Quantum Chemical Study of Defective Chromium Oxide

Richard Rivera, Soraya Jácome, Frank Maldonado, Arvids Stashans

***Abstract*—Through the use of first-principles calculations based on the Density Functional Theory (DFT) within the Generalized Gradient Approximation (GGA), a study of the defective α-Cr_2O_3 crystal has been performed. Structural, electronic and magnetic properties due to Ti, Ca and N impurities have been studied in the periodic crystalline structure. Ti-doped supercell shows that the nature of the chemical bonding in the neighbourhood of the impurity turns into more ionic one; the microstructure of the defective region displays a tendency of atomic movements away regarding the Ti imperfection. A metallic state is observed implying the n-type conductivity. Similar atomic rearrangements are found in the Ca-doped α-Cr_2O_3 supercell. No local energy levels within the band-gap are observed in this case. In the case of N-doped crystal some atoms move towards the impurity whereas the rest of them move outwards. Presence of the N atom reduces the band-gap width of the material. Finally, there are notable changes upon the magnetic properties of doped α-Cr_2O_3 crystals implying that chromium oxide might not act as an antiferromagnetic substance.**

***Index Terms*—α-Cr_2O_3, DFT, Impurity doping, Microstructure**

I. INTRODUCTION

Chromium oxide (α-Cr_2O_3) 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. It has a number of important applications, such as catalysts, solar thermal energy collectors black matrix films, liquid crystal displays, protective layers against corrosion and wear resistance of stainless steel and adhesion promoters [1]. Another attractive exploitation of the material is that the α-Cr2O3 thin films are being considered as electrochromic materials.

On the other hand, properties of materials and compounds are often controlled by defects and impurities. Alterations produced by the presence of point defects in a given compound could be of structural, electronic, optical or magnetic nature. Understanding the behaviour of point defects and impurities is essential to the successful application of any material. Purpose of the present work is to understand better at the fundamental quantum level the effects which N, Ti and Ca impurities incorporation might produce upon different features of chromium oxide thus helping to use this material more efficiently.

II. METHODOLOGY

The calculations have been carried out using *ab initio* DFT approach as it is implemented in the Vienna *ab initio* Simulation Package (VASP) [2] within the generalized gradient approximation (GGA) [3]. The projector augmented wave (PAW) pseudopotentials as proposed by Blöchl [4] and adapted by Kresse and Joubert [5] were utilized 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 6x6x6 for the 10-atom primitive unit cell of the rhombohedral α-Cr_2O_3. The previously mentioned parameters were obtained through the atomic relaxation until all the forces are less than 0.008eV/Å.

Principal magnetic configurations have been taken into consideration in order to find out the equilibrium ground state configuration of pure α-Cr_2O_3 crystal. The considered magnetic states for the crystal were the following: antiferromagnetic (AFM) --++, AFM -++-, AFM -+-+ and ferromagnetic FM ++++ configurations. It was found that the most favourable case is the one corresponding to the AFM -+-+ state. The detailed results of pure crystal calculations for different magnetic configurations were obtained before and can be found elsewhere [6,7].

α-Cr_2O_3 is an antiferromagnetic insulator forming borderline case between a charge transfer and Mott-Hubbard insulator. It is well known that density functional theory (DFT) experiences considerable difficulties when trying to achieve a correct description of such strongly correlated materials. 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 approximation, resulting in the so-called DFT+U method [8]. The corresponding equations describing this approach can be found elsewhere [9]. One of the significant corrections being provided by the DFT+U is a partial improvement for the band-gap width, which is underestimated by the standard DFT method. After testing some values for the U parameter corresponding to the d electrons of Cr atom, finally a value of U = 4 eV was obtained as a proper one for pure α-Cr_2O_3

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system (J = 0 has been utilised throughout the study). U parameter for the Ti 3d electrons were fitted before by Çelic *et al.* [10] and found equal to 4.5eV, which was adopted for the present work.

The equilibrium structural parameters have been computed by fitting the total energy of the system within a wide range of volumes. The optimum volume was found to be equal to 97.5 Å^3, which is close to the experimental findings of 96.5 Å^3 [11]. In order to study Ti, Ca and N impurities, 10-atom primitive unit cell was expanded eight times (2 x 2 x 2 extension) resulting in 80-atom supercell, and the MP k-point mesh of 4x4x4 was applied for the new cell.

III. RESULTS AND DISCUSSION

A. *Ti-doped α-Cr2O3*

Ti doping was done by replacing one of the lattice central host Cr atoms by the impurity. Due to the Ti atom inclusion in otherwise pure α-Cr_2O_3 structure, the atoms in its neighbourhood have tendency to displace themselves in order to find their new equilibrium positions. It was allowed both atomic and cell relaxation, but only defect nearest atomic shifts were encountered while the lattice parameters as well as cell volume remained unchanged due to Ti introduction. It is necessary to state that each Cr atom has six O atoms in its vicinity, three at 1.97 Å distance, and the other three at 2.03 Å distance (Table I, Fig. 1). There are two types of Cr atoms characterized by their magnetic moment, i.e. the first type of Cr atoms has a positive magnetic moment (case A) while the second one has a negative magnetic moment (case B). So, two separate cases have to be taken into consideration in order to study impurity doping in chromium-sublattice of the α-Cr_2O_3 crystalline structure. Nevertheless, it was found that results are practically identical for both doping options. It was found that O atoms have a slight tendency to increase their initial distances with respect to the impurity. In order to explain the reason of these motions, the Bader charge analysis [12] has been carried out. However, in order to understand better the atomic relaxation we also need to consider size of the atoms. The atomic radius of the Ti atom, 1.47 Å, is bigger than the corresponding number of replaced Cr atom, 1.27 Å. Consequently the impurity requires more space than the replaced chromium producing that the defect-closest O atoms move outwards with respect to the impurity. These movements practically are compensated by the Coulomb electrostatic attraction between the same O atom and the Ti atom. That is true since the Ti atom owns a bigger positive charge, +2.02 e, compared to that of the replaced Cr atom, +1.69 e, and one also has to consider the charge increase on the O atoms (Table I). That explains why the rearrangement of O atoms is rather small. It is important to note that not all of the O atoms displace themselves by the same distance. The defect-farthest O atoms, O (5), O (6) and O (7) atoms, move by a larger quantity than the closest ones. This behaviour could be explained again by the increase of electrostatic attractive interaction between the mentioned defect-closest O atoms and the impurity itself preventing the O (2), O (3) and O (4) atoms from larger shifts. In the case of Cr atoms we obtain defect-outward displacements due to the increase in the Coulomb electrostatic repulsion. Besides, Cr atoms are closer to the O atoms than to the impurity. So, they are attracted stronger to the O atoms, which are moving outwards with respect to the impurity. That is why Cr atoms are trying to preserve their initial distances with their neighbouring O atoms and displace themselves outwards from the Ti atom. One can notice that the Cr (8) atom has the largest shift from its initial placing, but it is also worth mentioning that this particular Cr atom is surrounded by the O atoms, O (5), O (6), and O (7) atoms (Table I, Fig. 1), which also display largest shifts. Thus this particular Cr atom behaves according to our explanation.

TABLE I.
CHARGES AND DISPLACEMENTS

Atom	Q1 (e)	Q2 (e)	ΔR (Å)
Ti (1)	–	2.02	–
O (2)	-1.12	-1.23	0.01
O (3)	-1.12	-1.22	0.03
O (4)	-1.12	-1.22	0.04
O (5)	-1.12	-1.22	0.06
O (6)	-1.12	-1.22	0.06
O (7)	-1.12	-1.21	0.07
Cr (8)	1.69	1.78	0.07
Cr (9)	1.69	1.78	0.02
Cr (10)	1.69	1.78	0.02
Cr (11)	1.69	1.78	0.03

Charges on atoms obtained by the Bader population analysis for the perfect (Q1) and Ti-doped (Q2) α-Cr_2O_3 crystals. The atomic displacements (ΔR) regarding the impurity for atoms within the defective region are also shown. Positive atomics displacements stand for the defect-outward movements. The atomic numeration corresponds to the one indicated in Fig. 1.

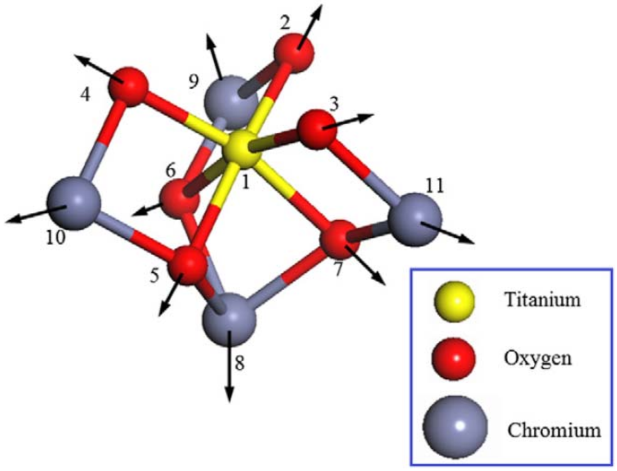

Fig. 1. Atomic displacements in the α-Cr2O3 crystalline lattice in the neighbourhood of the Ti dopant. Both Cr and O atoms have a tendency to move outwards with respect to the defect.

Fig. 2 displays the total density of states (DOS) for the Ti-doped chromium oxide. Introduction of Ti atom does not produce any local energy level within the band-gap of material. However, it is possible to observe that the Fermi level shifts to the bottom of the conduction band (CB). This implies that there is a free electron in the CB ensuring the n-

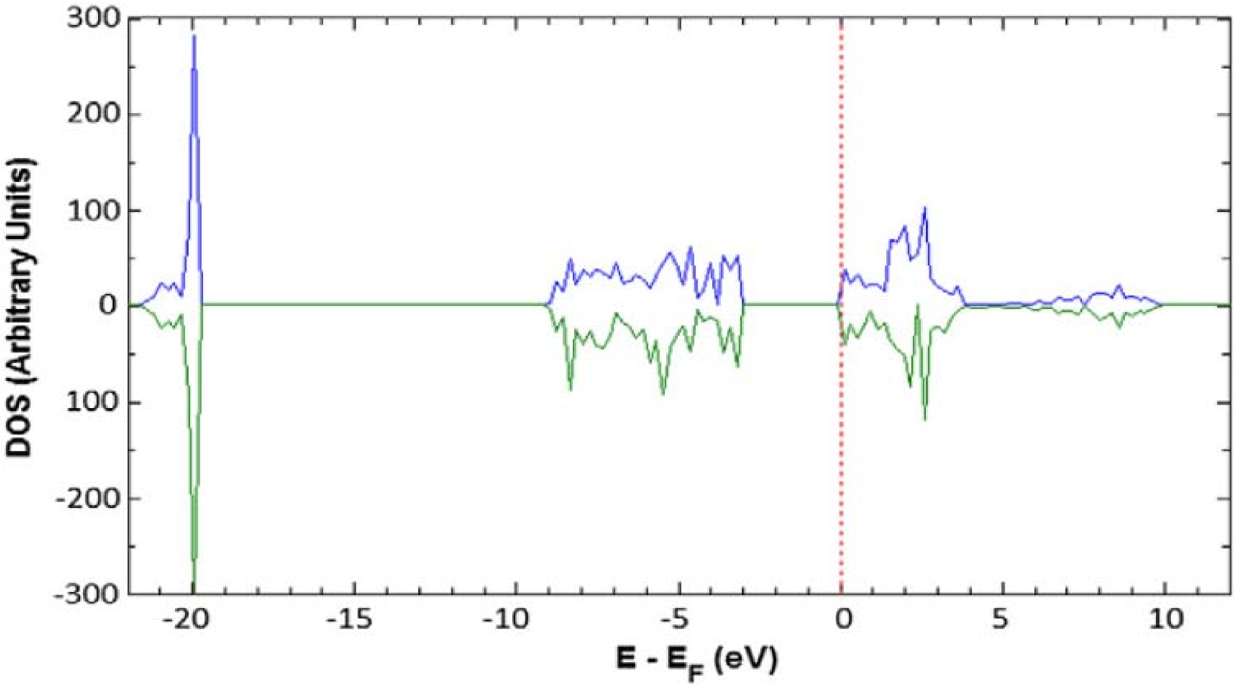

Fig. 2. DFT + U (U = 4 eV) computed total DOS for the AFM -+-+ state considering the case if Ti impurity replaces for a Cr atom possessing positive magnetic moment. The dotted line marks the Fermi level (E_F).

type electrical conductivity in agreement with the available experimental results [13].

Ti incorporation leads to the occurrence of a local magnetic moment in the chromium oxide lattice. In pure α-Cr_2O_3 crystal each Cr atom has a magnetic moment of $2.92\mu_B$. The impurity incorporation into the material affects the total magnetisation of supercell since Ti atom possesses a smaller magnetic moment, $0.88\mu_B$. In fact, the supercell magnetic moment after the doping is found to be equal to $-1.99\mu_B$. The major contribution to this value comes from the Cr atoms. Nevertheless, some non-negligible admixture towards the supercell magnetic moment is due to the O atoms.

B. *Ca-doped α-Cr2O3*

Ca impurity doping was done in a similar manner as described above Ti-doping. Again, full lattice relaxation was allowed, which included also possible volume changes for the supercell. General pattern of atomic movements resembles the one obtained previously (Fig. 1). However, we found that values of atomic displacements are larger (Table II) which might be due to the fact that Ca atom possesses a smaller positive charge, +1.46 e, than the replaced host Cr atom, +1.69 e.

Brief analysis of the electronic properties shows that Ca impurity incorporation does not produce any significant changes upon the DOS pattern. There are only some redistribution of electronic states within the upper valence band (VB) and CB.

Ca incorporation does lead to the occurrence of a local magnetic moment in the chromium oxide crystal because Ca atom initially possesses a negligible magnetic moment, $0.01\mu_B$. In fact, the supercell magnetic moment after the doping is found to be equal to $-1.99\mu_B$. The contributions to this value come not only from the Cr atoms. In particular, the defect-closest O atoms contribute with an amount of $0.30\ \mu_B$ towards the total magnetic moment and the other O atoms have slight contributions too. The important issue is related to the dopant influence on energetics of different magnetic configurations. We have performed calculations of Ca impurity incorporation not only in already described AFM-+-+ configuration, but also for AFM --++, AFM -++- and FM magnetic systems. As a result, we found that both AFM --++ and AFM -++- configurations have considerably higher energy whereas the FM state unexpectedly becomes the ground state configuration for the Ca-doped α-Cr_2O_3. According to our computations the FM state has 1.63 eV lower energy compared to the AFM -+-+ configuration. That implies, that α-Cr_2O_3, if doped with Ca impurity, does not behave any more as an AFM substance, it becomes ferromagnetic.

TABLE II.
CHARGES AND DISPLACEMENTS

Atom	Q1 (e)	Q2 (e)	ΔR(Å)
Ca (1)	–	1.46	–
O (2)	-1.12	-1.14	0.11
O (3)	-1.12	-1.14	0.14
O (4)	-1.12	-1.10	0.12
O (5)	-1.12	-1.09	0.28
O (6)	-1.12	-1.13	0.24
O (7)	-1.12	-1.13	0.28
Cr (8)	1.69	1.66	0.19
Cr (9)	1.69	1.79	0.07
Cr (10)	1.69	1.68	0.06
Cr (11)	1.69	1.78	0.06

Charges on atoms obtained by the Bader population analysis for the perfect (Q1) and Ca-doped (Q2) α-Cr_2O_3 crystal. The atomic displacements

(ΔR) for the atoms within the defective region are also shown. Positive atomics displacements stand for the defect-outward movements. The atomic numeration corresponds to the one indicated in Fig. 1.

C. *N-doped α-Cr2O3*

Introduction of N atom in the 80 atom supercell is done by replacing one of the supercell central O atoms by an N impurity. That leads to atomic relaxation in the vicinity of defect. According to our calculations (Table III, Fig. 3), Cr (2) and Cr (4) atoms reduce their initial distance with respect to the N impurity. Meanwhile, Cr (3) and Cr (5) atoms move away from it. Computed Bader charges show that the charge of the N atom, -1.06 e, is very similar to one of the replaced O atoms, -1.13 e implying small values of atomic shifts. Electron density redistribution, most likely from Cr *d* orbitals has to be taken into consideration in order to elucidate better the relaxation of Cr-sublattice. The movements of O atoms are rather irregular as well. Analysis of the positions of O atoms might shine some light on the local microstructure changes. The reason of peculiar O atoms motions is related to their chemical bonds with the neighbouring Cr atoms. Each Cr atom has four O atoms surrounding them in an almost perpendicular plane to the impurity. From these O atoms, two of them have a trend to reduce their initial distance regarding the N atom, while the other two tend to increase the atomic separation. The bonds between the Cr atoms and O atoms resemble the *d* type atomic orbitals, and the previously mentioned electron density redistribution might explain these movements.

TABLE III.
CHARGES AND DISPLACEMENTS

Atom	Q1 (*e*)	Q2 (*e*)	ΔR(Å)
N (1)	-	-1.06	-
Cr (2)	1.70	1.27	0.03
Cr (3)	1.69	1.69	-0.15
Cr (4)	1.70	1.57	0.12
Cr (5)	1.69	1.65	-0.03
O (6)	-1.13	-1.12	0.10
O (7)	-1.13	-1.13	-
O (8)	-1.13	-1.12	0.04
O (9)	-1.13	-1.14	-0.08
O (10)	-1.13	-1.16	-0.07
O (11)	-1.13	-1.13	-
O (12)	-1.13	-1.14	0.10
O (13)	-1.13	-1.14	-0.10
O (14)	-1.13	-1.10	-0.13
O (15)	-1.13	-1.10	-0.01
O (16)	-1.13	-1.09	0.09

Charges on atoms obtained by the Bader population analysis for the perfect (Q1) and N-doped (Q2) α-Cr$_2$O$_3$ crystals. The atomic displacements (ΔR) regarding the impurity for atoms within the defective region are also shown. Positive atomics displacements stand for the defect-outward movements. The atomic numeration corresponds to the one indicated in Fig. 3.

Fig. 4 shows total DOS pattern for the N-doped α-Cr$_2$O$_3$. Main N atom contributions are towards the top of the VB. The band-gap width is found to reduce from 3.21 eV (pure crystal) up to 3.09 eV (N-doped chromium oxide).

Introduction of the N atom produces some magnetic perturbations leading to the total magnetic moment of supercell being equal to +0.84 μ_B. The impurity has a contribution itself of +0.29 μ_B, and the impurity-closest Cr atom, the Cr (5) atom, reduces its magnetic moment from -2.92 μ_B to -2.57 μ_B. Small contributions of the O atoms towards the total magnetic moment is also observed.

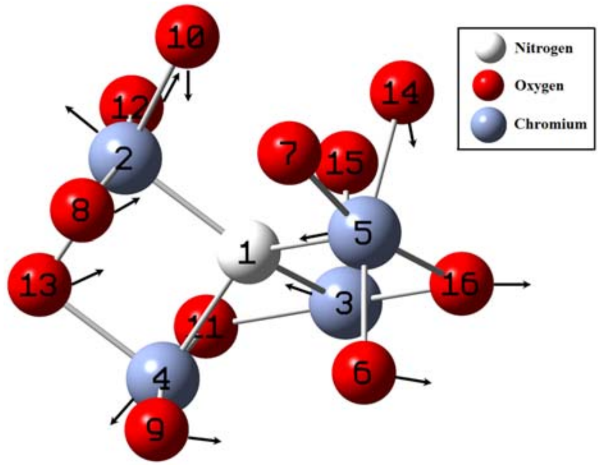

Fig 3. Atomic displacements in the α-Cr2O3 crystalline lattice in the neighbourhood of the N dopant.

IV. CONCLUSIONS

A quantum–mechanical study of impurity doped α-Cr$_2$O$_3$ crystals has been carried out using the first principles DFT within the GGA+*U* approach. The work allows getting a better idea of effects produced by some dopants upon the structural, electronic electrical and magnetic features of the material.

Calculated magnetic states as a function of volume for pure α-Cr$_2$O$_3$ material demonstrate the necessity of using an intra-atomic interaction for the strongly correlated *d* electrons, i.e. DFT+*U* approach, in order to give a reasonable description of such a system. The AFM-+-+ configuration has been found to be the ground state magnetic arrangement. The electronic band structure and the band-gap width being equal to 3.21 eV imply that the α-Cr$_2$O$_3$ crystal is an intermediate-type insulator between the charge transfer and Mott–Hubbard insulators. These obtained features are in close agreement with the available experimental data.

The revealed microstructure around the Ti defect consists in defect-closest atom displacements away with respect to the Ti impurity. The character of chemical bonding tends to become more ionic according to the obtained Bader population analysis. Ti impurity incorporation produces a local energy level within the band-gap of the material if Ti replaces for a Cr atom initially possessing a negative magnetic moment. This state is found for the β spin sub-system and is composed mainly of the Ti 3*d* atomic orbitals. Ti substitution for a Cr atom having either positive or negative magnetic moment, i.e. for both cases, yields a metallic state with the Fermi level position at the bottom of the CB. Free electron in the CB contributes towards the n-

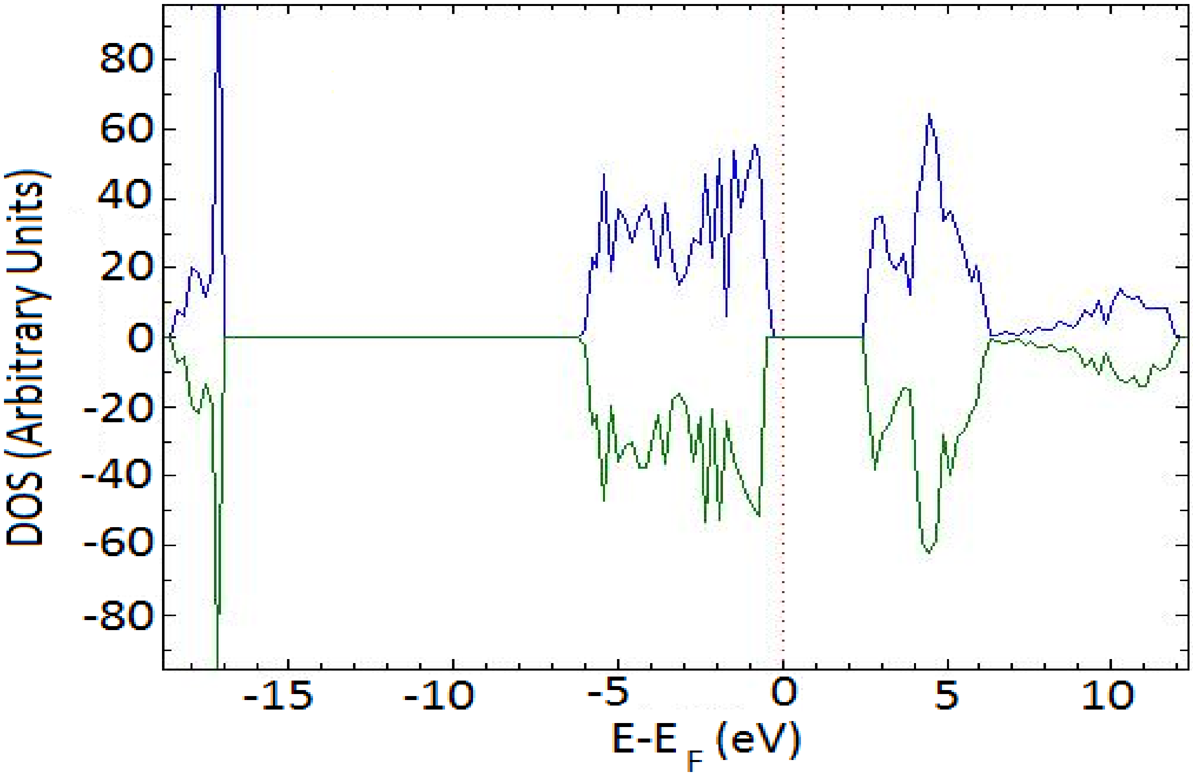

Fig. 4. DFT+U computed DOS for the AFM -+-+ state considering the case if N impurity replaces for a O atom. The dotted line marks the Fermi level (E_F).

type electrical conductivity in the material. Ti atom introduction leads to the occurrence of the local magnetic moment being equal to -1.99 μ_B. In both cases the main contribution towards the magnetic moment is because of the defect-neighbouring Cr atoms. Nevertheless, admixture of the nearest O atoms is not negligible and Ti defect itself contributes around 0.88 μ_B towards the total magnetic moment of the supercell.

Regarding the introduction of Ca impurity, we might state that computed atomic displacements around the single point defect shows the significance of ionic nature in the chemical bonding between the atoms. This is consistent with the calculated charges on atoms obtained by the Bader population analysis. Ca impurity incorporation does not produce any local one-electron energy levels within the gap between the upper valence band and the conduction band. Nevertheless, we observe the reduction in band-gap width by approximately 0.2 eV in case of the AFM -+-+ configuration and 0.4 eV for the FM arrangement. Additionally, some local-character changes within the band structure are observed. Ca atom introduction leads to the occurrence of the local magnetic moment being equal to -1.99μ_B with the main contribution towards the magnetic moment due to the defect-neighbouring Cr atoms. However, contribution of the nearest O atoms, found to be close to ±0.3μ_B, is not negligible. According to our outcomes, the Ca impurity incorporation produces the FM state being energetically favourable, 1.63eV, compared to the AFM -+-+ state. Thus the ground state configuration of the Ca-doped α-Cr2O3 is the FM arrangement.

If N-doped α-Cr_2O3 compound is analysed, the atomic displacements might be explained by a redistribution of the electronic density within the *d* atomic orbitals located on the Cr atoms. This redistribution affects the chemical bonding between Cr and O atoms located close to the N impurity. Presence of the nitrogen produces some contributions towards the top of the VB, with preference of the α spin. Also, the band-gap width is reduced due the N incorporation. The total magnetization of the crystal is affected when the N atom is introduced, which leads to a total magnetization being equal to +0.84 μ_B, with contributions from the impurity and its surroundings atoms.

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