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Local structure, magnetic and electronic properties of *N*-doped α-Cr_2O_3 from the first-principles

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ABSTRACT

First-principles calculations based on the density functional theory (DFT) within the generalized gradient approximation (GGA) have been used to study the defective α-Cr_2O_3 crystal. Structural, electronic and magnetic properties have been investigated in the periodic crystalline structure containing one and/or two *N* impurities. Local structure of defective region reveals a polarization around the impurity due to the atomic distortions. Presence of the *N* atom reduces the band-gap width of the material. The dopant might induce a local energy state within the band-gap region for some specific impurity concentrations. Discovered changes upon the magnetic properties imply that chromium oxide might not act as an antiferromagnetic substance in the presence of *N* imperfection.

1. Introduction

The corundum-type chromium oxide, α-Cr_2O_3, is of great interest, both from a scientific and a technological point of view. Chromium oxide is an important catalyst and a major constituent in many ceramics. The formation of a protective Cr_2O_3 overlayer is thought to be an important element in the corrosion resistance of Cr steels. It has a wide range of applications such as solar thermal energy collectors, black matrix films, liquid crystal displays [1,2], as well as protective layers against corrosion and wear resistance of stainless steel and adhesion promoters [3]. α-Cr_2O_3 has been also employed in spintronic devices like non-volatile magnetoelectric memories [4,5]. Another attractive employment of the material is its consideration as an electrochromic material.

From a theoretical point of view, the main interest in this compound lies in the role of strong electronic correlation which determines its physical properties. It is an antiferromagnetic (AFM) insulator forming borderline case between the charge transfer and Mott–Hubbard insulators [6]. It is well known that density functional theory (DFT) experiences considerable difficulties when trying to achieve a correct description of such strongly correlated materials. However, whereas transition metal monoxides have received a lot of attention as a paradigmatic case for studying strong electronic correlations [7], it is still current practice to treat the corundum-type transition metal oxides using standard DFT [8–11]. In our mind, the introduction 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 [12,13], is a way to correct major deficiencies in describing the strong repulsion between the *d*-electrons localized on metal atoms. We acquired very good results previously [14,15] by applying DFT + *U* approximation for the chromium oxide.

On the other hand, properties of materials and compounds are often controlled by the presence of various types of defects and lattice imperfections. Alterations produced by the point defects in a given crystal could be of structural, electronic, optical or magnetic nature. Understanding the behavior of point defects and impurities is essential for successful applications of any material. Nitrogen is of special importance for a number of applications based on the chromium oxide compounds. α-Cr_2O_3 thin films containing low nitrogen content exhibit better corrosion behavior in relation to their local structure [16]. Moreover, the resistivities of the samples are found to increase with *N* dopant due to decrease in the number of metallic bonds in the coating. *N* impurity doping produces stability improvement for the hole-transporting layer of organic solar cells based on amorphous chromium oxide [17]. Poorly conducting α-Cr_2O_3 compound when co-doped with magnesium and nitrogen produces transparent conductive oxide with a high performance [18]. It is believed that *N* atom incorporation enhances the specular transparency of the α-Cr_2O_3 films in the visible range of light. These and other facts point out the significance of *N* impurity

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incorporation in the chromium oxide and ask for the necessity to study the *N*-doped α-Cr_2O_3 at the fundamental quantum-mechanical scale. The purpose of our work is to understand better at the fundamental level the effects which *N* impurity incorporation might produce upon different features of chromium oxide thus helping to use this material more efficiently.

2. Methodology

Present study has been carried out using first-principles DFT approach as implemented in the Vienna *ab initio* Simulation Package (VASP) [19,20] and the generalized gradient approximation (GGA) [21]. The projector augmented wave (PAW) pseudo-potentials as proposed by Blöchl [22] and adapted by Kresse and Joubert [23] are utilized in our investigation.

A cut-off kinetic energy of 500 eV is used which allows convergence of the total energy to less than 1 meV/atom. Γ-centered 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-Cr_2O_3. Previously mentioned parameters have been obtained through the atomic relaxation until all the forces are found to be smaller than 0.008 eV/Å. 80-atom supercell has been employed to calculate *N* impurity with the corresponding MP *k*-point mesh being equal to 4 × 4 × 4.

Chromium oxide crystal is an AFM substance, which in principle can be found in three different AFM configurations: − − + +, − + + − and − + − +, where "+" and "−" denotes spin α and spin β for each one of the four Cr atoms, respectively. In our previous work [14] we encountered that the equilibrium magnetic configuration of primitive 10-atom unit cell in its pure state is the AFM − + − + configuration. The method to obtain the correct magnetic alignment consisted in the minimization of total energy of the system as a function of volume, and different spin states, α and β, have been considered for each one of the four Cr atoms entering the primitive unit cell of α-Cr_2O_3. Detailed description of the methodology to search for the equilibrium magnetic alignment for corundum-type crystals is given in our previous works [14,24]. Computed value of the magnetic moment for this configuration was found to be equal to 2.92 μ_B/Cr, which is very close to the corresponding experimental number of 2.76 μ_B/Cr [25]. The optimal volume for the equilibrium state was found to be equal to 97.5 $Å^3$ for the primitive unit cell of the rhombohedral α-Cr_2O_3, which is in a close concordance to the experimental findings of 96.5 $Å^3$ [26].

Due to the fact that Cr atoms possess *d*-electrons, it is necessary to remember that the DFT–GGA approach describes inappropriately the strong Coulomb repulsion between the *d* electrons localized on metal ions. One way to correct this deficiency is through the use of an intra-atomic interaction for the strongly correlated electrons by the UHF approximation resulting in the so-called DFT + *U* method [13]. The corresponding mathematical equations describing this approach can be found elsewhere [27]. A number of important studies have been performed so far to investigate α-Cr_2O_3 crystal bulk and surfaces and to prove that the DFT + *U* leads to a significantly improved description of the structural, magnetic and electronic properties of the material compared to the standard DFT approach. In our research we employed *U* = 4 eV as a proper value for our system (*J* = 0 has been utilized throughout the study), which was obtained in our previous computations [14,15,28]. DFT + *U* modification provides a band-gap width value being equal to 3.21 eV, which is really close to the experimental figure of 3.3 eV [25,29]. Total density of states (DOS) for the AFM − + − + magnetic state is depicted in Fig. 1. Partial DOS (Fig. 2) shows that lower valence band (VB) is due to the O 2*s* atomic orbitals (AOs), the upper VB is composed predominantly by the Cr 3*d* and O 2*p* states,

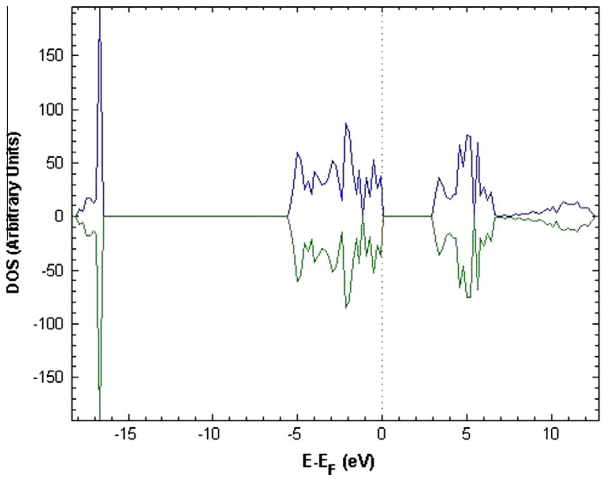

Fig. 1. DFT + *U* computed total DOS for pure chromium oxide considering energy-minimum AFM − + − + state. The dotted line marks the Fermi level (E_F).

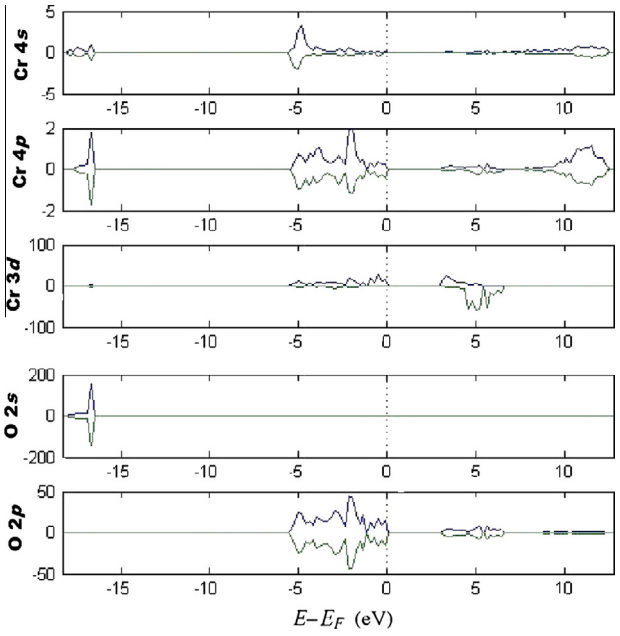

Fig. 2. DFT + *U* computed partial DOS for pure chromium oxide taking into consideration the AFM − + − + magnetic state. Main contribution from the Cr atoms, Cr 3*d* states, is found within the upper VB and the CB bottom, while the O 2*s* and 2*p* AOs contribute heavily to the lower and upper VB regions, respectively. The dotted line marks the Fermi level (E_F).

whereas bottom of the conduction band (CB) is almost completely formed by the Cr 3*d* AOs. There is notable admixture of the Cr 4*s* and 4*p* states at the upper VB region as well as some adding of the O 2*p* states at the CB bottom. Results on total and partial DOS are in complete accordance to the other available reports [30,31] on the band structure properties.

3. Results and discussion

As mentioned above, 80-atom supercell has been employed to study *N*-doping in the corundum-type chromium oxide. The cell was obtained as an eight times symmetric extension (2 × 2 × 2) of the primitive α-Cr_2O_3 cell. One of the O atoms located in the middle of the supercell was replaced by an *N* atom. Due to a rather big size of the supercell, used throughout the *N*-impurity computa-