Ab initio study of bulk and surface iron defects in SrTiO$_3$

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Abstract. Hybrid HF-DFT LCAO approach with B3PW exchange-correlation functional was employed for the calculations of bulk and surface Fe$^{4+}$ impurities in SrTiO$_3$ for various iron contents. Structural and energetic changes in the host material induced by defect incorporation were particularly addressed. The calculated Jahn-Teller distortion around the iron defects in the bulk were compared with recent experimental EXAFS results. It was found that the iron defects have propensity to segregate to the (001) surface and substantially reduce the basic properties of SrO-terminated surface.

1. Introduction
This study focuses on the first-principles modeling of substitutional iron defects in SrTiO$_3$ perovskite. This is performed using the CRYSTAL-2006 computer code [1] which offers a number of advantages for the quantum chemical investigation of solids. The package embraces the pure HF, DFT and the hybrid HF-DFT methodologies with the opportunity to use a wide range of functionals providing the flexibility to explore materials with diverse properties. Being the LCAO-based, the package is premier and versatile tool to perform an in-depth ab initio study of a wide spectrum of condensed matter properties in terms of local functions what is particularly fruitful in solid state chemistry. Furthermore, it enables one to carry out the simulation of systems of any periodicity ranging from 0D to 3D with rigorous exploitation of a given space symmetry. The latter point makes our study of bulk and surface defects symmetry-consistent within a periodic supercell approach.

The investigation of bulk Fe-doped SrTiO$_3$ which exemplifies an important acceptor-doped ceramic material with electrooptical applications [2] has been primarily inspired by the recent experimental study [3] of this system by means of a number of techniques which has unambiguously indicated the presence of the Jahn-Teller distortion around Fe$^{4+}$ centers substituting host Ti$^{4+}$ ions. The simulation of structural and electronic properties of the bulk iron impurities has been previously examined [4] for a whole range of iron concentrations $x$ in the SrFe$_x$Ti$_{1-x}$O$_3$ solid solutions. It has been shown that magnitude of the Jahn-Teller distortion around iron centers in terms of the static disorder component of the mean square relative atomic displacement $\text{MSRD}_{\text{stat}}$ increases with lowering the iron content, in accordance with the EXAFS data, and approaches the experimental estimate extrapolated to the single defect limit.
In this contribution, we present results of the study of iron defects both in the bulk and on the SrTiO$_3$ (001) surface using 3D- and 2D-supercell models, respectively, with emphasis on the comparison of bulk and surface defect properties. The question of a possible iron segregation from the bulk to the surface remains open and is particularly addressed in this study by comparing defect formation energies in the bulk and on the (001) surface with different terminations.

2. Computational details
In all calculations we exploited a periodic supercell approach which implies the use of a 3D extended unit cell for bulk and 2D extended unit cell for surface [5]. In the bulk simulations, we considered a number of 3D supercells where one substitutional iron defect was embedded in each supercell, thus modeling different iron concentrations (see [4] for details and Table 1 below). In the case of the (001) surface defects, we considered symmetrical seven-layer slab models with $2 \times 2$ and $3 \times 3$ unit cell extensions for SrO- and TiO$_2$-terminated surfaces. The iron defect, substituting for a host titanium, produces the surface defect with one dangling bond on the TiO$_2$-terminated surface and with all saturated bonds for the SrO-terminated model, being beneath the upper SrO plane. We found that the treatment of asymmetrical, six-layer stoichiometric model with SrO and TiO$_2$ terminations on the opposite sides of the slab did not affect our results significantly. Our preliminary calculation of a ten-layer slab showed that slabs with six- or seven-atomic planes are sufficient to account for the considered properties of the surface defects including segregation energies.

We have chosen the hybrid HF-DFT method with the B3PW functional [6] as it has been earlier successfully applied to the simulations of bulk and surface properties of a variety of perfect perovskites, including SrTiO$_3$ [7, 8, 9]. The Monkhorst-Pack [10] mesh of $2 \times 2 \times 2$ k-points was used in the 3D irreducible Brillouin zone (BZ) sampling for all iron contents except $C_{Fe} \geq 50\%$ where the denser meshes were employed. The number of sampling points in the 2D irreducible BZ was set to $4 \times 4$ for the $2 \times 2$ surface unit cell and $3 \times 3$ for the $3 \times 3$ one. We adopted the CRYSTAL-2006 default thresholds for the evaluation of mono- and bielectronic integrals as well as for the geometry optimization process. The bulk lattice constant of 3.892 Å optimized for pure SrTiO$_3$ was used in the calculations with small iron defect concentrations and the re-optimized constant of 3.874 Å for 50% iron content.

3. Bulk defects
It should be pointed out that the first ab initio study of Fe-doped SrTiO$_3$ has been carried out within the UHF method in [11] where the Jahn-Teller distortion around a single iron impurity has been predicted. In Figure 1 the sketches of the Jahn-Teller distorted FeO$_6$ octahedra and the splitting of Fe $3d$ energy levels before and after lattice relaxation are presented.

For the simulation of iron bulk defect we first performed the full optimization of atomic positions in a number of supercells which correspond to various iron contents. The oxygen displacements found in the first atomic shell around the iron impurity invariably show the same pattern for the Jahn-Teller distortion, namely, two elongated and four shortened Fe-O bonds, according to the D$_{4h}$ point symmetry. A comparison with experimental results derived from the recent EXAFS data [3] can be done based on the static disorder component of the mean square relative displacements

$$MSRD_{stat} = \frac{m(r_m - r_0)^2 + n(r_n - r_0)^2}{m + n},$$

where $m=4$ and $n=2$ are the numbers of changed bond lengths, $r_0$, $r_m$ and $r_n$ are the lengths of ideal and two types of distorted bonds, respectively.

In Table 1 we summarize the results concerning oxygen displacements around the iron defect and defect formation energies for the chosen supercells. It is seen that MSRD$_{stat}$ increases with
Figure 1. Schematic view of the relaxation of six nearest oxygen atoms around Fe\(^{4+}\) impurity and the splitting of iron energy levels in cubic (O\(_h\)) and tetragonal (D\(_{4h}\)) crystalline field symmetries.

Table 1. The displacements of oxygen atoms in the first shell of the iron impurity for different iron concentrations \(C_{Fe}\). Inwards relaxation means displacement towards the iron center. \(N\) denotes the number of atoms in the supercell and \(d\) is the distance between the closest isolated iron defects. \(E_f\) is iron formation energy.

| \(N\)  | Extension         | \(C_{Fe}\) (%) | \(d\) (Å) | Oxygen shifts (Å) | MSRD\(_{stat}\) \(
\times 10^{-3}\) (Å\(^2\)) | \(E_f\) (eV) |
|-------|------------------|----------------|--------|-----------------|----------------|--------|
| 10    | \(\sqrt{2} \times \sqrt{2} \times \sqrt{2}\) | 50.0          | 5.48   | 0.0489 0.0665 | 2.96 1.59       |
| 80    | \(2\sqrt{2} \times 2\sqrt{2} \times 2\sqrt{2}\) | 6.25          | 11.01  | 0.0545 0.0681 | 3.34 1.78       |
| 135   | \(3 \times 3 \times 3\) | 3.70          | 11.68  | 0.0580 0.0660 | 3.42 1.78       |
| 160   | \(2\sqrt{3} \times 2\sqrt{3} \times 2\sqrt{3}\) | 3.125         | 13.48  | 0.0570 0.0690 | 3.53 1.78       |
| 270   | \(3\sqrt{2} \times 3\sqrt{2} \times 3\sqrt{2}\) | 1.85          | 16.51  | 0.0495 0.0795 | 3.70\(^a\) 1.79 |

\(^a\) The estimate of MSRD\(_{stat}\) from the EXAFS experiment\(^{[3]}\) extrapolated to the dilute limit yields 0.006 Å\(^2\).

lowering the iron content, thus correctly reproducing the trend obtained from EXAFS data, and approaches the experimental estimate for the dilute defect limit.

It should be noted that the dispersion of the iron band within the band gap is almost negligible (0.01 eV) for 270-atom supercell meaning that the defect-defect interaction is practically eliminated. The width of the iron band for higher iron contents increases up to 0.12 eV for 6.25% iron and merges with the top of valence band for 50% iron concentration indicating the metallic nature of highly iron-doped SrTiO\(_3\). The absence of the Jahn-Teller distortion in the limiting case of pure SrFeO\(_3\) has been proved on the energetically most favorable ferromagnetic state by performing the full optimization of an initial distorted geometry.

The calculated projected density of electronic states (PDOS) reveals that O 2p orbitals give a dominant contribution to the top of valence band while Fe 3d (\(e_g\)) states form the defect band level within the band gap for a slightly doped system, are broadened for moderate concentrations and finally merge with O 2p in the pre-Fermi level region for a highly doped SrTiO\(_3\) (\(C_{Fe} \geq 50\%\)). Such a Fe-O mixing suppresses the Jahn-Teller distortion as an iron content increases.

The assessment of the formation energy for substitutional iron impurity was done as

\[
E_f = E(def) - E(Fe) + E(Ti) - E(per),
\]

where \(E(Fe)\) and \(E(Ti)\) are the energies of iron and titanium atoms in the gas phase, while
Table 2. The Mulliken effective atomic charges $q$ (in e) in perfect SrTiO$_3$, SrFeO$_3$ and 80-atom supercell with iron impurity. M denotes Ti or Fe atom in bulk crystals and Fe atom in the supercell.

| Crystal                  | q(Sr) | q(M) | q(O) |
|--------------------------|-------|------|------|
| SrTiO$_3$                | 1.87  | 2.36 | -1.41|
| SrFeO$_3$                | 1.88  | 2.26 | -1.38|
| SrFe$_{0.0625}$Ti$_{0.9375}$O$_3$ | 1.87  | 2.28 | -1.39 (O$_{x,y}$) -1.43 (O$_z$) |

$E(\text{def})$ and $E(\text{per})$ are total energies for defective and perfect crystals, respectively. It is seen from Table 1 that the $E_f$ becomes practically constant for iron concentrations less than 6.25%.

The calculated Mulliken effective atomic charges for the two limiting cases of bulk SrTiO$_3$ and SrFeO$_3$ as well as for an in-between solid solution are listed in Table 2. They reflect the fact of a more covalent character of SrFeO$_3$ crystal compared to SrTiO$_3$. In both solids the effective charges are far smaller than formal (ionic) charges, due to Ti-O, Fe-O bond covalency whereas Sr remains close to Sr$^{2+}$ ion.

4. The (001) surface defects

The simulations of the iron substitutional defects on the SrTiO$_3$ (001) surfaces were carried out on two symmetrical slabs containing seven atomic layers and terminated by either SrO or TiO$_2$ planes. In Figure 2 three upper layers of SrO- (a) and TiO$_2$-terminated (b) iron-doped surfaces are displayed. It should be noted that the introduction of the surface defect does not change the primary pattern of the atomic displacements known from the calculation of pure (001) surface relaxation [8]. As has been revealed there, the most displaced atoms are surface (for SrO termination) and subsurface (for TiO$_2$ termination) strontium atoms which relax inwards and outwards the slab center, respectively, and show displacements which are by several orders of magnitude larger than other atoms. However, the iron impurity incorporation induces also the atomic displacements not only in the vertical direction: the oxygen displacements found in the first atomic shell of the surface iron defect are reported in Table 3 and schematically shown in Figure 2.

Figure 2. Three upper atomic layers of SrO- (a) and TiO$_2$-terminated (b) surfaces with the iron defect. Only the directions of displacements for the most relaxed strontium atoms and the nearest to the iron defects oxygen atoms are schematically indicated.
Table 3. The displacements of oxygen atoms in the first atomic shell of the iron impurity for different iron concentrations $C_{Fe}$. Inward relaxation means displacement towards the iron defect. $E_f$ is iron formation energy.

| Extension | Termination | $C_{Fe}$ (%) | $d$ (Å) | Oxygen shifts (Å) | $E_f$ (eV) |
|-----------|-------------|--------------|---------|-------------------|------------|
|           |             |              |         | **Inward** | **Outward** |          |          |
| 2×2       | SrO         | 25.0         | 7.78    | 0.0778$^a$ | 0.0000     | 1.47     |          |
|           | TiO$_2$     |              |         | 0.0370$^b$ |            |          |          |
| 3×3       | SrO         | 11.1         | 11.68   | 0.0788$^a$ | 0.0092     | 1.47     |          |
|           | TiO$_2$     |              |         | 0.0395$^b$ |            |          |          |

$^a$ Oxygen atom in the upper plane.
$^b$ Oxygen atom in the third plane.

Table 4. The Mulliken effective atomic charges (in e) for the undoped and doped (001) surfaces.

| Termination | Plane | Doped surface | Undoped surface |
|-------------|-------|---------------|-----------------|
|             |       | Ion Charge    | Ion Charge      |
| SrO         | 1     | Sr 1.85       | Sr 1.85         |
|             |       | O $-1.36$     | O $-1.52$       |
|             | 2     | Fe 2.28       | Ti 2.37         |
|             |       | O $-1.47$     | O $-1.44$       |
| TiO$_2$     | 1     | Fe 2.22       | Ti 2.29         |
|             |       | O $-1.29$     | O $-1.30$       |
|             | 2     | Sr 1.85       | Sr 1.85         |
|             |       | O $-1.44$     | O $-1.37$       |

In this table we also present iron formation energies computed in the same manner as for the bulk. From a comparison of bulk and surface values one can conclude that there is a perceptible driving force for iron impurities to segregate to both SrO and TiO$_2$ surfaces, with a slight energy preference in the latter case.

It is interesting to compare the calculated Mulliken atomic charges for perfect and defective surfaces listed in Table 4. As known from the simulations of bare and water-covered nondefective SrTiO$_3$ surfaces [8, 12], SrO-terminated surface reveals the more basic nature of the top oxygen atoms making the dissociative type of water adsorption on SrO-terminated surface more probable than on the TiO$_2$-terminated one. This is clearly reflected here by the oxygen charges on both surfaces being more negative for SrO plane. However, the iron defect substituted for titanium in the second layer significantly reduces the charge of the top oxygen, what, in turn, should lead to less basic properties of SrO-terminated surface in the iron-doped material.

5. Conclusions

The first-principles calculations within the hybrid HF-DFT LCAO approach using the B3PW functional have demonstrated that the Jahn-Teller lattice distortion around the Fe$^{4+}$ impurity in the bulk SrTiO$_3$ increases with lowering the iron concentration, corroborating recent EXAFS experiments. A comparison of the iron formation energies in the bulk and on the (001) surfaces shows the propensity of Fe$^{4+}$ to segregate to both the SrO- and TiO$_2$-terminated surfaces, with a slight energy preference in the latter case. The atomic displacements around the surface iron defects show a more complex pattern than in the bulk due to combination of the two effects,
namely, the Jahn-Teller distortion and the surface relaxation. The Mulliken population analysis indicates that the presence of Fe$^{4+}$ impurities in the subsurface plane significantly reduces the charge of the top oxygen in the SrO surface plane above these impurity defects (in comparison to the substituted Ti$^{4+}$), thus severely diminishing its basic properties.

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