13] obtained more reasonable results for the electronic band structure of Cr₂O₃ by performing GGA+U where the simplified
(spherically averaged) U − J a correction was used [9]. Shi et al. [5] found a good agreement between the experimental and their LSDA+U calculations for structural, spectral, and magnetic properties with the same values of U and J which are close to those found from the constrained occupation method within DFT. Although, several efforts are in practice for the correct description of the physical properties of strongly correlated Cr$_2$O$_3$ using DFT, further investigations are thoroughly in need to understand the real picture of its electronic structure to exploit and engineer its properties for further applications. In this work, we calculate the magnetic properties, the density of states (DOS) and the band structure of Cr$_2$O$_3$ using full potential linearized augmented plane wave (FP-LAPW) method at the level GGA and GGA+U for precise description of its results. To understand the electronic properties of Cr$_2$O$_3$, spin polarized total and partial density of states are calculated. The paper is designed such that section 2 presents the computational methods used. The results obtained in the present work with their discussion are presented in section 3. Where in section 4, conclusion based on the present study is given.

2 Computational Methods

The LAPW method is considered as the most accurate approach for electronic structure calculations of the crystals [1, 14]. LAPW solves the Kohn-Sham equations for self consistently for the ground state density, total energy, and (Kohn-Sham) eigenvalues (energy bands) of a many-electron system (here a crystal) by introducing a LAPW basis set. The present first principles calculations have been performed using the state of the art FP-LAPW method [15-16] as incorporated in the WIEN2k code [17]. In this methodology/computational code, the unit cell is divided into (I) non-overlapping atomic spheres (centered at the atomic sites) and (II) an interstitial region. In the two types of regions different basis sets are used.

For these calculations, the structure of Cr$_2$O$_3$ have been built by taking the experimental data of the lattice constants and atomic positions from the reference [18]. For the exchange correlation potential treatment, we used the Perdew et al proposed GGA which can better reproduce the exchange potential [19]. Additional U-parameter has been used for the treatment of correlation effects. The Monkhorst-Pack scheme [20] based on the (8x8x8) k-points grid was employed for the Brillouin-zone integrals using the tetrahedron method with Blöch corrections [21]. To achieve energy eigenvalues convergence, the wave functions in the interstitial regions were expanded in plane waves with a cut-off $K_{max} = 9/RMT$, where RMT denotes the smallest atomic sphere radius and $K_{max}$ gives the magnitude of the largest K vector in the plane wave expansion. The muffin-tin radii were assumed to be (1.84) atomic unit (a.u.) for Cr, and 1.66 a.u for O. The valence wave functions inside the spheres are expanded up to $l_{max}=10$, while the charge density was Fourier expanded up to $G_{max} =14$ (a.u.)$^{-1}$. Self-consistency is obtained using k-points in the irreducible Brillouin zone (IBZ). The BZ integration was carried out using the tetrahedron method [22-24]. The band structure and density of states (DOS) are calculated. The self-consistent calculations are considered to be converging if the total energy of the system is stable.

3 Result and Discussion

The electronic structure and magnetic properties of Cr$_2$O$_3$ are investigated by means of the FP-LAPW method [25-26] within GGA and GGA+U. It is known that these PDOS contributions could be used to predict the behavior of different atoms in possible transition from nonmagnetic state to magnetic state. The coulomb repulsion of electrons can prevent formation of band states, stabilizing localized electron states. The d-levels in most of the transition metal oxides are partially filled; therefore the band theory predicts electron delocalization. The delocalization is resulted in the higher binding energies of d-electrons compared to its real value. In such cases, the bandgap is mostly affected by the presence of a delocalized d-orbital with higher binding energies in the valence band. To understand the electronic properties of Cr$_2$O$_3$, we determined
the spin polarized total and partial density of states (DOS) as plotted in Figure (1). GGA+U. The total DOS above in Figure (1a) are dominated by the Cr 3d, Cr dx2y2dxy, Cr p and O p. The DOS profile shows that a comparatively narrower at the deep valence band centered at ~ -18.8 eV is contributed by the Cr-s and O-p states. The partial DOS of Cr2O3 clearly shows a strong hybridization among O 2p and Cr 3d electrons in the energy regime ~8 to -3 eV in the valence band. Moreover, the DOS for majority spin components in this energy regime is quantitatively nearly equivalent minority spin components that apparently do not contribute to the magnetic moment in Cr2O3. The reduced magnetic moment in Cr2O3 due to the hybridization of Cr 3d and O 2p states has also been reported in [27]. Cr-3d PDOS contributions to the density of states in Cr2O3 are shown in Figure (1d). The DOS shows a significant and broadened structure for majority spin component in the vicinity of Fermi level. However, the DOS at the corresponding energy is negligible for minority spin states. The unbalanced majority and minority spin DOS in the vicinity may be the reason of the observed magnetic moment in Cr2O3. Moreover, the electronic structures reflect significantly wider energy band gap for minority spin component compared to majority spins. Table 1 presents the calculated bandgaps of Cr2O3 in the present work in comparison to the other results calculated with different exchange functionals and experiment. The band structures of Cr2O3 along the symmetry lines of the Brillouin zone for the spin-up and spin-down cases are shown in figure (2). The band structures of Cr-3d for the spin-up are shown in figure (3). The band structures spin up of partial d Cr atom are shown in figure (4).

**Figure 1.** The spin polarized total and partial DOS of Cr2O3 determined with GGA+U.

| Table 1: Experimental and calculated bandgaps (ev) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Bandgap         | GGA+U (Present) | HF              | LDA/GGA         | DFT+U           | HSE             | B3LYP           | sX              | Expt.           |
| Cr2O3 Up        | 15[28]          | 1.5[12]         | 2.9[29]         | 4.4[30]         | 3.4 [31]        | 3.31 [32]       | 3.4 [33-34]     |
| Cr2O3 Dn        | 3               |                 |                 |                 |                 |                 |                 |                 |
Table 2: Magnetic moments (µB) for transition metals atoms (Cr2O3)

| µB     | GGA+U(Present) | LDA/GGA | DFT+U  | HSE    | sX     | Expt. |
|--------|----------------|---------|--------|--------|--------|-------|
| Cr2O3  | 2.55           | 2.76[35]| 2.9 [29]| 2.92 [30] | 3.52 [32]| 3.8 [12]|

Figure 2. The spin polarized band structure of Cr2O3 determined with GGA+U

Figure 3. The total spin-dn band structure of Cr atom.

Figure 4. Spin-up band structure of partial d Cr atom.

4 Conclusion

A quantum-mechanical study of chromium-oxide crystal has been carried out using the first-principles DFT methodology within the GGA and GGA+U approximation. We investigated the structural and electronic properties of the corundum (Cr2O3) by means of the FLAPW method. Results give a better idea of effects produced by GGA+U method upon the structural, electronic, electrical and magnetic features of the material. Calculated magnetic moments of Cr2O3 demonstrate the importance of GGA+U method. Local magnetic moment of (2.55µB) is calculated for Cr atom in Cr2O3 compounds. We prove that, the anti-bonding character in the Cr 3d–O 2p hybridization appearing in the energy band gap plays an important role in the phase and structural stability.
References

[1] Schober H, May T, Dorner B, Straubenberger U and Morrii Y 1995 Zeitschrift Fr Physik B Condensed Matter 98 197-205

[2] Alstrup N C, Langvad N and Chorkendorf I 1994 Surface and Interface Analysis 22 441-444

[3] Figueiredo M O, dos Santos A C, Carneim M J, Abbate M, de Groot F M F, Petersen H and Braun W 1994 The Analyst 119 609

[4] Ryan M P, Newman R C and Thompson G E 1994 Philosophical Magazine Part B 70 241-251

[5] Shi S, Wysocki A L and Belashchenko K D 2009 Physical Review B 79

[6] FUJITA M, INUKAI K, SAKIDA S, NANBA T, OMAYOJI I, YAMAGUCHI A and MIURA Y 2007 Journal of the Society of Materials Science, Japan 56 526-530

[7] Jacob K T 1978 Journal of The Electrochemical Society 125 175

[8] ROY D M and BARKS R E 1972 Nature Physical Science 235 118-119

[9] Wang Jin, Li Chun-Mei, Ao Jing, Li Feng, Chen Zhi-Qian, Acta Phys Sin, 2013, Vol. 62 , Issue (8): 087102, School of Materials Science and Engineering, Southwest University, Chongqing 400715, China,

[10] Catti M, Sandrone G, Valerio G and Dovesi R 1996 Journal of Physics and Chemistry of Solids 57 1735-1741

[11] Chao Z, Chun-Lei W, Ji-Chao L and Kun Y 2007 Chinese Physics 16 1422-1428

[12] Dobin A Y, Duan W and Wentzovitch R M 2000 Physical Review B 62 11997-12000

[13] Rohrbach A, Hafner J and Kresse G 2004 Physical Review B 70

[14] Singh D J 1994 Planewaves, Pseudopotentials and the LAPW Method (Springer US) pp 35-43

[15] Gao S 2003 Computer Physics Communications 153 190-198

[16] Schwarz K 2003 Journal of Solid State Chemistry 176 319-328

[17] P. Blaha, K. Schwarz, G. K. H. Madsen, K. Vosicka, J. Luitz, Wien2k, Karlheinz Schwarz, Technische Universitat Wien, Austria “an Augmented Plane Wave + Local orbitals program for calculating crystal properties”, (2001).

[18] Zhang R, Liu Y, Ye J, Yang W, Ma Y and Gao S 2007 Journal of Alloys and Compounds 427 78-81

[19] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 Physical Review B 46 6671-6687

[20] Monkhorst H J and Pack J D 1976 Physical Review B 13 5188-5192

[21] Blchl P E 1994 Physical Review B 50 17953-17979

[22] Jepson O and Anderson O 1971 Solid State Communications 9 1763-1767

[23] Lehmann G and Taut M 1972 Physica Status Solidi (b) 54 469-477

[24] Wilson J and Yoc A 1969 Advances in Physics 18 193-335

[25] Polman E A, Fransen T and Gellings P J 1989 Journal of Physics: Condensed Matter 1 4497-4510

[26] Stringer J 1989 Materials Science and Engineering: A 120-121 129-137

[27] Zimmermann R, Steiner P und Hufer S 1996 Journal of Electron Spectroscopy and Related Phenomena 78 49-52

[28] Catti M, Sandrone G and Dovesi R 1997 Physical Review B 55 16122-16131

[29] Mosey N J, Liao P and Carter E A 2008 The Journal of Chemical Physics 129 014103

[30] Moore E A 2007 Physical Review B 76

[31] Engel E and Schmid R N 2009 Physical Review Letters 103

[32] Guo Y, Clark S J and Robertson J 2012 Journal of Physics: Condensed Matter 24 325504
[33] Cheng C S, Gomi H and Sakata H 1996 Physica Status Solidi (a) 155 417-425
[34] Crawford J A and Vest R W 1964 Journal of Applied Physics 35 2413-2418
[35] Zeiger H J 1975 Physical Review B 11 5132-5144