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Defects in TiO_2 Crystals

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***Abstract*-TiO_2 crystals, anatase and rutile, have been studied using Density Functional Theory (DFT) and the Generalized Gradient Approximation (GGA). Also, the intra-atomic interaction term for strongly correlated d-electrons (DFT+U approximation) has been utilized for a proper description of the Ti d-electrons. The presence of some impurities in the otherwise pure crystal affects the structural, electronic and magnetic properties of the TiO_2. The presence of a Fe atom in the anatase structure produces shifts of the Ti atoms towards it whereas the majority of O atoms move away. Also, it exhibits n-type electrical conductivity. When a Sc atom is present in the same structure, Ti atoms are not moving while the O atoms move outwards with respect to the impurity. There are no changes in the electrical conductivity. In the case of Fe atom incorporation into the rutile structure, the host Ti atoms move towards the point defect and O atoms move outwards, obviously due to the electrostatic forces. The band-gap reduction has been observed for this particular case. Finally, the presence of a Sc atom in the rutile crystalline lattice produces a local microstructure with all defect-surrounding atoms displacing themselves outwards the defect, most due to the reduction of the charge in the defective region. A small band-gap reduction (14%) has been also found in this case.**

***Index Terms*—TiO_2; impurity doping; acceptor-type defect; physical properties.**

I. INTRODUCTION

Titanium dioxide (TiO_2) belongs to the transition metal oxides, and is one of the most studied materials. Its applications include heterogeneous catalysis, gas sensor devices, photo-catalysis, solar energy production, and some other ones [1, 2]. This material can be found in two different stable structures: rutile and anatase, each one with their own characteristics.

Properties of both structures of the TiO_2 crystal depend on different kind of defects and impurities that may be present in the materials. These defects could affect the structural, electronic, magnetic and optical properties of the TiO_2. In order to find other successful applications of this material, it is of necessity to try to understand the behaviour of impurities affecting its properties. The present work is an attempt to understand better what is happening at the fundamental quantum level in the crystals when there are some impurities, Fe and Sc atoms, present in the otherwise pure lattices.

II. METHODOLOGY

Calculations have been carried out through the use of the Vienna *ab initio* Simulation Package (VASP), software based on the DFT approach. The interaction between the core electrons and the valence electrons is implemented through the Projector Augmented Wave (PAW) method [4], and the Perdew–Burke–Ernzerhof (PBE) [5] GGA exchange-correlation functionals has been utilized throughout the investigation.

Calculations of anatase structure were carried out using a cut-off kinetic energy of 500 eV by converging the total energy of the system to less than 1meV/atom. Γ-centred Monkhorst-Pack (MP) grid with a 0.03 $Å^{-1}$ separation is applied, which corresponds to a *k*-point mesh of 9 x 9 x 4 for the 12-atom primitive unit cell of the anatase TiO_2. For the rutile structure, a cut-off kinetic energy of 450 eV was implemented by converging the total energy of the system to less than 1meV/atom. Γ-centred MP grid with a 0.04 $Å^{-1}$ separation is applied, which corresponds to a *k*-point mesh of 6 x 6 x 9 for the 6-atom primitive unit cell of the rutile TiO_2. The previously mentioned parameters were obtained through the atomic relaxation until all the forces are < 0.008 eV/Å, and the equilibrium state of the system is achieved.

DFT has some difficulties describing the strong correlation of Ti-*d* electrons, and, in order to take into account these issues, an intra-site Coulomb repulsion *U*-term has been included. Such an inclusion results in the so-called DFT+*U* method [6]. Some test calculations showed that $U = 3.5$ eV is the most appropriate value for our systems. This parameter has a strong effect on the band-gap width, which experimentally is 3.2 eV for anatase (calculated value is 2.72 eV) and 3.0 eV for rutile (computed value is 2.52 eV) [1]. Larger values of parameter *U* would allow to obtain band-gap width even closer to the experimental findings but would have a negative impact on the equilibrium structural parameters, so we did not enlarge further the magnitude of this parameter. The obtained lattice parameters are $a = 3.81$ Å and $c = 9.70$ Å for anatase and $a = 4.65$ Å and $c = 3.01$ Å for rutile, which are in very close concordance with the available experimental data [1].

Once all above-described computational parameters are found, the effects of Fe- and Sc-doping within both structures have been studied. In order to carry out the corresponding simulations, anatase primitive cell has been expanded nine times (3 x 3 x 1 expansion) resulting in 108-atom supercell with a *k*-point mesh being equal to 3 x 3 x 4. Similarly, the rutile structure has been expanded sixteen times (2 x 2 x 4 expansion), resulting in 96-atom supercell with a new *k*-point mesh being equal to 3 x 3 x 2.

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III. RESULTS AND DISCUSSION

A. *Fe-doped anatase*

One of the Ti atoms located in the central part of the crystal was replaced by a Fe atom. Once the Fe atom is incorporated in the structure, the atoms in its neighbourhood move themselves in order to find new equilibrium positions. Table I and Fig. 1 show the displacements of atoms, with Ti atoms moving towards the impurity and the O atoms having a trend to move outwards the imperfection, except for the O (10) and O (11) atoms. In order to explain these motions, Bader charge analysis [7] was carried out. The charge of the Fe atom is smaller than the replaced titanium, and the atomic charges on the Fe-surrounding Ti atoms have decreased. This means that the nature of the chemical bonding has become more covalent. Also, the covalent radius of the iron is smaller than that of the corresponding Titanium atom. In the case of O atoms, all of them has a decrease in their atomic charge, specially the O (10) and O (11) atoms. These two oxygens move towards the impurity position, contrary to the rest of the O atoms. Since both mentioned O atoms are positioned between Ti atoms (Fig. 1) they apparently try to preserve their initial distance regarding the titaniums, which are moving towards the impurity.

Calculated Density of States (DOS) pattern is shown in Fig. 2. The Fe atom has some contributions in the upper valence band (VB), especially for α spin sub-system, and also there are contributions in the conduction band (CB), mainly for β spin. The most important outcome is the presence of a local energy level just above the top of the upper VB. This result implies possible enhancement of electrical conductivity in the Fe-doped material. Analysis shows that this local state is hybridized with present contributions of the Fe 3*d* atomic orbitals (AOs) and O 2*p* AOs.

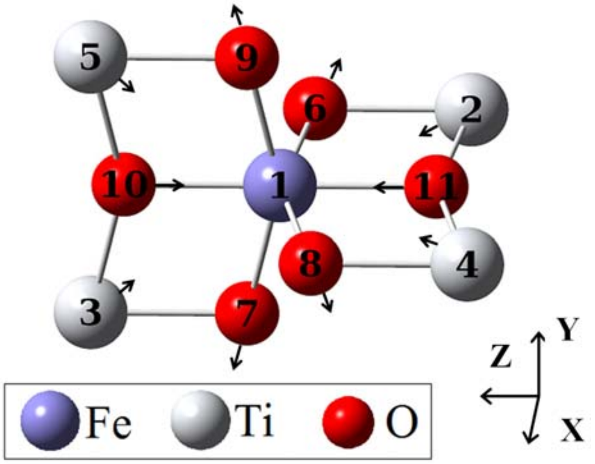

Fig. 1. Atomic displacements in the anatase crystalline lattice in the neighbourhood of the Fe dopant. Ti atoms move towards the impurity, O atoms move in the opposite direction except the O (10) and O (11) atoms.

Since the iron has magnetic properties its presence in the lattice leads to the occurrence of a local magnetic moment. In fact, the supercell magnetic moment after the doping is found to be equal to 3.94 μ_B. The major contribution to this value comes from the impurity, 3.7 μ_B, and some small contributions from Ti and O atoms too.

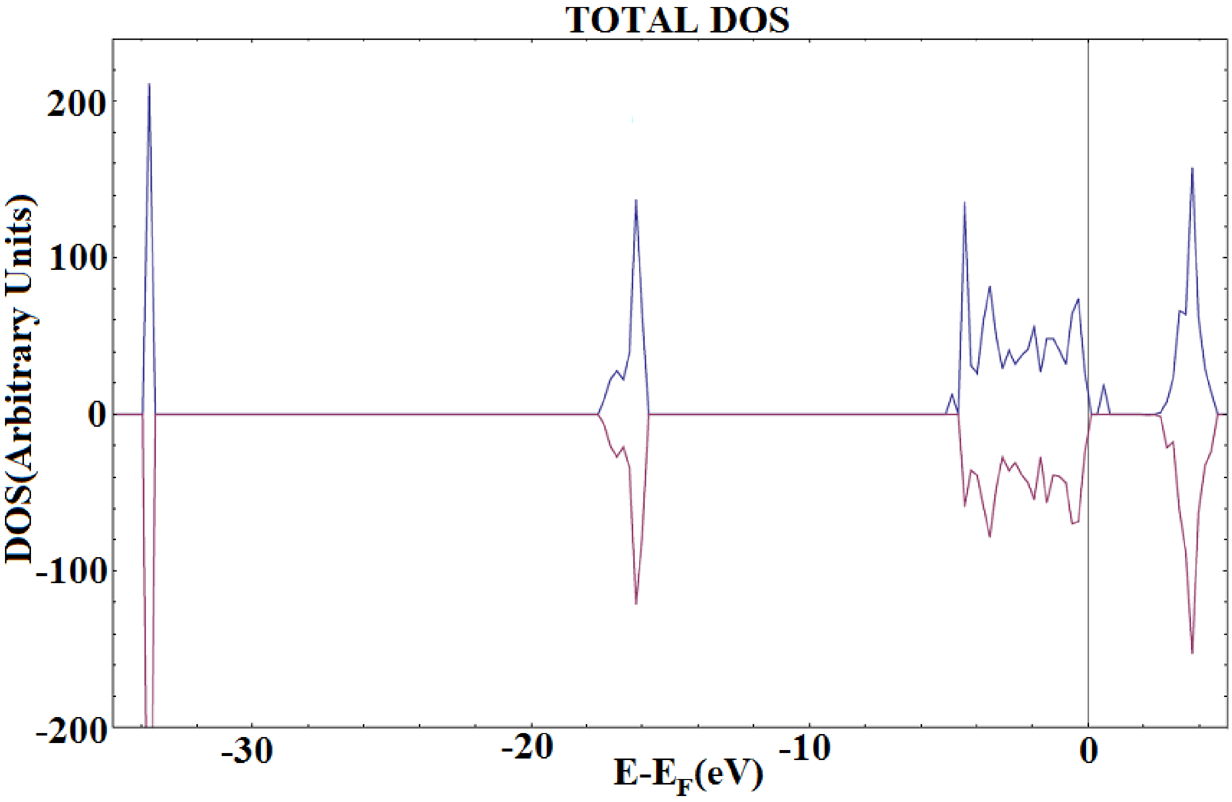

Fig. 2. Total DOS of the Fe-doped anatase structure. The vertical line marks the Fermi level (E_F).

TABLE I
CHARGES AND DISPLACEMENTS

Atoms	Q1 (e)	Q2 (e)	ΔR (Å)
Fe(1)	2.36	1.96	-
Ti(2)	2.36	2.13	-0.02
Ti(3)	2.36	2.11	-0.02
Ti(4)	2.36	2.13	-0.02
Ti(5)	2.36	2.11	-0.02
O(6)	-1.18	-1.07	0.02
O(7)	-1.18	-1.07	0.02
O(8)	-1.18	-1.07	0.02
O(9)	-1.18	-1.07	0.02
O(10)	-1.18	-0.95	-0.12
O(11)	-1.18	-0.96	-0.12

Charges on atoms obtained through the Bader population analysis for the perfect (Q1) and Fe-doped (Q2) anatase crystals, respectively. The atomic displacements (ΔR) regarding the impurity for 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. 1.

B. *Sc-doped anatase*

The substitution of a central Ti atom by a scandium produces a Sc-doped anatase crystal. The atoms in the surroundings of the impurity move in an attempt to find their new equilibrium positions. The movements of the atoms are shown in table II and Fig 3. It is possible to see that the Ti atoms conserve their initial distance with respect to the defect; meanwhile the O atoms move outwards it. The Bader charge analysis shows that the atomic charge on the impurity is smaller than that of the replaced Ti atom and the defect-neighbouring atoms have a small change in their charge value. The Coulomb attraction between the O atoms and the Sc impurity thus is smaller, and the O atoms move outwards the point defect.

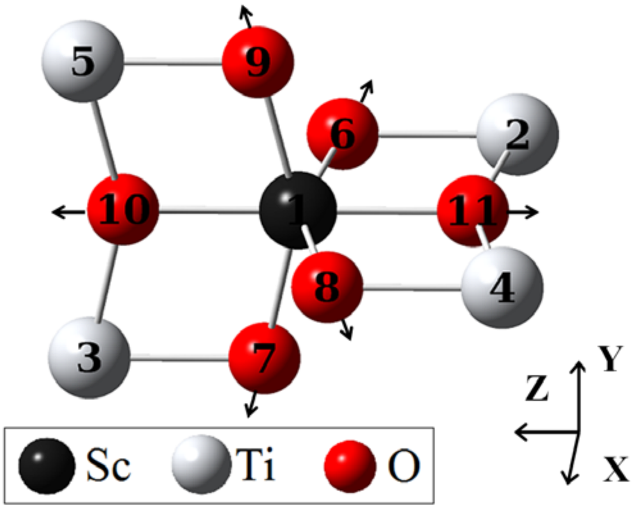

Fig. 3. Atomic displacements in the anatase crystalline lattice in the neighbourhood of the Sc impurity.

Analysis of the DOS pattern (Fig. 4) shows that the

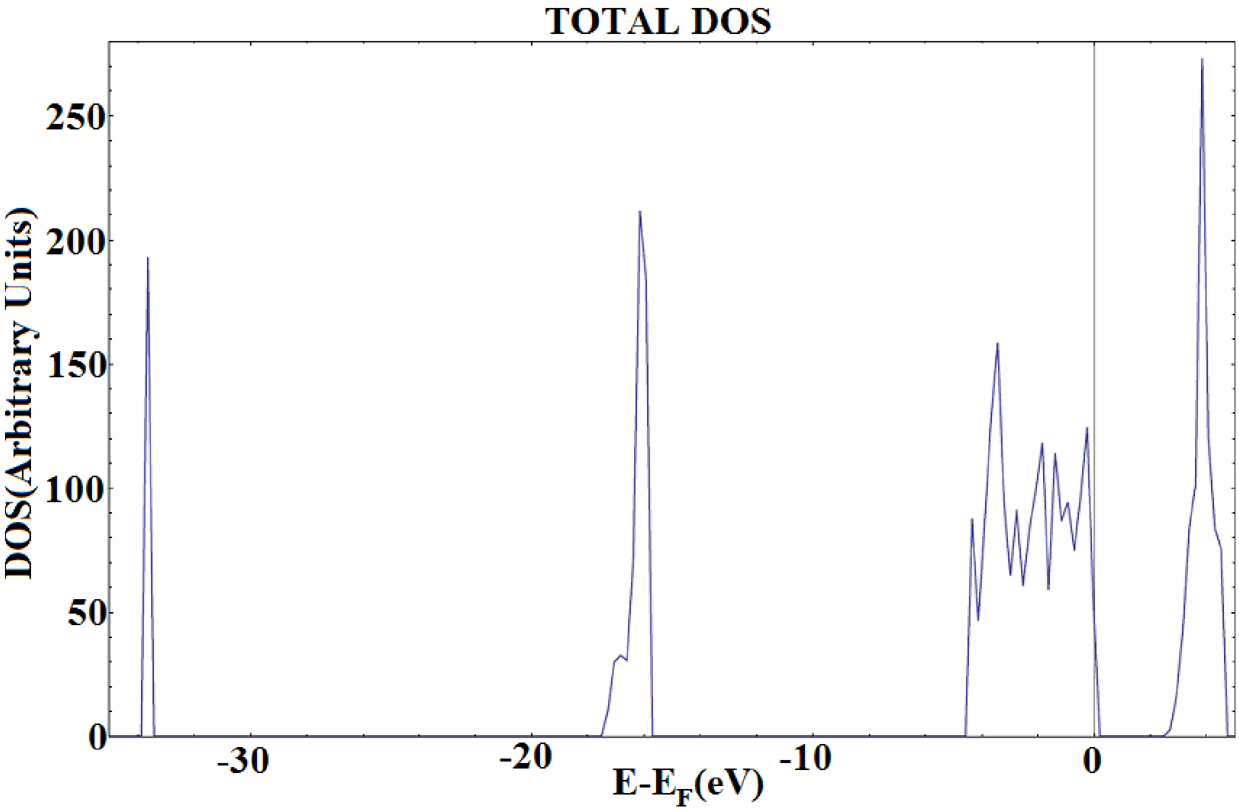

Fig. 4. Total DOS of the Sc-doped anatase structure. The vertical line marks the Fermi level (E_F).

presence of the Sc atom has no affected the energetic bands of the system. The impurity has some small contributions in the upper VB and the CB, but there is no any local energy level within the band-gap region. The width of the band-gap magnitude has not changed, which means that one should not expect any changes in the electrical conductivity of Sc-doped material.

TABLE II
CHARGES AND DISPLACEMENTS

Atoms	Q1 (e)	Q2 (e)	ΔR (Å)
Sc(1)	2.36	2.04	-
Ti(2)	2.36	2.32	-
Ti(3)	2.36	2.32	-
Ti(4)	2.36	2.32	-
Ti(5)	2.36	2.32	-
O(6)	-1.18	-1.16	0.08
O(7)	-1.18	-1.16	0.08
O(8)	-1.18	-1.16	0.08
O(9)	-1.18	-1.16	0.08
O(10)	-1.18	-1.17	0.13
O(11)	-1.18	-1.16	0.13

Charges on atoms obtained through the Bader population analysis for the perfect (Q1) and Sc-doped (Q2) anatase crystals, respectively. The atomic displacements (ΔR) regarding the impurity for 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.

C. *Fe-doped rutile*

Fe-doping in rutile was done in a similar manner as in anatase crystal described before. Table III and Fig. 5 show the movements of the defect-nearest atoms. The closest Ti atoms move slightly towards the impurity and the O atoms increase their initial bond lengths regarding the impurity. The Bader charge analysis shows that the charge on the Ti atoms is almost the same, and the atomic charge within the defective region is somewhat smaller than the corresponding value in the pure undoped material. Besides, the covalent radius of the Fe atom is smaller than that of the host Ti atom as explained before. That implies why the Ti atoms have moved closer to the impurity. The O atoms have reduced their initial charge, especially O (8) and O (9) atoms, and the Coulomb attraction between them and the impurity Fe atom has decreased. Hence, the O atoms move outwards the defect.

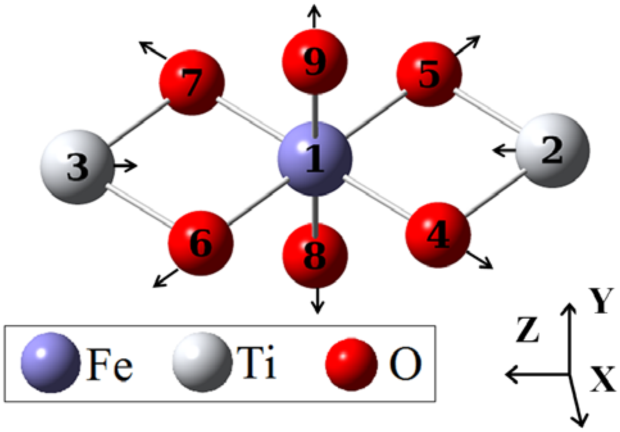

Fig. 5. Atomic displacements in the rutile crystalline lattice in the surroundings of the Fe impurity.

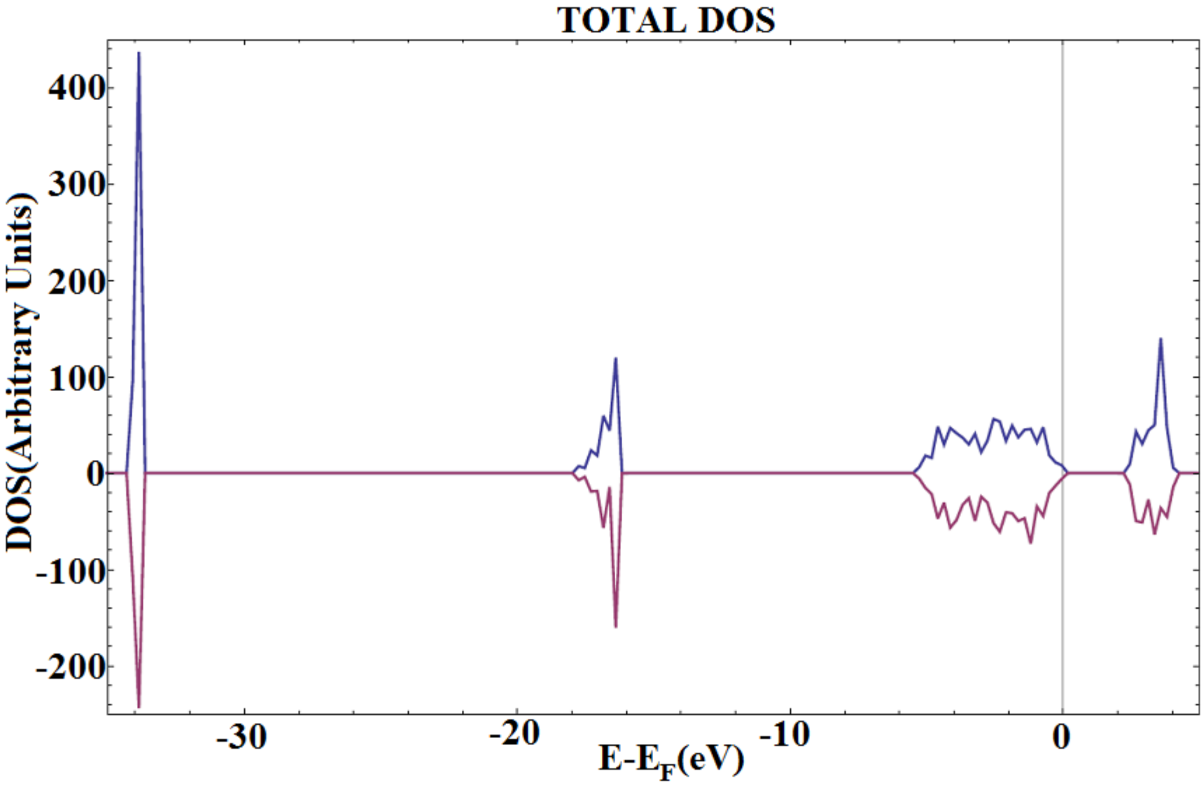

Fig. 6. Total DOS of the Fe-doped rutile structure. The vertical line marks the Fermi level (E_F).

TABLE III
CHARGES AND DISPLACEMENTS

Atoms	Q1 (e)	Q2 (e)	ΔR (Å)
Fe(1)	2.36	1.96	-
Ti(2)	2.36	2.37	-0.02
Ti(3)	2.36	2.37	-0.02
O(4)	-1.18	-1.16	0.04
O(5)	-1.18	-1.18	0.04
O(6)	-1.18	-1.15	0.04
O(7)	-1.18	-1.17	0.04
O(8)	-1.19	-0.94	0.03
O(9)	-1.19	-0.94	0.03

Charges on atoms obtained through the Bader population analysis for the perfect (Q1) and Fe-doped (Q2) rutile crystals, respectively. The atomic displacements (ΔR) regarding the impurity for 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. 5.

Fig. 6 shows the DOS of the system. The presence of the Fe impurity produces some local contributions in the upper VB, especially for α spin, and some contributions in the CB, mainly for β spin. There is no any local energy level in the band-gap of the crystal. However, one can observe a slight decrease, about 9%, of the band-gap width, which means a small contribution towards the enhancement of electrical conductivity.

Fe atom is an element that has magnetic properties and its presence leads to the occurrence of a local magnetic moment in the lattice. The supercell magnetic moment after the introduction of the impurity is found to be equal to 4.91 μ_B. The main contribution to this value is from the Fe impurity, 4.25 μ_B, with some small admixture coming from Ti and O atoms.

D. *Sc-doped rutile*

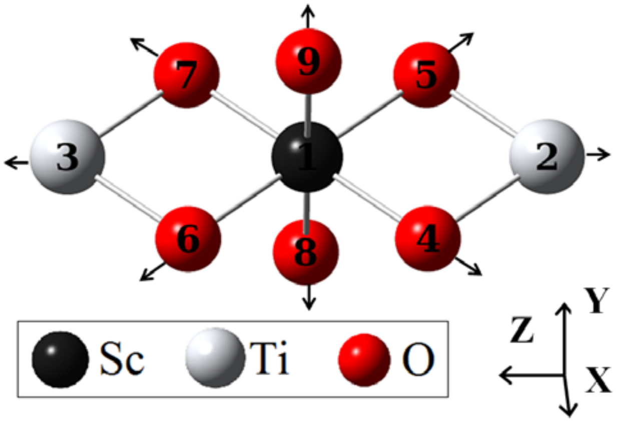

Fig. 7. Atomic displacements in the rutile crystalline lattice in the surroundings of the Sc impurity.

Sc impurity doping was done in a similar manner as described above. The allowed full lattice relaxation shows that all the atoms near the vicinity of the impurity are moving towards the inserted defect (Table IV and Fig. 7). Bader charge analysis shows that the charges on the atoms are almost the same as for the pure rutile crystal. The atomic charge on the Sc atom is smaller than that of the replaced Ti atom. That is why the Ti atoms move slightly towards it is due to the reduction of the Coulomb electrostatic repulsion whereas the O atoms are increasing their initial bond-length distances towards the impurity because of the same reason.

TABLE IV
CHARGES AND DISPLACEMENTS

Atoms	Q1 (e)	Q2 (e)	ΔR (Å)
Sc(1)	2.36	2.04	-
Ti(2)	2.36	2.36	0.01
Ti(3)	2.36	2.36	0.01
O(4)	-1.18	-1.18	0.11
O(5)	-1.18	-1.18	0.11
O(6)	-1.18	-1.18	0.11
O(7)	-1.18	-1.18	0.11
O(8)	-1.19	-1.18	0.08
O(9)	-1.19	-1.18	0.08

Charges on atoms obtained through the Bader population analysis for the perfect (Q1) and Sc-doped (Q2) rutile crystals, respectively. The atomic displacements (ΔR) regarding the impurity for 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. 7.

The DOS of the Sc-doped rutile is shown in Fig. 8. The presence of the scandium has no major influence upon the energetic bands of the system. The impurity has some small contributions in the upper VB and the CB. The width of the band-gap region is found to decrease, about 14%, which might improve slightly the electrical conductivity.

IV. CONCLUSIONS

Through the use of the DFT+*U*, a quantum-mechanical study of both structures of TiO_2, anatase and rutile, has been carried out, in the presence of Fe and Sc impurities. The obtained structural parameters for pure crystals are in a close agreement with the available experimental results.

The analysis of the results in the anatase structure shows that the presence of an iron impurity produces the movement of the atoms in its neighbourhood. Atomic charges computed through the Bader analysis show that the chemical bonding around the defective region has become more covalent. Hence, the Ti atoms move closer to the impurity, and most of the O atoms increase their initial distance till the Fe atom. The DOS pattern shows the presence of a local level in the band gap close to the top of the upper VB, which have contributions of Fe 3*d* states and O 2*p* AOs. That might enhance electrical conductivity. Also, the Fe-doped anatase supercell presents a total magnetic moment of 3.94 μ_B, with main contribution from the dopant, 3.7 μ_B.

Regarding the introduction of a scandium atom in the anatase structure we can conclude that the Ti atoms conserve their initial distances till the single point defect whereas the O atoms move outwards it. The charge of the impurity, smaller than the replaced Ti atom, produces a decrease in the Coulomb interaction in the defective region. The DOS for this case show that there are no any changes

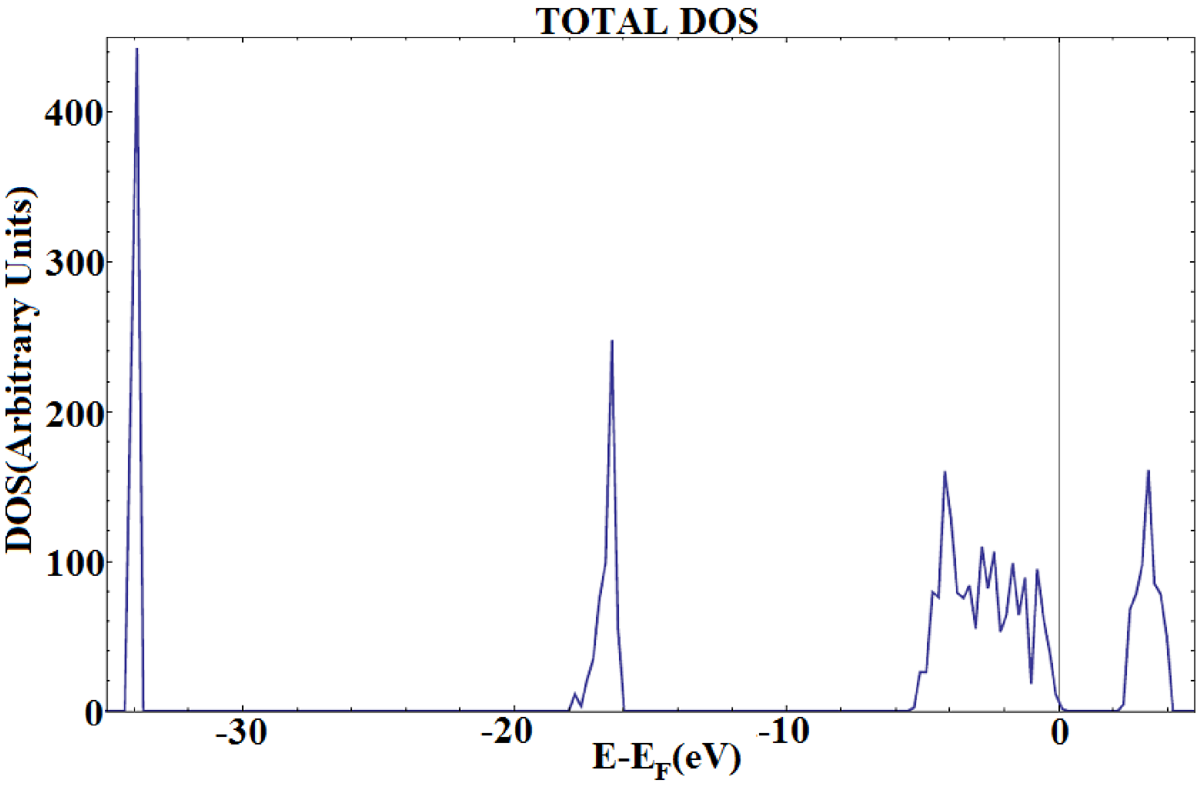

Fig. 8. Total DOS of the Sc-doped rutile structure. The vertical line marks the Fermi level (E_F).

upon the electrical conductivity since the Sc atom does not produce any local level or changes the band-gap width.

Rutile structure containing an iron impurity shows that Ti atoms shift themselves towards the defect, whilst the O atoms move away regarding the defect. That might be due to the reduction of atomic charge because of the doping. The DOS of the system show some contributions of the impurity atom in the upper VB for α spin and some Fe admixture in the CB for β spin. A slight decrease, approximately by 9%, has been observed. The supercell magnetic moment is found to be equal to 4.9 μ_B that is mainly due to the Fe atom contributing 4.25 μ_B.

Sc-doping in the rutile structure produces movements of Ti atoms slightly away from the impurity, and the O atoms move outwards the defect as well. Bader charge analysis shows a smaller charge on the defect, so the Coulomb attraction with the O atoms tends to decrease. The Ti atoms try to preserve their respective Ti-O distances and move outwards the point defect. DOS analysis implies a reduction of the band-gap width by approximately 14%.

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