

A first-principles study of dilute solutions of oxygen in titanium

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Solutions of oxygen in titanium are investigated through density functional calculations. This method provides an accuracy comparable to the experimental determination of the enthalpy of dissolution of O in α -Ti but not for β -Ti solutions. The insertion of an O atom induces an increase in the electronic density around the O atom and a diffuse decrease in the electronic density in the lattice. Two oxygen sites sharing a face of two adjoining Ti octahedra cannot be simultaneously occupied.

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The rapid development of nanostructured Ti-based materials [1] has been impressive in recent years. The use of multiscale simulations, which is the most appealing approach for the study of these materials, requires the availability of reliable ab initio methods to deal with defects. In the first part of this paper, we shall discuss mainly the ability of ab initio methods to determine the enthalpy of formation of defects. This point is timely as the calorimetric methods that are most suitable [2] for determining the formation enthalpies of defects in metal–oxygen systems are less and less available. In the second part of this paper, we shall examine the geometric and electronic perturbations caused by the insertion of an O atom in Ti. We have used the Vienna Ab initio Simulation Package (VASP) [3,4] which is based on the density functional theory. Technical choices made in the use of this package have been detailed elsewhere [5,6]. A cutoff energy for the plane-wave basis equal to 400 eV has been chosen. We have considered 10 valence electrons for Ti and six valence electrons for O.

As it is stable up to 1152 K [7], the hexagonal close-packed (hcp) structure (α phase) is the easiest Ti structure to study using a DFT program at 0 K. We have used two supercells: an orthorhomboid with 48 Ti atoms (four layers of 12 atoms) and a hexagonal prism

with 64 Ti atoms (four layers of 16 atoms). In both cases, the product of the number of k points times the number of Ti atoms has been chosen equal to 384. We have calculated the energy minima for both Ti_n and Ti_nO supercells under the hexagonal compact symmetry constraint, allowing the parameters a and c to vary independently. For both supercells, the atomic volume of pure Ti has been found equal to 17.28 \AA^3 with $c/a = 1.58$ in agreement with experiments [8] instead of the ratio 1.633 expected for ideal hcp structures. This implies that the octahedra are not quite regular: the lengths of the edges are either 2.87 or 2.93 Å. The incorporation of one O atom in our supercells provokes a moderate lattice expansion corresponding to a partial molar volume of O equal to 2.6 cm^3 . The Ti–O distance, which is equal to 2.05 Å in the unrelaxed crystal, increases by 0.03 Å. This result differs from the statement of Lado-Tourino and Tsobnang [9] who find that relaxation provokes a decrease of the Ti–O distance.

As detailed in Tétot et al. [10], two calibration methods have been used, yielding slightly different results, the so-called chemical calibration being probably more accurate. As it will be discussed later, the choice of a reference state plays an essential role in the ability of local density approximation (LDA) and generalized gradient approximation (GGA) functionals to calculate the energies of formation of defects, and so we present them in detail. As shown in Table 1, three processes may be considered to describe the oxidation process. Process (A), which considers the reaction of atomic O with Ti is

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Table 1. Calculated vs. experimental heat releases for the three processes considered

Process	Experiment (chemical calibration)	GGA calculation at 0 K	Difference LDA–GGA
$\frac{1}{x}\text{Ti} + \text{O} \rightarrow \frac{1}{x}\text{TiO}_x$	–9.01	–8.82	–1.37
$\frac{1}{x}\text{Ti} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{x}\text{TiO}_x$	–6.50	–5.75	–0.75
$(\frac{1}{x} - \frac{1}{2})\text{Ti} + \frac{1}{2}\text{TiO}_2 \rightarrow \frac{1}{x}\text{TiO}_x$	–1.45	–1.08	–0.25

Process (A) (atomic O reference), process (B) (reference O₂), process (C) (comproportionation). Energies are in eV.

the more direct one. We shall use it in the discussion of the oxidation of β -Ti. The heat effect associated with process (B) is half the partial molar enthalpy of mixing of O₂ ($\Delta H(\text{O}_2)$) and is the quantity which is measured in the high-temperature calorimeter. The heat effect associated with process (C) may be written:

$$1/2[\Delta H(\text{O}_2) - \Delta_f H_T^0(\text{TiO}_2)] \quad (1)$$

In this expression, $\Delta_f H_T^0(\text{TiO}_2)$ is the formation enthalpy of TiO₂ at temperature T . This quantity is only weakly temperature dependent as the number of oscillators remains constant in the transformation (C) while the number of gaseous species remains zero. This is not the case for processes (A) and (B). Results are reported in Table 1 and in Figure 1.

As pointed out by Crocombette et al. [11], interstitial O is easier to form with LDA than with GGA. Our simulations confirm this result in this particular case. The discrepancies between LDA and GGA strongly decrease when both reference states are condensed phases. This feature was also present in the study of O solutions in Si [5]. Moreover, the agreement with experiment is very good when the comproportionation process is used. It is noteworthy that the relaxation energy is rather small (0.085 eV).

Now let us turn to β solutions. In the interest of simplicity, we have used process (A) which uses atomic O as a reference and GGA functionals to study the dissolution of O in β -Ti. In spite of its metastability at low temperatures, no difficulty occurs for pure β -Ti which can be relaxed at 0 K without loss of the initial symmetry of the crystal. The energy of transition per atom at 0 K β to α is found to be somewhat more exothermic

(–0.104 eV) than the experimental value of –0.045 eV at 1152 K determined by Kaschnitz and Reiter [7].

Things are quite different for O solutions: The insertion of O breaks the initial symmetry and makes the transition towards a more stable phase easier. If no relaxation is allowed, the insertion of O is found to be exothermic but with a heat release (5.52 eV) much smaller than found in α phase (8.74 eV). This is not too surprising because of the unfavorable values of the Ti–O distances (two values equal to 1.63 Å and four other ones equal to 2.30) in the flattened octahedrons of the body-centered cubic (bcc) lattices compared to the six Ti–O distances equal to 2.05 Å in the α phase.

Full relaxation cannot lead to the α phase since the applied supercells for the β phase are not commensurate with the α phase.

In fact, what we obtain in our simulations are structures intermediate between α and β structures: in order to ascertain this point, we have relaxed at constant volume several supercells with different numbers of Ti atoms under the cubic symmetry constraint. In any case the calculated heat effect is intermediate between:

- The expected value for the β phase (–9.12 eV mol^{–1}). This value is obtained from Table 1 by adding the experimental difference of $\frac{1}{2}\Delta H(\text{O}_2)$ in the α and β phases. (–0.30 eV) to the calculated GGA value for the α phase.
- The heat released from a two-step unrealistic process.
 1. Transformation of the whole sample from β structure to α structure (martensitic transformation). This step corresponds to a heat release equal to $n_{\text{Ti}} \cdot \Delta H$ transition.
 2. The dissolution of O in α -Ti: $\frac{1}{2}\Delta H(\text{O}_2)$.

These quantities have been reported in Table 2. If the O is removed from the sample, it is noteworthy that the final energy per Ti atom (after relaxation) is smaller than the initial energy of pure β -Ti by an amount independent of the size of the sample as long as we are using a supercell with $8n$ Ti atoms (with $n = 1, 2, 4, 8$). The calculation using a 54-atom cell provides a somewhat smaller energy decrease.

Let us now examine the electronic perturbation caused by the insertion of an O atom into a Ti lattice (α or β). In order to obtain a picture of the electronic transfer due to the insertion of O, we have used the difference between full self-consistent charge densities (Ti₄₈O) on the one hand and superposed self-consistent charge densities of Ti₄₈ and of one atomic density for a spinless isolated O atom on the other hand. In the remaining part of this paper, we shall call this quantity $\Delta\rho$. The essential feature is an enhancement of the electronic density in the vicinity of the O atom which pro-

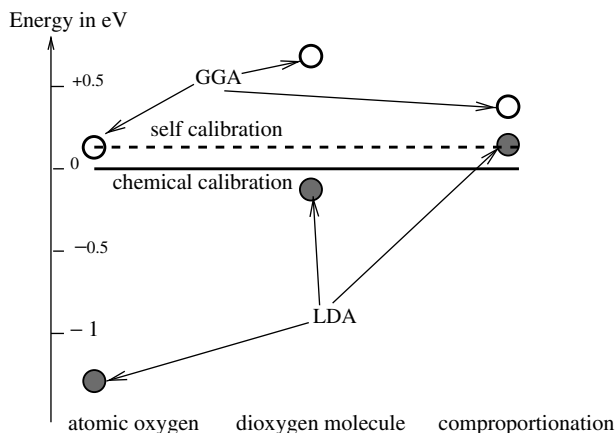


Figure 1. The difference between the experimental and calculated heat of reactions for solutions of O in α -Ti as a function of the approximation (GGA vs. LDA) and of the reference state. Negative values indicate a more exothermic O dissolution than experimentally observed.

Table 2. Computed heat effects of dissolution of O in β -Ti

n Ti/supercell:	8	16	32	54	64
Shape of the supercell:	rh	Cube	rh	Cube	rh
Unrelaxed heat	−5.55	−5.53	−5.53	−5.47	−5.51
Relaxation energy	−3.67	−4.00	−4.90	−5.28	−6.50
Expected value	−9.12	−9.12	−9.12	−9.12	−9.12
Calculated heat effect	−9.22	−9.53	−10.43	−10.75	−12.01
Limiting unrealistic case	−9.63	−10.43	−12.03	−14.23	−15.23
ΔE_{Ti} after removal of O	−0.050	−0.049	−0.048	−0.040	−0.049

All energies are in eV. Supercells are either cubes or rhomboedra (rh). The reactants are atomic O and pure Ti. The heat release calculated in our simulations as well as that calculated in the limiting unrealistic case increase strongly as the number of Ti atoms increases. ΔE_{Ti} is the change of energy per Ti atom after addition and removal of one O atom in the supercell.

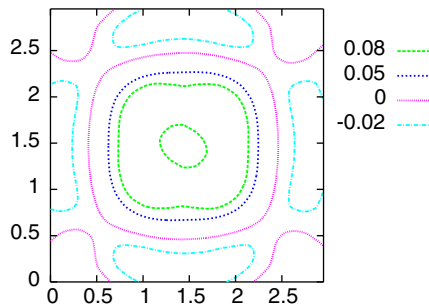
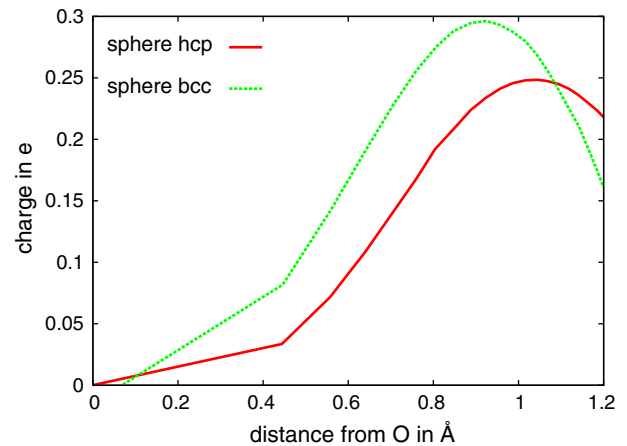
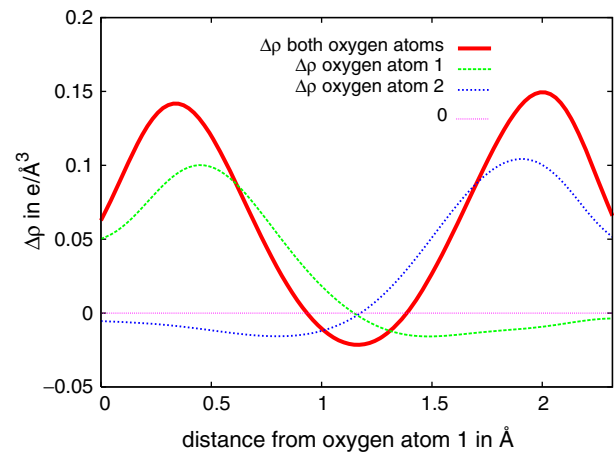
vokes a diffuse decrease in the electronic density in the lattice as may be seen in Figure 2; the electronic density near Ti atoms remains essentially unchanged.

Using these electronic density calculations, in order to make this observation more quantitative, in Figure 3 we have plotted the electronic charge inside spheres of increasing radii. We can visualize the O as a sphere of radius 1.05 Å and charge 0.25 e in α -Ti and as a sphere of radius 0.9 Å and charge 0.3 e in β -Ti. In fact $\Delta\rho$ is not quite spherical as apparent in Figure 2. In other words, the insertion of an atomic O acts as a perturbation, creating a small island of negative ion. This process is largely exothermic. This effect is more visible for a bcc lattice, which may be understood as a consequence of the larger value of $\langle \frac{1}{d(\text{Ti-O})} \rangle$ in bcc lattices which increases the electronic transfer.

O atoms are located inside Ti octahedra. Interstitials in first, second and third neighbor positions share, respectively, a face, an edge and a vertex. From crystallographic studies [12], Dubertret has concluded that in α -Ti, two O sites sharing a face cannot be simultaneously occupied. In the following, we have explored this observation in more details.

The deformation of electronic clouds involving two O atoms in first neighbor positions is shown in Figure 4. We observe a strong repulsion between them.

The distance between two O atoms in first nearest neighbor positions increases strongly because of the relaxation (from 2.32 to 2.51 Å) but only slightly otherwise.

**Figure 2.** $\Delta\rho$ (in $\text{e}\text{\AA}^{-3}$) in a plane containing the interstitial O atom and four Ti atoms in α -Ti (unrelaxed lattice) at the corners of the square. Distances are in Å.**Figure 3.** Electronic charge inside spheres of increasing radii due to the insertion of O.**Figure 4.** Deformation of the electronic cloud near two O atoms. We have considered two O atoms in first nearest neighbor positions. As expected, the figure is symmetrical. If atoms 1 and 2 do not interact, $\Delta\rho$ is smoothly decreasing as we go from one atom to the other. If both atoms are simultaneously present in the lattice, we observe an outward move of the electronic clouds.

Let us define the interaction energy between two O atoms by

$$E_{\text{interaction}} = E(\text{Ti}_{48}\text{O}_2) + E(\text{Ti}_{48}) - 2E(\text{Ti}_{48}\text{O}) \quad (2)$$

In this way, we find an interaction energy between first nearest neighbors equal to 0.64 eV for the unrelaxed lattice; this value drops to 0.51 eV if relaxation is allowed. It is of interest to compare this value to the values for O atoms in second and third nearest neighbor positions in a relaxed lattice, which are only 0.08 and 0.04 eV, respectively. This large value, which may be explained by a strong electrostatic repulsion between O negative electronic atmospheres, is consistent with the observation of Dubertret [12] and with the blocking model of Boureau and Campserveux [13].

As a conclusion, in this paper, we have demonstrated several points:

- DFT calculations yield an accuracy comparable to the best experimental determinations of the defect formation energy at least for a system stable at 0 K.
- For systems not stable at 0 K, things are more complicated. For metastable systems with high activation energy, the situation is identical to the case of stable systems. Different structures may be safely studied [14]. This is not the case for unstable systems such as β solutions of O in Ti at 0 K. The system has to cope with the symmetry constraints and the thermodynamic constraint with no activation barrier. It is not easy to extract information from the resulting configuration. Nevertheless, a lot of information concerning unrelaxed structures which is not available from experiments can be obtained, such as electronic structure and the energy of defective structures.
- In order to get precise results, it is necessary to consider all reactants and products in the solid phase. An additional advantage of this method is that discrepancies between GGA and LDA are greatly reduced.
- Strong repulsive interactions observed in crystallographic studies between first nearest neighbors can be explained by electrostatic effects.

- The insertion of an O provokes a localized electronic perturbation around the O atom, which brings some legitimacy to pair potentials including effective O–O interactions. A study based on such potentials in order to explain order–disorder transitions is in progress and the preliminary results are encouraging.

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