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Structure, electronic and magnetic properties of Ca-doped chromium oxide studied by the DFT method

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ABSTRACT

Using first-principles density functional theory calculations within the generalised gradient approximation (GGA) as well as GGA+*U* method we study Ca-doped α -Cr₂O₃ crystal. Structural, electronic and magnetic properties due to the singular impurity incorporation have been investigated and discussed in detail. Atomic shifts as well as computed Bader charges on atoms imply the importance of ionic nature in the atomic interactions in chromium oxide. The study improves our knowledge on how the crystalline lattice reacts on the presence of a Ca dopant. According to our research it is found that Ca impurity incorporation produces some local changes upon the electronic band structure of the material without occurrence of local states within the band-gap. It is found that Ca incorporation produces change in magnetic behaviour of the crystal: it becomes ferromagnetic.

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1. Introduction

Chromium oxide (α -Cr₂O₃) is rather interesting material and belongs to the family of transition metal oxides. It is a wide band-gap semiconductor since its direct band-gap width is equal to 3.3 eV [1,2]. It has a wide range of applications, i.e. being used as catalysts, solar thermal energy collectors, as well as in black matrix films, liquid crystal displays [3,4], protective layers (corrosion and wear resistance of stainless steel) [5] and adhesion promoters [5]. α -Cr₂O₃ is also employed in spintronic devices such as non-volatile magnetoelectric memories [6,7]. Another attractive exploitation of the material is that the α -Cr₂O₃ thin films are being considered as electrochromic materials. There are many crystalline modifications of the chromium oxide, such as Cr₂O₃(corundum), CrO₂(rutile), Cr₅O₁₂(three-dimensional framework), Cr₂O₅ and CrO₃(unconnected strings of CrO₄ tetrahedral). However, the only stable bulk oxide form is Cr₂O₃, which is a magnetic dielectric with the corundum structure [3]. In the α -Cr₂O₃ corundum structure, the O atoms form a hexagonal close-packing array. The metal atoms occupy two thirds of the octahedral interstices between two layers. α -Cr₂O₃ might be described by the rhombohedral primitive unit cell, where Cr atoms are eight-coordinated with oxygens in two oxygen layers.

Several experimental studies have been performed with Ca impurity in the α -Cr₂O₃ crystals together with the other impurity atoms [8–11]. Nevertheless, to our knowledge no experimental or theoretical investigations have been carried out to determine solely Ca effect on different features in the chromium oxide. The present investigation has a purpose to find out the effects of Ca influence upon structural, electronic and magnetic properties of corundum-type chromium oxide.

2. Methodology

The present calculations have been carried out using first-principles density functional theory (DFT) approach as it is implemented in the Vienna ab initio Simulation Package (VASP) [12,13] computer code and the generalised gradient approximation (GGA) [14]. The projector augmented wave (PAW) pseudo-potentials as proposed by Blöchl [15] and adapted by Kresse and Joubert [16] were utilised in our investigation.

A cut-off kinetic energy of 500 eV is used by converging the total energy to less than 1 meV/atom. Γ -centred Monkhorst-Pack (MP) grid with a 0.045 Å⁻¹ separation is applied, which corresponds to a *k*-point mesh of 6 × 6 × 6 for the 10-atom primitive unit cell of the rhombohedral α -Cr₂O₃. Previously mentioned parameters were obtained through the atomic relaxation until all the forces are less than 0.008 eV/Å.

Chromium oxide crystal is an antiferromagnetic (AFM) substance, which in principle can be found in three different AFM

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configurations: $---+$, $--+$ and $---+$, where “+” and “-” denotes spin α and spin β atomic state, respectively. In one of our previous works [17] we found that the equilibrium magnetic configuration of this material in its pure state is the AFM $---+$ configuration. The computed magnetic moment for this configuration was found to be equal to $2.92\mu_B/\text{Cr}$, which is very close to the corresponding experimental value of $2.76\mu_B/\text{Cr}$ [1]. The optimum volume for the equilibrium state was found to be equal to 97.5 \AA^3 , which is in concordance to the experimental findings of 96.5 \AA^3 [18].

The $\alpha\text{-Cr}_2\text{O}_3$ has a classification as an intermediate-type insulator being placed in between the charge-transfer insulator and the Mott–Hubbard insulator. This is supported by photoemission and electron-energy-loss spectroscopy studies [19] as well as X-ray photoemission experiments [20]. Because of this fact, it is necessary to take into account that the DFT–GGA describes inappropriately the strong Coulomb repulsion between the d electrons localised on metal ions. One way to correct this deficiency is through the use of an intra-atomic interaction for the strongly correlated electrons by an unrestricted Hartree–Fock (UHF) approximation, resulting in the so-called DFT+ U method [21,22]. The corresponding equations describing this approach can be found elsewhere [23]. A number of important studies have been performed before to investigate $\alpha\text{-Cr}_2\text{O}_3$ crystal bulk and surfaces proving that DFT+ U leads to a significantly improved description of the structural, magnetic and electronic properties of the material compared to the standard DFT approach. Some examples include work of the influence of strong electronic correlation on main physical and chemical properties in chromium oxide [24], investigation of electronic structure and magnetism in corundum-type Cr_2O_3 [25], calculation of adsorption of different species on the chromium oxide (0 0 0 1) surfaces [26,27]. In our research we employed $U=4 \text{ eV}$ as a proper value for our system ($J=0$ has been utilised throughout the study). Thus, our DFT+ U modification provides a band-gap width value being equal to 3.21 eV , which is really very close to the experimental figure of 3.3 eV [1,2] and also agrees well with 3.0 eV band-gap width found in Ref. [24]. Density of states (DOS) for the AFM $---+$ magnetic state is depicted in Fig. 1. The upper valence band (VB) is dominated by the Cr 3d states, with some admixture of the O 2p states, whereas the bottom of the conduction band (CB) is almost completely formed by the Cr 3d states. These results are in complete concordance to another available reports [24,28] on band structure properties. Please note that results in Ref. 28 were obtained by different theoretical approach. Finally, we can state that U approximation has to be used even in case of the all-electron full-potential linearised augmented plane wave method as implemented in the WIEN2K computer code [29].

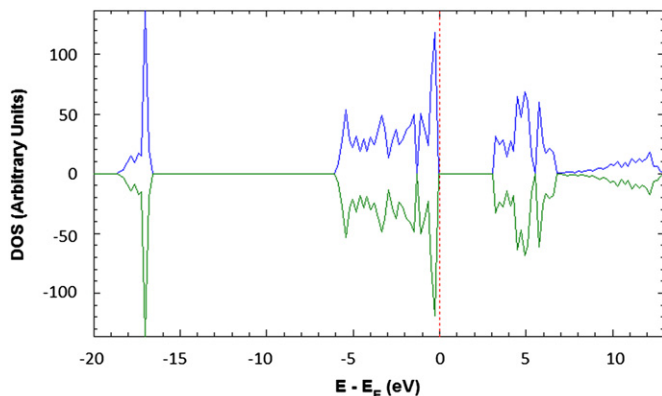


Fig. 1. DFT+ U computed DOS for the AFM $---+$ state. The dotted line marks the Fermi level (E_F).

Recently performed studies of chromium oxide [30] by the WIEN2K computer code shows that using an additional on-site Coulomb interaction with $U=4.5 \text{ eV}$ and $J=1.0 \text{ eV}$, it is feasible to obtain experimental band-gap width in the $\alpha\text{-Cr}_2\text{O}_3$ material.

3. Results and discussion

3.1. Geometry of Ca-doped $\alpha\text{-Cr}_2\text{O}_3$

In order to study Ca impurity in the $\alpha\text{-Cr}_2\text{O}_3$, 10-atom primitive unit cell was expanded eight times ($2 \times 2 \times 2$ extension) resulting in 80-atom supercell, and the MP k -point mesh of $4 \times 4 \times 4$ was applied for the new cell. Due to large size of supercell used throughout the Ca-impurity computations, the closest distance between two Ca impurities are equal to 10.75 \AA . Thus we eliminate the possibility of any mutual Ca–Ca interaction within the chromium oxide crystal. In order to be completely sure of isolated point defect model, we performed some extra computations using a 120-atom supercell being constructed from the hexagonal unit cell of the chromium oxide with $a+b$, $a-b$, c lattice vectors and exploiting the MP k -point mesh of $4 \times 5 \times 3$. Results obtained from the 120-atom supercell were identical to those of the 80-atom system. Therefore, we can state that a single-point defect within a periodic computational model has been used throughout the present work. As a consequence of such an approach, the incorporated defect produces only local effects on both structural and electronic properties of a given crystal.

As a result of Ca atom inclusion in the otherwise pure $\alpha\text{-Cr}_2\text{O}_3$ structure, the atoms in its neighbourhood have tendency to displace themselves in order to find their new equilibrium positions. Full lattice relaxation was allowed, which included also possible volume changes for the supercell. It is necessary to state that each Cr atom has six O atoms in its vicinity, three at 1.97 \AA distance, and the other three at 2.03 \AA distance (Table 1, Figs. 2 and 3). There are two types of Cr atoms characterised by the magnetic moment, i.e. first kind of Cr atoms has a positive magnetic moment (case A) while another one has a negative magnetic moment (case B). Thus, two separate cases have to be taken into consideration to study impurity doping in the $\alpha\text{-Cr}_2\text{O}_3$ crystalline lattice.

In case A of the supercell, i.e. when the Ca atom replaces for a Cr atom possessing a positive magnetic moment, the O atoms have a tendency to increase their initial distances with respect to the impurity as it is shown in Table 1 and Fig. 3. In order to explain the reason of these motions, the Bader charge analysis [31] has been carried out. Through the employment of this

Table 1

Charges on atoms obtained by the Bader population analysis for the perfect (Q_1) and Ca-doped (Q_2) $\alpha\text{-Cr}_2\text{O}_3$ crystal. The initial distance to the impurity (R_1) and the atomic displacements (ΔR) for the atoms within the defective region are also shown. Positive atomic displacements stand for the defect-outward movements. The atomic numeration corresponds to the one indicated in Fig. 3.

Atom	Q_1 (e)	Q_2 (e)	R_1 (Å)	ΔR (Å)
Ca (1)	–	1.46	–	–
O (2)	–1.12	–1.14	1.97	0.11
O (3)	–1.12	–1.14	1.97	0.14
O (4)	–1.12	–1.10	1.97	0.12
O (5)	–1.12	–1.09	2.03	0.28
O (6)	–1.12	–1.13	2.03	0.24
O (7)	–1.12	–1.13	2.03	0.28
Cr (8)	1.69	1.66	2.68	0.19
Cr (9)	1.69	1.79	2.90	0.07
Cr (10)	1.69	1.68	2.90	0.06
Cr (11)	1.69	1.78	2.90	0.06

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