

Electronic, structural, and magnetic effects of 3d transition metals in hematite

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We present a density-functional theory study on the electronic structure of pure and 3d transition metal (TM) (Sc, Ti, Cr, Mn, and Ni) incorporated α -Fe₂O₃. We find that the incorporation of 3d TMs in α -Fe₂O₃ has two main effects such as: (1) the valence and conduction band edges are modified. In particular, the incorporation of Ti provides electron carriers and reduces the electron effective mass, which will improve the electrical conductivity of α -Fe₂O₃. (2) The unit cell volume changes systematically such as: the incorporation of Sc increases the volume, whereas the incorporation of Ti, Cr, Mn, and Ni reduces the volume monotonically, which can affect the hopping probability of localized charge carriers (polarons). We discuss the importance of these results in terms of the utilization of hematite as a visible-light photocatalyst. © 2010 American Institute of Physics. [doi:10.1063/1.3432736]

I. INTRODUCTION

Semiconductor materials for economical photoelectrochemical (PEC) production of hydrogen using solar energy have attracted great attention since the demonstration of water splitting using a TiO₂ photoanode illuminated with ultraviolet light almost forty years ago by Fujishima and Honda.¹ To realize low-cost PEC production of hydrogen, the semiconductor materials must be abundant, inexpensive, stable in aqueous solutions, and yet have high solar-to-hydrogen conversion efficiency. However, so far, no single material has been found that meets all these criteria, even though more than 200 semiconducting materials have been studied as potential photocatalysts.^{2,3}

Hematite (α -Fe₂O₃) has been considered a promising material that may potentially meet the above-mentioned criteria because of the following advantages:^{2,4} α -Fe₂O₃ is inexpensive, abundant, nontoxic, and stable in most alkaline electrolytes. It has a bandgap of 2.2 eV, which is capable of absorbing roughly 40% of the solar spectrum, leading to a maximum theoretical solar-to-hydrogen conversion efficiency of about 13% under AM1.5 illumination (the global standard spectral irradiance). Its valence band edge position matches the H₂O/O₂ oxidation potential for efficient oxygen evolution, and its conduction band edge position is just slightly lower than the hydrogen reduction potential. However, despite these favorable characteristics, the maximum experimental solar-to-chemical efficiency reported in the literature for hematite is less than 3%.⁵ The extremely low

electrical conductivity and the indirect bandgap (weak optical absorption) are the two most critical factors that limit the PEC performance of α -Fe₂O₃.^{6,7}

The PEC performance of α -Fe₂O₃ has been shown to be affected dramatically by the incorporation of transition metal (TM) and post-TM elements at concentrations of several percent.^{8–15} The incorporation of 3d metals has demonstrated particularly interesting effects. For example, the incorporation of Ti and Cr in α -Fe₂O₃ has led to significantly enhanced photocurrents.^{10,12} The incorporation of impurities may affect the properties of synthesized materials in many ways, such as structure, morphology, electronic nature, and catalytic behavior. In this paper, we study how the electronic structure, magnetic properties, and crystal volume of α -Fe₂O₃ can be changed by the incorporation of some 3d TMs (Sc, Ti, Cr, Mn, and Ni) using the first-principles density-functional theory (DFT). We find that the conduction band edge of α -Fe₂O₃ is highly localized, leading to a heavy electron effective mass and, therefore, very low electron conductivity. This is consistent with the fact that α -Fe₂O₃ has achieved solar-to-hydrogen conversion efficiencies well below its theoretical limit.

The incorporation of 3d TM in α -Fe₂O₃ has two main effects such as: (1) the valence and conduction band edges are modified. In particular, the incorporation of Ti and Cr reduces the electron effective mass, which would improve the electron conductivity of α -Fe₂O₃ and hence explain why the incorporation of Ti and Cr in α -Fe₂O₃ has led to significantly enhanced photocurrents. (2) The incorporation of Sc increases the unit cell volume, whereas, the incorporation of Ti, Cr, Mn, and Ni reduces the volume monotonically. As the transport properties of α -Fe₂O₃ are limited by small polaron (trapped charge carrier) mobility, the volume change may also affect the electrical conductivity through altering the hopping probabilities.

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II. METHOD

We have employed DFT to calculate the electronic properties of the bulk and defective α -Fe₂O₃ structures. The calculations were performed using the local spin density approximation¹⁶ to DFT with the projector augmented wave (PAW) method^{17,18} within the Vienna *ab initio* simulation package (VASP 4.6.21).^{19,20} A well-converged plane-wave cut-off energy of 500 eV was used, and the ion positions and volumes of the supercells were always relaxed by minimizing the force on each of the atoms and stress on the cell. For α -Fe₂O₃ because Fe *d* bands are strongly correlated, we adopted the LSDA+*U* (Ref. 21) approach with *U*=5.5 eV for the Fe *d* and dopant 3*d* bands. We have tested with several *U*-values and their implication on the volume of the cell: *U*=5.5 eV provides a reasonable description of the bandgap and a better lattice-constant compared to experiment; larger *U* values give rise to too small a cell volume due to the higher localization of the Fe *d* electrons. Bandyopadhyay *et al.*²² employing a similar methodology found that *U*=5 eV provides a good description of the bandgap and magnetic moment of Fe, while higher values of *U* gave a larger bandgap than the experimental one, almost by 0.4 eV. Additional studies have shown before (with VASP, Ref. 23), that at around *U*=5 eV, the Fe–Fe distance approaches the experimental value, which is important, as the polaron conductivity in α -Fe₂O₃ depends on this distance. On the other hand, without the Coulomb *U* correction, the magnetic ordering of α -Fe₂O₃ is not well described and the bandgap is highly underestimated. With *U*, the bandgap (separation of the occupied and unoccupied Kohn–Sham eigenvalues) is found to be 1.72 eV, close to the experimental bandgap of 2.2 eV.

The primitive unit cell of α -Fe₂O₃ has rhombohedral symmetry (the corundum structure, space group 167). Each Fe is coordinated by six oxygen atoms in a distorted octahedron and each O has four Fe neighbors. To accommodate the layered antiferromagnetic (AFM) ordering observed in α -Fe₂O₃ at low temperature, the hexagonal lattice containing three primitive cells (12 Fe atoms and 18 O atoms) was used in this study. In the hexagonal lattice (Fig. 1) each layer of Fe atoms is separated by a plane of O atoms. The coupling between the Fe atoms within each layer is ferromagnetic, whereas, the coupling between the layers is AFM below 960 K.²⁴ This particular magnetic configuration plays an important role in determining the conduction properties of this material. For 3*d* TM incorporation, one of the six spin-down Fe atoms are substituted by a 3*d* TM atom, which corresponds to 8.3% substitution at the Fe site. The volume and internal positions of the defective cell were fully relaxed to release the external pressure, simulating isobaric defect formation above the impurity limit.

III. RESULTS AND DISCUSSION

The Fe (4*s*²3*d*⁶) atom has a formal Fe³⁺ (*d*⁵) ionization state in α -Fe₂O₃, which is in a high spin magnetic configuration giving a nominal local magnetic moment of 5 μ_B per ion but these spins are ordered to give an overall type II AFM ground state (Fig. 1). Figure 2(a) shows the electronic band structure, and Fig. 2(b) contains the calculated partial

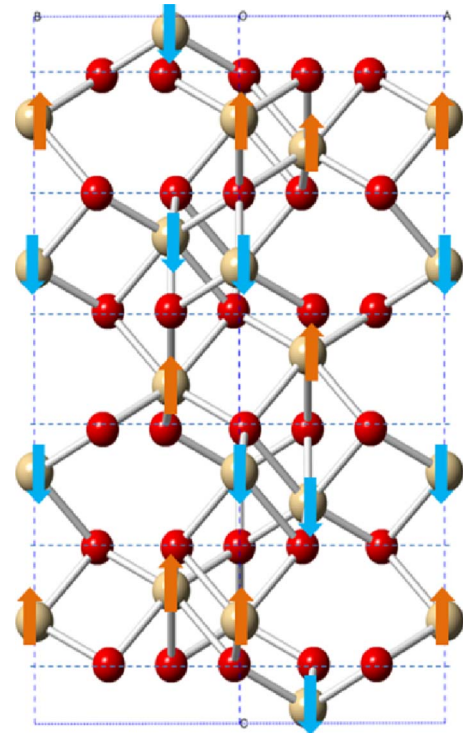


FIG. 1. (Color online) Hexagonal Fe₂O₃ lattice with AFM spin arrangements indicated by up and down arrows at the Fe sites. Small and large balls are oxygen and iron atoms, respectively.

(ion and angular momentum projected) density of states (p-DOS) plot for α -Fe₂O₃. The valence band maximum (VBM) has mostly O *p* and Fe *d* character and the conduction band minimum (CBM) has mostly minority-spin Fe *d* character. Due to these orbital features, the band structure of α -Fe₂O₃ has an almost dispersionless CBM between the *M* and *K* points in the first Brillouin zone. This indicates that pure α -Fe₂O₃ has extremely heavy carrier effective masses, which will result in low mobility for the electrons. This is consistent with the fact that the conducting mechanism in α -Fe₂O₃ is polaronic (localized electron carriers), which has been previously modeled using Marcus' theory,²⁵ and is one of the main reasons why low solar-to-hydrogen conversion efficiency has been obtained with α -Fe₂O₃ despite its favorable bandgap. The lower part of the conduction band between Γ and *A* is also very flat and at higher energy compared to the CBM. It implies that interlayer conduction along the *z*-direction will be severely suppressed; the conductivity is known to be highly anisotropic, being significantly higher within the layers in the *a*-*b* plane.²⁵ Thus, electron conduction in α -Fe₂O₃ essentially occurs along the same layers where all the Fe atoms have the same magnetic moment. On the other hand, the VBM, which lies between *M* and *K* points, has some dispersion feature due to the favorable *p*-*d* hybridization between the O *p* and Fe *d* states. Therefore, holes have a lower effective mass, which would suggest a higher mobility compared to electrons, neglecting the nature of their polaronic distortion.

We now discuss how the electronic structure may be modified by incorporation of 3*d* TMs. We have considered the 3*d* TMs of Sc, Ti, Cr, Mn, and Ni. From Sc to Ni, the

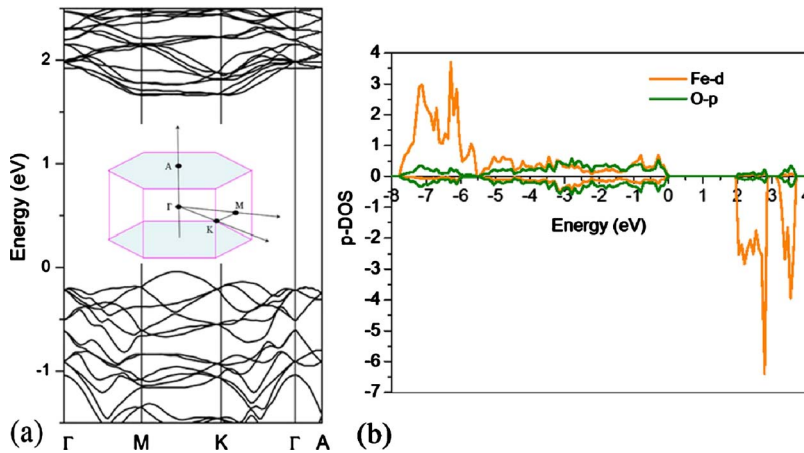


FIG. 2. (Color online) (a) Calculated electronic band structure and (b) p-DOS plot for pure α -Fe₂O₃. The inset in Fig. 2(a) shows the first Brillouin zone and special points used for the band structure plot. The highest occupied state is set to 0 eV.

number of d electrons increases, whereas, the electronegativity increases and the d orbital becomes more localized.²⁶ As a result, the effect of incorporation of these $3d$ TMs in α -Fe₂O₃ can be explained following these trends.

α -Fe₂O₃:Sc. Sc ($4s^2 3d^1$) is isovalent to Fe: a Sc³⁺ (d^0) ion at an Fe³⁺ site formally loses its three valence electrons, which results in a closed shell electronic configuration. The total magnetic moment of the defective Fe₂O₃ cell is derived from an unpaired Fe³⁺ (d^5) ion giving $5 \mu_B$. Figure 3 shows the calculated band structure of α -Fe₂O₃:Sc for spin-up (left panel) and spin-down (right panel) states. The bandgaps are 1.65 eV and 1.79 eV for spin-up and spin-down bands, respectively, which can be compared to the calculated bandgap for pure α -Fe₂O₃ (1.72 eV). There is almost no change in the features of the CBM because it still has Fe $3d$ character and the Sc $3d$ bands are positioned at higher energy. This means that the heavy effective mass for electrons remains unchanged. Therefore, incorporation of Sc into α -Fe₂O₃ may reduce the bandgap slightly, thus enhancing photon absorption; but it would not affect the intrinsic electronic conductivity of α -Fe₂O₃.

α -Fe₂O₃:Ti. Ti ($4s^2 3d^2$) has four valence electrons and favors a 4+ charge state. Substitution of the Ti⁴⁺ (d^0) ion at an Fe³⁺ site results in one conduction band electron. Figure 4 shows the calculated band structure of α -Fe₂O₃:Ti for spin-up (left panel) and spin down (right panel). From the

band structure, we see that the conduction band is partially occupied and the CBM of the α -Fe₂O₃:Ti system is heavily modified by Ti s and d orbitals. In this case, the CBM becomes more dispersive than that of the pristine α -Fe₂O₃, indicating that alloying with Ti may reduce the effective mass for electrons, and the additional conduction electrons (n -type charge carriers) will further aid electron transport rates. The delocalization of the CBM state is further confirmed by the fact that the local magnetic moment of Ti is less than $-0.1 \mu_B$, although the total magnetic moment of the cell is $4 \mu_B$. This is because the conduction band of α -Fe₂O₃ is lower than that of TiO₂, i.e., Fe₂O₃ has a larger electron affinity.²⁷ The surplus electron will not be trapped on the Ti impurity center to form a Ti³⁺ (d^1) species but will be donated to the Fe host. The spin-up CBM does not show much change from that of the pure α -Fe₂O₃. However, two filled defects levels above the original VBM are found, which are derived from hybridized O p and Ti d states. Considering these two bands as part of the new valence band (in the case of the Fe_{2-x}Ti_xO₃ alloy), the bandgap for the spin-up channel is 1.19 eV, which is much lower than that of pure α -Fe₂O₃: low energy photon absorption will be enhanced.

α -Fe₂O₃:Cr. The Cr ($4s^2 3d^4$) atom in the Cr³⁺ (d^3) ionic charge state in α -Fe₂O₃ can put three d electrons in the Cr t_{2d} state and the unoccupied e_d state will be separated to

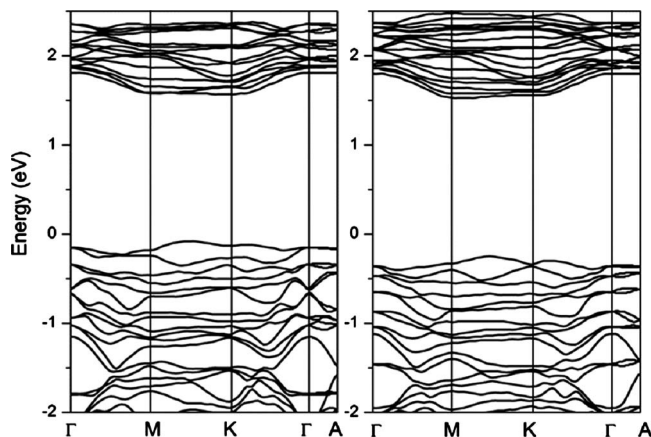


FIG. 3. Calculated electronic band structure for α -Fe₂O₃:Sc. Left panel: spin-up; right panel: spin-down states. The highest occupied state is set to 0 eV.

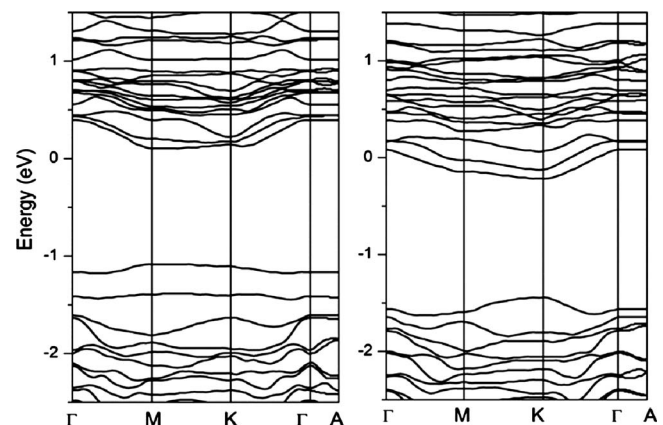


FIG. 4. Calculated electronic band structure for α -Fe₂O₃:Ti. Left panel: spin-up; right panel: spin-down bands. The highest occupied state is set to 0 eV.

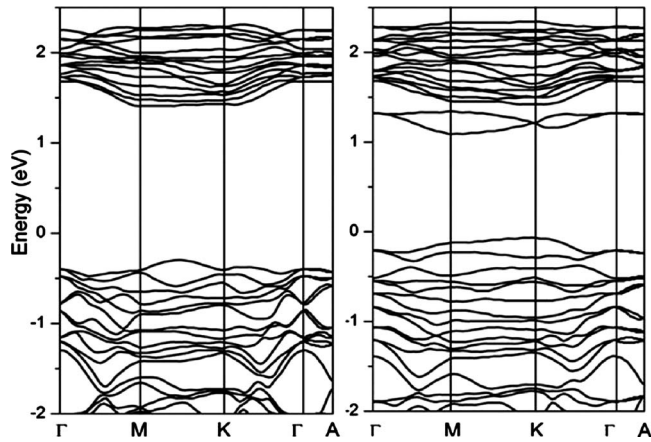


FIG. 5. Calculated electronic band structure for $\alpha\text{-Fe}_2\text{O}_3\text{:Cr}$. Left panel: spin-up; right panel: spin-down bands. The highest occupied state is set to 0 eV.

higher energies by the octahedral crystal-field splitting. The calculated band structures for spin-up (left panel) and spin down (right panel) of $\alpha\text{-Fe}_2\text{O}_3\text{:Cr}$ are shown in Fig. 5. As discussed above, the bandgap for the spin-up channel is almost the same as that for pure $\alpha\text{-Fe}_2\text{O}_3$; but in the spin-down channel, the bandgap (1.17 eV) is much smaller than the pure host due to the strong localization of the occupied spin-down t_{2d} state. The local moment at the Cr site is close to $-3 \mu_B$ (replacing an Fe ion of $-5 \mu_B$) and the total moment of the cell is, therefore, $2 \mu_B$. If the concentration of Cr is increased, i.e., in the alloying regime, these Cr e_d and s orbital derived states will become the bottom of conduction band of $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$. The new CBM has more dispersion and it could, therefore, enhance the conductivity by improving electron mobility; however, the bandwidth does remain relatively narrow.

$\alpha\text{-Fe}_2\text{O}_3\text{:Mn}$. Mn ($4s^23d^5$) has one more d electron than Cr; thus, when Cr^{3+} is replaced by Mn^{3+} (d^4), part of the spin-down e_d band just below the CBM will become filled. The local magnetic moment of Mn will increase to about $-4 \mu_B$, and the total magnetic moment of the defective cell is reduced to about $1 \mu_B$. This small total magnetic moment indicates that the spin-splitting between the spin-up and spin-down bands is small, so both CBMs for spin-up and spin-down states are occupied, which renders it as an n -type material. On the other hand, the Mn d band does not contribute much to the VBM. The bandgaps for spin-up and spin down are 1.17 eV and 1.35 eV, respectively. Our calculated band structure for $\alpha\text{-Fe}_2\text{O}_3\text{:Mn}$, as shown in Fig. 6, is slightly different from the previously published band structure,²⁸ which shows a partially filled band at the middle of the bandgap. We find that we can also obtain this feature if the volume of the supercell with substitutional Mn was not relaxed. After volume relaxation, this mid-gap partially occupied band splits into filled and empty states deep in the bandgap, which suggests that Mn will be susceptible to oxidation toward Mn^{4+} or reduction toward Mn^{2+} .

$\alpha\text{-Fe}_2\text{O}_3\text{:Ni}$. Ni ($4s^23d^8$) substitution on the spin-down Fe site in $\alpha\text{-Fe}_2\text{O}_3$ has a formal Ni^{3+} (d^7) ionic state. The band structures are shown in Fig. 7. Due to large crystal-field splitting, both the spin-up and spin-down Ni t_{2d} states are

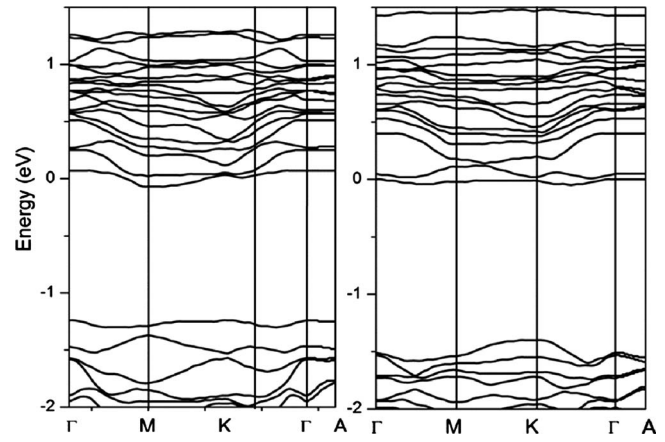


FIG. 6. Calculated electronic band structure for $\alpha\text{-Fe}_2\text{O}_3\text{:Mn}$. Left panel: spin-up; right panel: spin-down bands. The highest occupied state is set to 0 eV.

fully occupied, with the remaining seventh electron occupying one of the spin-down Ni e_d states. Therefore, the local magnetic moment at the Ni site is close to $-1 \mu_B$ and the total magnetic moment per cell is $4 \mu_B$. The spin-down Ni e_d state appears in the middle of the gap; the lower state is fully occupied, whereas, the upper state is empty. This half-filled Ni-derived band in the middle of the bandgap makes $\alpha\text{-Fe}_2\text{O}_3\text{:Ni}$ a good candidate as an intermediate-bandgap material if charge compensation by intrinsic defects (such as oxygen vacancies) to produce the more stable Ni^{2+} species can be avoided. The two states above the VBM in the spin-up channel are also mainly derived from Ni d . Considering these two states as part of a new alloy valence band, the bandgap in the spin-up band structure would be 1.34 eV.

The trend for the incorporation of 3d TMs in $\alpha\text{-Fe}_2\text{O}_3$ can be further characterized from the DOS plots. Figure 8 shows the total DOS plots for pure $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ incorporated with other 3d TMs. These DOS plots are aligned with respect to the O $1s$ core level to show the relative shift in the states. Here, it is assumed that the deep O $1s$ level is an appropriate reference energy level, as its actualizations due to different dopants in $\alpha\text{-Fe}_2\text{O}_3$ can be neglected far from dopant site. The Fermi level, defined as the highest

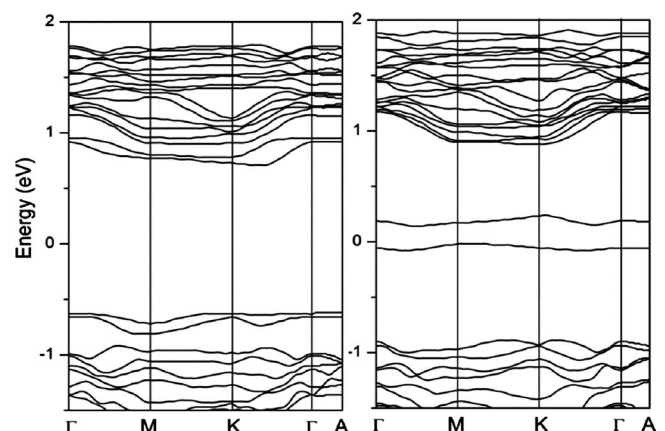


FIG. 7. Calculated electronic band structure for $\alpha\text{-Fe}_2\text{O}_3\text{:Ni}$. Left panel: spin-up; right panel: spin-down bands. The highest occupied state is set to 0 eV.

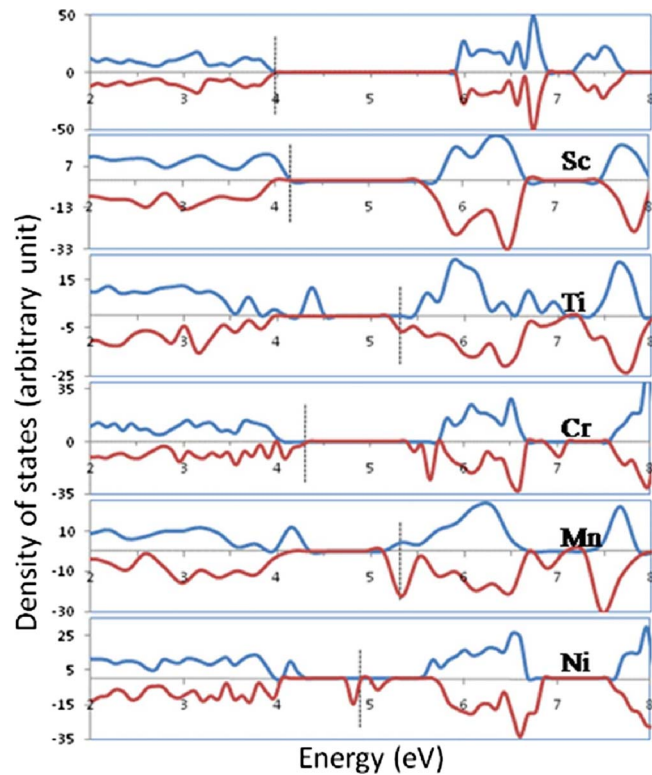


FIG. 8. (Color online) Total electronic DOS plot for pure $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ incorporated with Sc, Ti, Cr, Mn, and Ni at substitutional sites. The states are aligned with respect to the O $1s$ core level and the highest occupied state is indicated by the dashed vertical line in each case.

occupied state, is marked by the dashed line in each case. The DOS plots clearly show the trend of the effects of TMs on the electronic structure of $\alpha\text{-Fe}_2\text{O}_3$. Whereas the Sc derived band is well mixed with the original conduction band of $\alpha\text{-Fe}_2\text{O}_3$, Ni produces two states in the middle of the gap. This trend is consistent with the fact that the d orbitals become increasingly localized from Sc to Ni. Among all the considered $3d$ TMs, the Ti and Cr derived bands exhibit the most dispersive features, indicating that the incorporation of Ti and Cr should lead to a lower effective mass for electrons, and, therefore, should somewhat enhance the electrical conductivity.

Further, we find that the incorporation of $3d$ TMs leads to significant volume changes in the defective cell. Except for the larger Sc cation, the incorporation of other TMs results in a volume reduction, as shown in Fig. 9. For Sc substitution, the volume is increased by about 1.4% at the calculated defect concentration. The largest volume reduction (about 2%) was found for Ni substitution, which is related to the strong localization of the Ni d orbital. As the dominant contribution of electrical conduction in $\alpha\text{-Fe}_2\text{O}_3$ is through small polaron hopping, the volume decrease is likely to aid the conductivity both through a shorter hopping distance and harder phonon frequencies. A recent experimental and theoretical study of group 13 elements doped in $\alpha\text{-Fe}_2\text{O}_3$ also showed similar behavior.²⁹

It should be mentioned here, that the local distortions created by the TM doping in $\alpha\text{-Fe}_2\text{O}_3$ are small due to the low cation size mismatch. For example, for Ti-doped $\alpha\text{-Fe}_2\text{O}_3$, the two different local bond angles for O–Ti–O are

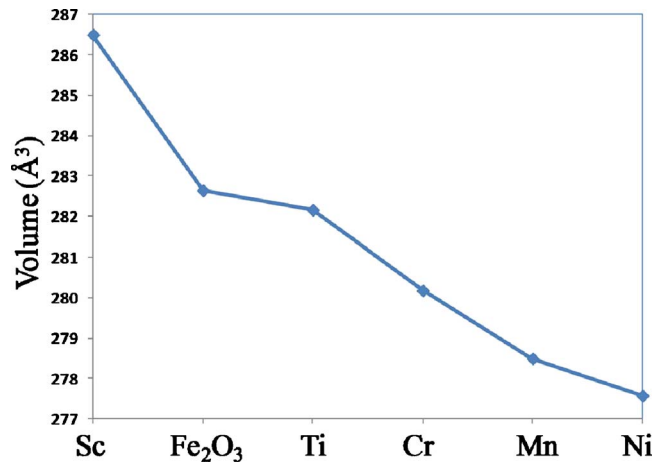


FIG. 9. (Color online) Calculated volumes for defective supercells containing $3d$ TM substitutions in Fe_2O_3 . Fe_2O_3 represents pure $\alpha\text{-Fe}_2\text{O}_3$.

81.4° and 86.2° , compared to the undoped angles of 78.2° and 86.1° , respectively. On the other hand, the same layer Fe–Fe distances decrease (where the electron hopping mainly takes place); for Ti-doped and undoped cases, the Fe–Fe distances are 2.89 \AA and 2.97 \AA , respectively. So, in the present case of TM doping, it can be argued that, as the TM dopants are localized in nature and do not inflict much lattice distortion, the local chemical environment for Fe to Fe intralayer hopping sufficiently far from the dopant sites would not change much except for the reduced Fe–Fe distances due to the volume decrement. Therefore, lattice strain, in the form of reduced Fe–Fe distances, may also contribute to improved photon conversion efficiencies in the doped systems, through improved mobility of electrical charge carriers.

It should be pointed out that the incorporation of $3d$ TMs may result in additional effects besides those discussed above. For example, the incorporation of impurities can change the morphology, stoichiometry, crystallinity, and grain size of synthesized materials. The incorporated $3d$ TMs could also favor segregation to the material surface, and some of the $3d$ TMs are potential catalysts for the processes involved in hydrogen and oxygen evolution, which may affect the PEC performance of the synthesized materials. Thus, all possible effects should be considered so that the PEC performance of a material may be evaluated adequately. Nevertheless, the above calculated electronic structure and volume change provide initial insight into the understating how the incorporation of $3d$ TMs may affect the conductivity of $\alpha\text{-Fe}_2\text{O}_3$ and lead to the optimization of iron oxide as a cheap visible-light photocatalyst.

IV. CONCLUSIONS

We have studied the properties of $\alpha\text{-Fe}_2\text{O}_3$ on the incorporation of substitutional $3d$ TM cations. We have shown that the incorporation of some $3d$ TMs act as electron donors and reduce the effective mass for electrons and hence can promote the electrical conductivity; therefore, it may help to increase the solar-to-hydrogen conversion efficiency by facilitating the separation and transport of photogenerated

charge carriers. Furthermore, we have found that the incorporation of some 3d TMs will lead to a net volume reduction, which may affect the polaron hopping probabilities in $\alpha\text{-Fe}_2\text{O}_3$. Our results suggest that among all the considered 3d TMs, the incorporation of Ti would lead to the greatest increase in electrical conductivity, and, therefore, to the greatest enhancement of PEC performance.

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