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Use of a variable-charge interatomic potential for atomistic simulations of bulk, oxygen vacancies, and surfaces of rutile TiO_2

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In this paper, interatomic potential models used for atomistic simulations of insulating oxides are revisited through the example of TiO_2 rutile. The cohesive energy of oxides comprises an electrostatic part and a short-range part whose relative importance differs with the models. The electrostatic part can be evaluated by considering either point fixed atomic charges or, alternatively, charges that are allowed to vary in response to the local atomic environment, with a shielding correction to coulombic interactions at short range. We deeply analyzed this latter approach in the framework of the Rappé and Goddard QEq charge equilibration scheme. We conclude that it is an efficient model to describe heterogeneous situations due to point defects or surfaces. Moreover, whatever the description of the electrostatic part of the energy is, several short-range interatomic potentials are found to describe in an acceptable way the crystal bulk properties (cohesive energy, elastic constants, etc). To compare the efficiency of various short-range potentials, we selected the TiO_2 rutile whose experimental formation energy of the oxygen vacancy is available. By combining it with the cohesive energy, we have been able to accurately analyze the energetics of TiO_2 as a function of those potentials. In this paper we show first that Morse potential is not adapted to oxygen-oxygen interactions and that pair-wise potentials between Ti-O pairs are not suitable to describe defects. As a result, we propose a model that combines the QEq description for electrostatic energy, a Buckingham potential for O-O interactions and a *N*-body potential for the covalent part of the Ti-O interactions. This model efficiency has been tested on bulk, oxygen vacancy, and surfaces of rutile and turned out to provide results which fit very satisfactorily the experimental data.

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I. INTRODUCTION

As oxides play a major role in materials science, it is of great interest to perform atomistic simulations on a great number of atoms at finite temperature and as a function of oxygen chemical potential, which is not conceivable by means of *ab initio* techniques yet. This requires a realistic and operational interatomic potential model (IPM). Until recently, most of the IPMs for oxides were based on the Born-Madelung cohesive description of ionic solid. This involves to consider coulomb interactions between fixed formal point charges, often including a shell model[1] to take the polarizability of ions into account, and a repulsive term using some combination of Born-Mayer and van der Waals potentials, acting at short range (see, for example, Refs. 2–4, and references therein). Beyond bulk and surface properties of pure or doped materials, there is a need to model materials in which heterogeneous interfaces occur. As a matter of fact, properties of oxide/oxide and metal/oxide interfaces govern a number of technologically important devices, including thermal barriers, gas sensors, fuel cells, catalytic devices, etc. It is clear, in this case, that the picture of fixed charges (formal or not) is incorrect. A model allowing charges to vary in response to changes in the local environment of the ions is then needed. Based on the earlier work by Mortier and others[5,6] and on the QEq charge equilibration scheme of Rappé and Goddard,[7] many variable-charge models have been proposed.[8–15] These models mainly differ from, first, the predicted ion charges, that depend on the QEq parameters and, second, from the type of short-range potentials to be employed. The more recent models use a two-body Morse potential in a so-called "MS-Q" model.[9,13,15]

Our studies on oxides are aimed at simulating the oxide/oxide and metal/oxide interfaces taking place in thin layer materials synthesized in our laboratory. More precisely, we are interested in the dependence of chemical and structural properties of the interfaces on temperature and partial pressure of oxygen, including the important role of point defects. We were first interested in TiO_2 because it holds an important place in material science due to the wide range of technical fields where it is employed (for a recent review see Ref. 16). Moreover, the rutile polymorph of TiO_2 can be considered as a model oxide for several reasons: (i) it is one of the most investigated systems, experimentally and theoretically, both for bulk and surface properties,[16] (ii) it has relatively strong covalent characteristics, (iii) although it seems simple to model theoretically, its open structure based on tetragonal centered titanium cell poses problems with regard to more compact structures, and (iv) the formation energy of an oxygen vacancy has been measured accurately,[17,18] which is not often the case. Further, this energy has been reproduced with a very good precision by *ab initio* calculations.[19] In contrast, whatever the set of potential parameters may be, the MS-Q models proposed for TiO_2, (Refs. 13 and 15) do not allow us to obtain a satisfactory value for the formation energy of an oxygen vacancy. We therefore revisited these MS-Q models in order to analyze the reasons of their failure. In this paper, we present a detailed analysis of the energetics of TiO_2, including that of oxygen vacancy, in the framework of various models. Our analysis led us to propose several major improvements of the MS-Q model, in particular, the use of *N*-body short range potentials which is in agreement with the description of the covalent character of the Ti-O bond by

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means of the second moment approximation of the tight-binding scheme.[20]

The structure of the paper is as follows. In Sec. II, we recall the main differences between the fully ionic description of the fixed formal charge model and the QEq scheme with two aims in view. First, this is useful to discuss some arguments developed in Ref. 15 about the QEq scheme, which is done in Sec. III. Second, this allows us to examine the pieces that go into the calculation of the energy of the oxygen vacancy and the role that this calculation plays in checking the model. In Sec. III, we discuss the MS-Q models proposed[13,15] and their limitations. In Sec. IV, we propose some improvements to these models and present results on bulk, oxygen vacancy, and surfaces of rutile TiO_2 and on bulk anatase and brookite, the two other natural polymorphs of TiO_2. All our calculations were performed using a general Monte Carlo code (SMASH)[21] that we developed. Many calculations were checked using GULP (Ref. 22) and DL_POLY[23] codes.

II. FIXED FORMAL CHARGE MODEL VS. QEq SCHEME

By definition, the cohesion of a solid is the formation of this solid from gaseous atoms, taken as zero of energy. For ionic solids, a stage of the formation consists in creating ions by transfer of electrons. In the case of a perfect TiO_2 crystal, this can be written as

$$\mathrm{Ti}(g) + 2\mathrm{O}(g) \overset{(1a)}{\rightarrow} \mathrm{Ti}^{4q+} + 2\mathrm{O}^{2q-} \overset{(1b)}{\rightarrow} \mathrm{TiO}_2(s), \qquad (1)$$

where q is the charge transfer by unit charge between cations and anions ($q \in \{0,1\}$). The cohesive energy, corresponding to the whole process (1), is $E_{\mathrm{coh}}=-19.9$ eV/TiO_2 formula.[24]

A. The fixed formal charge model (FFCM)

The formal charges of the ions Ti ($q_{\mathrm{Ti}}=+4$) and O ($q_{\mathrm{O}}=-2$) correspond to $q=1$ in the process (1). In this case, the ionic energy of the process (1a), E^{ion}, is known experimentally and is the sum of the four first ionization energies of titanium (91.1 eV)[24] minus twice the first and second electron affinities of oxygen $-2(1.46-8.75) \approx 14.6$ eV,[25] that is to say $E^{\mathrm{ion}}=105.7$ eV in all.

The lattice energy, corresponding to the process (1b), is $E_{\mathrm{latt}}=E_{\mathrm{coh}}-E^{\mathrm{ion}}=-19.9-105.7=-125.6$ eV. E_{latt} is the sum of the Madelung energy (E^M) and of the short-range energy ($E^{\mathrm{SR}}_{\mathrm{coh}}$). Classically, E^M may be simply evaluated by

$$E^M = \frac{\alpha_M \times q_{\mathrm{Ti}} \times q_{\mathrm{O}}}{2 \times r_0} = -142.4 \text{ eV}, \qquad (2)$$

where $\alpha_M=4.82$ is the Madelung constant of the rutile structure with respect to the first neighbor distance Ti-O, $r_0=1.95$ Å (on average). Thus, the short-range energy, $E^{\mathrm{SR}}_{\mathrm{coh}}=E_{\mathrm{latt}}-E^M=16.8$ eV is positive (repulsive). To sum up, in the FFCM, the cohesive energy of rutile is the sum of a large cohesive electrostatic part $E^{\mathrm{elec}}_{\mathrm{coh}}=E^{\mathrm{ion}}+E^M$, and a repulsive short-range part

$$E_{\mathrm{coh}} = E^{\mathrm{elec}}_{\mathrm{coh}} + E^{\mathrm{SR}}_{\mathrm{coh}} = -36.7 + 16.8 \text{ eV} = -19.9 \text{ eV}. \qquad (3)$$

Now, a convenient way to sharpen the energetics analysis of rutile TiO_2 is to focus on the formation, at constant pressure, of an oxygen vacancy V_{O} for which the formation energy is known: $E_{V_{\mathrm{O}}}=7.5$ eV.[17–19] Usually, in the framework of the FFCM, this energy corresponds to the following process:

$$2\mathrm{Ti}^{4+} + \mathrm{O}^{2-} \rightarrow \mathrm{O}(g) + 2\mathrm{Ti}^{3+} + V_{\mathrm{O}}. \qquad (4)$$

$E_{V_{\mathrm{O}}}$ has three components: an ionic component $E^{\mathrm{ion}}_{V_{\mathrm{O}}}$ to form one neutral oxygen from one oxygen ion and two Ti^{3+} from two Ti^{4+}, a loss in Madelung energy $E^M_{V_{\mathrm{O}}}$ and a short-range interaction part $E^{\mathrm{SR}}_{V_{\mathrm{O}}}$. The ionic term is known ($E^{\mathrm{ion}}_{V_{\mathrm{O}}}=-93.8$ eV)[24,25] and $E^M_{V_{\mathrm{O}}}$ can be evaluated by Monte Carlo simulations: $E^M_{V_{\mathrm{O}}} \approx 108$ eV for relaxed energy. One can then deduce

$$E^{\mathrm{SR}}_{V_{\mathrm{O}}} = E_{V_{\mathrm{O}}} - E^{\mathrm{ion}}_{V_{\mathrm{O}}} - E^M_{V_{\mathrm{O}}} \approx -6.5 \text{ eV}. \qquad (5)$$

Now, it is convenient to assume that almost all of the short-range interactions are due to the first neighbors (this is confirmed in all our calculations). In TiO_2, a titanium atom has 6 oxygen atoms at first neighbors and an oxygen atom has 3 titanium atoms and 11 oxygen atoms at first neighbors (these 11 oxygen atoms lie between 2.57 and 2.95 Å, and we consider a single shell of neighbors at a mean distance of 2.77 Å). Note that the Ti-Ti short range interactions are neglected, as in a number of models (see Ref. 2, and references therein). Limiting ourselves to these shells and assuming pair interactions, the short-range part of the cohesive energy $E^{\mathrm{SR}}_{\mathrm{coh}}$ and of the energy of formation of the oxygen vacancy $E^{\mathrm{SR}}_{V_{\mathrm{O}}}$ can be expressed, respectively,

$$E^{\mathrm{SR}}_{\mathrm{coh}} = 6V_{\mathrm{Ti\text{-}O}} + 11V_{\mathrm{O\text{-}O}} \approx 16.8 \text{ eV} \qquad (6)$$

and

$$E^{\mathrm{SR}}_{V_{\mathrm{O}}} = -3V_{\mathrm{Ti\text{-}O}} - 11V_{\mathrm{O\text{-}O}} \approx -6.5 \text{ eV}, \qquad (7)$$

where $V_{\mathrm{Ti\text{-}O}}$ and $V_{\mathrm{O\text{-}O}}$ are the short-range pair interactions between first neighbor Ti-O and O-O pair, respectively. Equations (6) and (7) lead to

$$E^{\mathrm{SR}}_{\mathrm{coh}} + E^{\mathrm{SR}}_{V_{\mathrm{O}}} = 3V_{\mathrm{Ti\text{-}O}} \approx 10.3 \text{ eV}, \qquad (8)$$

and therefore to

$$V_{\mathrm{Ti\text{-}O}} \approx 3.5 \text{ eV} \quad \text{and} \quad V_{\mathrm{O\text{-}O}} \approx -0.35 \text{ eV}. \qquad (9)$$

In the FFCM, short-range Ti-O interactions must be repulsive and O-O interactions attractive, which is not intuitive.

Let us consider, for example, the often cited Catlow *et al.*,[2] model. Buckingham potentials are used for Ti-O and O-O pair interactions (see Fig. 1). At first neighbor, the O-O interaction is slightly attractive (−0.06 eV), because of the predominance of the Van der Waals term, and the first neighbor interaction of the Ti-O pair is repulsive (5.3 eV) and represents 95% of the short range energy. The sign of the interactions is in agreement with Eq. (9), but the model clearly overestimates short-range repulsive interactions. These interactions lead to $E^{\mathrm{SR}}_{\mathrm{coh}}=31$ eV [Eq. (6)],

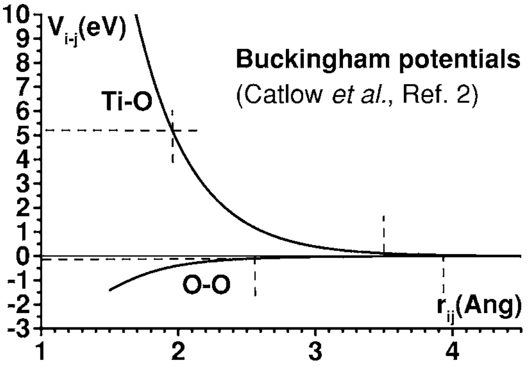


FIG. 1. Short-range Buckingham potentials used in the fixed formal charge model of Ref. 2. Ti-Ti interactions are neglected in this model. Dashed lines refer to first and second neighbor shells.

overestimating $E_{\text{coh}}^{\text{SR}}$ by 15 eV, which represents the difference between calculated and experimental lattice energy (−110 eV instead of −125.6 eV[2]) or, equivalently, between calculated and experimental cohesive energy ($E_{\text{coh}}=-4$ eV instead of −19.9 eV). In the same way, the model leads to $E_{V_{\text{O}}}^{\text{SR}}=-15$ eV, which yields, by use of Eq. (5), $E_{V_{\text{O}}}\approx-1$ eV. This negative value, not physically correct, was confirmed by our Monte Carlo calculations at constant pressure, whether or not shell model was included. Note that the original result in Ref. 2 (positive vacancy energy) was obtained by static simulations using the Mott-Littleton method at constant volume. This exemplifies the important role that point defect data can play to check potentials.

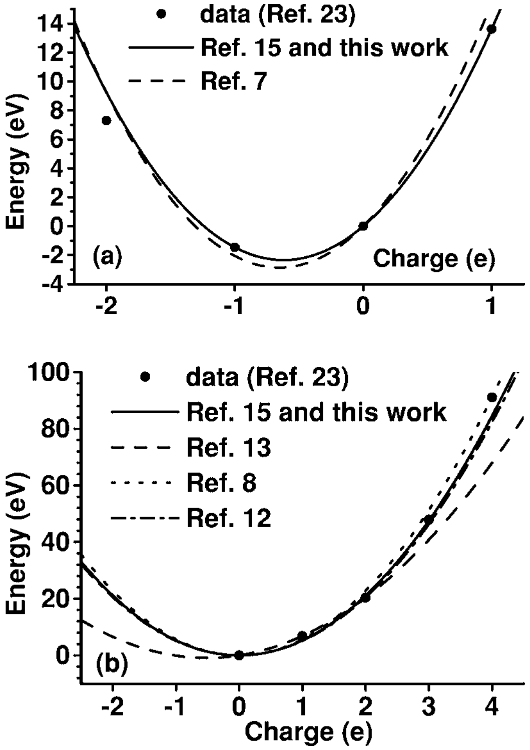
Thus, the parameters of the potentials have to be better fitted to make the FFCM usable. Nevertheless, even in these conditions, the latter model has an important shortcoming: it does not allow the charge transfer when a source of heterogeneity occurs (point defect, surface, interface). In the preceding, we considered that the charge transfer during the formation of an oxygen vacancy is carried out by forming two reduced cations at first neighbor, even though the charges may be delocalized in reality, at least between the three Ti first neighbors of the vacancy. Concerning the surfaces the charge transfer do not exceed ten percent (with respect to the charges of the bulk) and could be neglected as a first approximation. Nevertheless, we shall see in the following that this charge transfer has a noticeable effect on the atomic relaxations near the surface. Last but not least, if one considers an interface between a metal and an oxide or between two oxides, a fixed charge model is clearly inappropriate. Now, studying such interfaces is one of our ultimate goals, and we need for that a model that permits to calculate the atomic charges with respect to the local environment of the atoms. Such a model is discussed in the next section.

B. The QEq scheme

The QEq scheme is based on the electronegativity equalization principle of Rappé and Goddard:[7]

$$\mu=\mu_i=\frac{\partial E_{\text{coh}}^{\text{elec}}}{\partial q_i}, \tag{10}$$

where $E_{\text{coh}}^{\text{elec}}=E^{\text{ion}}+E^{M}$ is the electrostatic part of the cohesive energy, q_i the charge on the ion i, and μ_i the electronegativity. In other words, at equilibrium, the charges q_i carried by the ions are those that minimize $E_{\text{coh}}^{\text{elec}}$ with the condition $\Sigma q_i=0$. These charges are smaller than the formal charges and therefore, the parameter q in Eq. (1) is smaller than 1. A number of models based on this scheme have been developed for different systems: for example oxides[8–15] and liquid water.[26]


(a)

(b)

FIG. 2. Atomic self-energy of ion (a) O, (b) Ti as a function of charge.

Calculation of $E_{\text{coh}}^{\text{elec}}$ requires that the energy E^{ion} of the process (1a) be evaluated first for $q<1$ and then the electrostatic interaction E^{M}.

$E^{\text{ion}}=2E_{\text{O}}+E_{\text{Ti}}$ where E_{O} (E_{Ti}) is the self-energy of an oxygen (titanium) ion with a charge q_{O} (q_{Ti}) not known *a priori* (the relation $2q_{\text{O}}+q_{\text{Ti}}=0$ must be fulfilled). The self-energy of oxygen and titanium ions as a function of charge is shown in Fig. 2. Following Rappé and Goddard,[7] the self-energy of the ion i can be expressed to the second order as

$$E_i=E_i(0)+\chi_i^0 q_i+\frac{1}{2}J_i^0 q_i^2, \tag{11}$$

where χ_i^0 and J_i^0 are related to electronegativity and hardness, respectively. These parameters can be derived from atomic data as in the original work of Rappé and Goddard.[7] Nevertheless, the values used by these authors for oxygen do not fit very well the data of Fig. 2(a). For this reason, most of the authors consider χ_i^0 and J_i^0 as adjustable parameters.[8,15] We acted in the same way. Moreover, it has to be noted that the minimum of the function $E_i=f(q_i)$ corresponds to $q_i=0$ for metals [see Fig. 2(b)] that leads to $\chi_i^0=0$ (whereas for oxygen the minimum lies between $q_{\text{O}}=0$ and $q_{\text{O}}=-1$). J_i^0 is then adjusted to reproduce the curve $E_i=f(q_i)$ in the vicinity of

TABLE I. QEq parameters for Ti and O used in this study.

	O	Ti
χ^0 (eV)	7.543	0.0
J^0 (eV)	12.162	10.572
R_A (Å) (MB-Q model)	0.63	0.75
R_A (Å) (SMB-Q model)	0.6	0.77

the expected charge of the metal ion (between 2 and 3 for Ti, see further).

The electrostatic interaction depends on the form of the Coulomb potential J_{ij} between ions i and j. For large separation r_{ij}, classically we have $J_{ij}=14.4/r_{ij}$ (where the conversion factor 14.4 allows r_0 to be in Å and J_{ij} in eV). In the QEq scheme, for distances such that the electronic distributions of ions overlap, the classical Coulomb potential (corresponding to point charges) is replaced by the Coulomb integral between two single *s*-type Slater orbitals

$$\rho_i(r)=N_n r^{n-1} e^{-\zeta r}, \tag{12}$$

where N_n is the normalization constant and n is the quantum number of the outer valence orbital. The exponent ζ is given by

$$\zeta=(2n+1)/(4R_A), \tag{13}$$

where R_A is the covalent radius for atom A in the original QEq formulation.[7] In the present study, following Thomas *et al.*[15] we use R_{O} and R_{Ti} as adjustable parameters which are determined by the bulk equilibrium atomic charges. Assigning a charge to an atom in an ionocovalent compound is somewhat arbitrary. Nevertheless, in order to use tractable models, it is necessary to associate a fictitious charge to each atom, which is necessarily smaller than the formal charge. A starting point may be *ab initio* calculated Mulliken charges[27] which varies from 2.23 to 2.82 for Ti in rutile.[12,15,28–30] J_i^0 is therefore adjusted for $q_{\mathrm{Ti}} \in \{2,3\}$. This leads to the QEq parameters reported in Table I for oxygen and titanium. J_{ij} as a function of r_{ij}, corresponding to these QEq parameters, are plotted in Fig. 3.

The main consequence of the decrease of the ion charges and of the shielding of the Coulomb interaction is to drastically decrease the absolute value of the electrostatic part of the cohesive energy $|E_{\mathrm{coh}}^{\mathrm{elec}}|$, which becomes smaller than the absolute value of the total cohesive energy $|E_{\mathrm{coh}}|$. Therefore, the short-range part $E_{\mathrm{coh}}^{\mathrm{SR}}$ changes sign with respect to the FFCM and becomes negative (cohesive). Moreover, the short-range part of the formation energy of the oxygen vacancy $E_{V_{\mathrm{O}}}^{\mathrm{SR}}$ becomes positive, of the order of 4 eV. This implies that now $V_{\mathrm{Ti\text{-}O}}$ must be negative and cannot longer be described with a Buckingham potential. As for $V_{\mathrm{O\text{-}O}}$, it must be slightly positive. This is a radical change with regard to the preceding model.

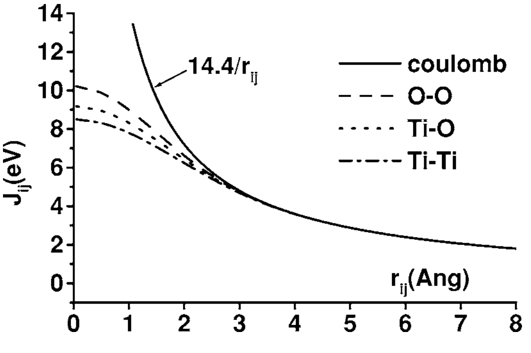


FIG. 3. J_{ij} in the QEq scheme corresponding to the QEq parameters χ^0 and J^0 displayed in Table I.

III. THE MS-Q MODEL

The most recent QEq-type model applied to $\mathrm{TiO_2}$, is the MS-Q model by Swamy and Gale (SG).[13,14] It is based on the work by Demilrap *et al.*[9] on $\mathrm{SiO_2}$, where the original QEq scheme of Rappé and Goddard is combined with short-range Morse potentials[31] of the form

$$V_{ij}(r_{ij})=D_{ij}([1-e^{-a_{ij}(r_{ij}-r_{ij}^0)}]^2-1) \tag{14}$$

or, equivalently,

$$V_{ij}(r_{ij})=D_{ij}e^{-2a_{ij}(r_{ij}-r_{ij}^0)}-2D_{ij}e^{-a_{ij}(r_{ij}-r_{ij}^0)}, \tag{15}$$

where D_{ij}, a_{ij} and r_{ij}^0 are positive adjustable parameters. r_{ij}^0 is the equilibrium intermolecular separation when dealing with diatomic molecules. $V_{ij}(r_{ij})$ has a minimum $(=-D_{ij})$ when $r_{ij}=r_{ij}^0$. The crystal structures and bulk moduli of eleven $\mathrm{TiO_2}$ polymorphs were quite satisfactorily reproduced with this model[14] which, nevertheless, suffers from some shortcomings. On the one hand, the charges yielded by the QEq parameters used by the authors are very low: $q_{\mathrm{Ti}} \approx +1.15$. Consequently, the absolute value of the cohesive energy of rutile is underestimated ($|E_{\mathrm{coh}}|=8$ eV instead of 19.9 eV). On the other hand, the surface formation energies are not correctly reproduced [the (110) surface is slightly less stable than the (100) one].[32] In fact, Monte Carlo simulations show that the (110) surface is not stable at all: the outer oxygen atoms move away from the surface without finding an equilibrium position.

The SG's MS-Q model was analyzed by Thomas *et al.* (TMB).[15] Their conclusions are rather unfavorable to the QEq scheme and have to be discussed again. First, the authors observed that the results of the SG's MS-Q model are almost identical to the predictions of a MS model, which is simply the MS-Q model without electrostatic forces. They concluded that the short-range Morse potentials are largely responsible for the results yielded by the MS-Q model and that charges have little effect, which limits the transferability of models based on the QEq scheme and calls into question their functional form. If this observation is effectively corroborated in the case of the SG's MS-Q model by our Monte Carlo calculations, this is no longer the case for the improved model (MSB-Q) proposed further. This result is therefore not general and the functional form of the QEq scheme is therefore not implicated; in our opinion, the observations of TBM are due to the combination of two effects present in the SG's MS-Q model: the Morse potentials (particularly the Ti-O potential) impose bond lengths against electrostatic forces manifestly too weak.

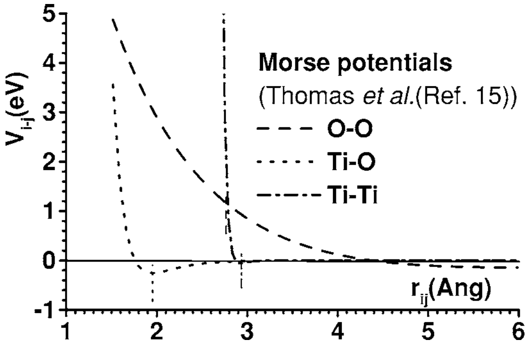


FIG. 4. Morse potentials used by Thomas *et al.* (Ref. 15) in their MSQ model. Vertical lines indicate the first neighbor distance for each pair of atoms.

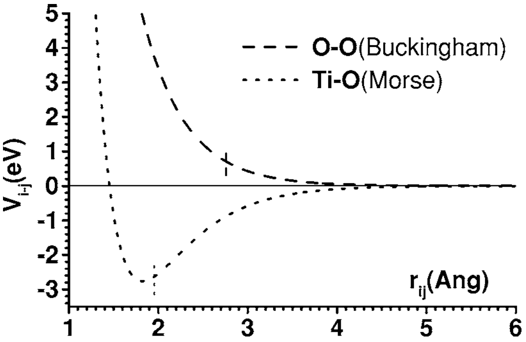


FIG. 5. Morse-Buckingham potentials used in our MB-Q model. Vertical lines indicate the first neighbor distance for each pair of atoms.

Another important point discussed by TMB is the question of the transferability of the MS-Q model and more generally of the QEq-type models. First, let it be emphasized that, whatever the fitted parameters may be (those of the SG model[13] or those of the modified TMB one[15]), the Morse character has an effect only upon the Ti-O bond. As a matter of fact, as shown in Fig. 4, on the one hand, the Ti-Ti interactions are negligible and, on the other hand, the O-O interactions are repulsive at short range, due to the very large value of r^0_{OO} with respect to the first neighbor O-O distance (3.7 and 5.98 Å in the two models respectively, compared to 2.77 Å). We shall show further that, for this reason, a Morse-type potential is not adapted for O-O interactions. Now, the Morse potential for the Ti-O bond [see Eq. (15)] is divided into a repulsive term and an attractive one, the latter describing the electronic delocalization between Ti and O, or, in other words, the covalent character of the bond. This term must tend towards zero for fully ionic compounds and, coherently, does not appear in fully ionic models like the FFCM. In ionocovalent cases, this term depends on the covalent character of the bond that is estimated by the charge transfer $2-|q_{\mathrm{O}x}|$. Therefore, an IPM cannot be transferable between oxides of different stoichiometries. For example, the titanium oxides $\mathrm{TiO_2}$, $\mathrm{Ti_3O_5}$, $\mathrm{Ti_2O_3}$ and TiO have not the same charge states. The Ti-O bond over the series, which goes from insulator to metallic conductor, cannot be modeled by the same IPM. Moreover, as discussed in Ref. 33, cation-cation interactions are also expected to be dependent on the electronic state ($\mathrm{Ti^{4+}}, \mathrm{Ti^{3+}}, \mathrm{Ti^{2+}}$) of the cations. The fact that there are not outer d electrons in $\mathrm{Ti^{4+}}$ ions explains why $\mathrm{Ti^{4+}}$-$\mathrm{Ti^{4+}}$ interactions are negligible in $\mathrm{TiO_2}$ polymorphs, which is not the case for other stoichiometries. On the other hand, an IPM can be transferable to different polymorphs when the bond character is similar. This is the case for the $\mathrm{TiO_2}$ polymorphs considered by SG.

As already mentioned, TMB (Ref. 15) revisited the SG's MS-Q model, first by fitting again the QEq parameters to obtain $q_{\mathrm{Ti}}=+2.23$ in $\mathrm{TiO_2}$, which is undoubtedly more realistic than the SG's value ($q_{\mathrm{Ti}}=+1.15$). Secondly, they also fitted again the Morse parameters (see Fig. 4), which allows them to obtain a better cohesive energy than SG, $E_{\mathrm{coh}} \approx -24.2$ eV, divided into −8 eV for the electrostatic part and −16 eV for the short-range part. Now, at first neighbor, their model yields $V_{\text{Ti-O}}=-0.25$ eV and $V_{\text{O-O}}=1.16$ eV (the Ti-Ti interactions are insignificant, see Fig. 4), which leads, from Eq. (6), to $E^{\mathrm{SR}}_{\mathrm{coh}}=11.3$ eV for the short-range cohesive energy. This high positive value is completely in disagreement with the fact that the greatest part of the short-range energy (−16 eV) must be yielded by first neighbors. The short-range cohesive energy becomes negative only for $r_{ij} \geqslant 8$ Å and decreases up to the cut off radius $r_c=12.2$ Å. This behavior is clearly unphysical and is due to the negative contribution of O-O interactions for $r_{ij} \geqslant 4.5$ Å (see Fig. 4). As already mentioned, this situation is due to the fitted value of r^0_{OO} (5.98 Å) of the Morse potential, which is very large in comparison with the first neighbor O-O distance (2.77 Å). This behavior is in fact always observed, more or less pronounced, when describing O-O interactions with Morse-type potential:[9,13,15] in all models, $V_{\text{O-O}}$ is positive at first neighbor and becomes negative at much longer range, which ensures the stability of the compound. One can conclude that the Morse-type potential is ill suited to describe the O-O interactions. As a matter of fact, there is no physical reason to explain this change of sign. In order to ensure repulsive O-O interactions it is better to use a Buckingham potential. Moreover, Ti-Ti interactions can be neglected in $\mathrm{TiO_2}$ polymorphs. On these bases, we improved the MS-Q model in two steps, as presented in the next section.

IV. IMPROVEMENTS OF THE MS-Q MODEL

A. The MB-Q model

First, we used a mixed Morse-Buckingham-QEq model (MB-Q model): short range Ti-O interactions are described by a Morse potential, O-O interactions by a Buckingham potential, Ti-Ti interactions are neglected and the QEq scheme is implemented as described in Sec. II B. The QEq parameters χ^0_i and J^0_i are given in Table I. Using the code SMASH,[21] potential parameters are adjusted in order to reproduce the lattice parameters a, c, u (u is the internal coordinate for oxygen), the cohesive energy, six elastic constants plus the bulk modulus of the relaxed structure of rutile. The Morse-Buckingham potentials are shown in Fig. 5, the parameters are listed in Table II and the calculated lattice properties that derive from the model are listed in Table III (third column). These properties fit satisfactorily the experimental data (Table III, second column). From this model we calcu-

TABLE II. Fitted potential parameters of the MB-Q model for TiO_2 rutile.

Ti-O (Morse parameters)		O-O (Buckingham parameters)	
D (eV)	2.7593	A (eV)	215.1638
a (Å^{-1})	1.8687	ρ (Å)	0.4824
r^0 (Å)	1.8248	C (eV)	0.0

lated the energy and the volume of formation of an oxygen vacancy, the energy of formation of the three relaxed surfaces (110), (100), and (001), the linear coefficients of thermal expansion parallel and perpendicular to the c axis between 2 and 300 K (α_a and α_c, respectively), as well as the heat capacity C_P (see Table IV, third column). The defect formation energies (vacancy and surfaces) were calculated with allowing the charges to relax around the defect up to a cutoff radius of 6 Å, which ensures the convergence of the charges toward the bulk values. The Coulomb energy was calculated by means of the charge neutrality method of Wolf *et al.*[36] that is very well adapted to nonperiodic systems and that avoids carrying on calculations in the reciprocal space. The obtained results are good in some cases and not for others. The good hierarchy observed between the energies of the three surfaces is a positive point. In contrast, the results concerning the oxygen vacancy are not satisfactory, particularly the low value of the formation energy ($E_{V_O}=1.6$ eV instead of 7.5 eV). From the detailed analysis of the energetics reported in Table V, it can be seen that the low value of E_{V_O} is mainly due to the very low value of the short-range part $E^{SR}_{V_O}$, and also to the loss of energy during relaxation.

TABLE III. Observed and calculated crystal properties used to fit the potential parameters of the MB-Q and of the SMB-Q models for TiO_2 rutile.

		Calculated	
	Experimental	(MB-Q model)	(SMB-Q model)
q_{Ti}		2.48	2.51
a (Å)	4.594[a]	4.594 (0%)	4.581 (−0.3%)
c (Å)	2.959[a]	2.944 (−0.5%)	2.966 (+0.2%)
u	0.3053[a]	0.3020 (−1%)	0.3025 (−0.9%)
E_{coh} (eV)	−19.9[b]	−19.7 (−1%)	−19.9 (0%)
E^{elec}_{coh} (eV)		−9.3	−9.45
E^{SR}_{coh} (eV)		−10.4	−10.45
C_{11} (GPa)	268.0[c]	299.0 (+11%)	293.0 (+9%)
C_{33} (GPa)	484.0	407.0 (−16%)	400.0 (−17%)
C_{12} (GPa)	175.0	177.0 (+1%)	203.0 (+16%)
C_{23} (GPa)	147.0	145.0 (−1%)	164.0 (+11%)
C_{66} (GPa)	190.0	177.0 (−7%)	183.0 (−3.5%)
C_{44} (GPa)	124.0	145.0 (+17%)	128.0 (+3%)
B (GPa)	211.0	216.0 (+2%)	228.0 (+8%)

[a] Ref. 42.
[b] Ref. 24.
[c] Elastic constants from Ref. 34.

TABLE IV. Energy and volume of the oxygen vacancy, surface energies, thermal expansions and heat capacity of TiO_2 rutile calculated with the MB-Q model and the SMB-Q model, compared with experimental (^{ex}) or *ab initio* (^{ab}) data.

		Calculated	
	Experimental or *ab initio*	(MB-Q model)	(SMB-Q model)
E_{V_O} (eV)	^{ex,ab}7.5[a],[b]	1.6 (−80%)	4.8 (−36%)
V_{V_O} (Å^3)	^{ab}4.[b]	−5.0(sign)	+1. (−75%)
$E_{(110)}$ (j m^{-2})	^{ab}0.9[c]	0.49 (−45%)	0.68 (−24%)
$E_{(100)}$ (j m^{-2})	^{ab}1.12[c]	0.64 (−43%)	0.85 (−24%)
$E_{(001)}$ (j m^{-2})	^{ab}1.7[c]	2.0 (+18%)	1.74 (+2%)
α_a (10^{-6}, °C^{-1})	^{ex}7.3[d] (30–650 °C)	2.6 (−64%)	10.0(+37%)
α_c (10^{-6}, °C^{-1})	^{ex}8.8[d] (30–650 °C)	9.3 (+5%)	16.0(+82%)
C_P (J mol^{-1} K^{-1})	^{ex}55.0[d] (298 K)	40.0(−27%)	50.0(−10%)

[a] Refs. 17 and 18.
[b] Ref. 19.
[c] Ref. 35.
[d] Ref. 16.

At first neighbors, the interaction energies given by the model (parameters in Table II) are $V_{\text{Ti-O}}=-2.64$ eV ($r_{ij}=1.95$ Å) and $V_{\text{O-O}}=0.69$ eV ($r_{ij}=2.77$ Å). Using Eq. (6), these interactions yield $E^{SR}_{coh}=-8.25$ eV at first neighbors, that is to say 80% of the total short-range cohesive energy. It is therefore pertinent, in the following, to discuss 80% of the expected value of E_{V_O}, at first neighbors, that is to say 6 eV. In these conditions, a value of $E^{SR}_{V_O}$ (unrelaxed) of, at least, 4 eV instead of 1 eV obtained here is required in order to compensate the relaxation. Applying Eqs. (6)–(8) with $E^{SR}_{coh}=-8.25$ eV and $E^{SR}_{V_O}=4$ eV leads to $V_{\text{Ti-O}}\approx-1.4$ eV and $V_{\text{O-O}}\approx0.02$ eV at first neighbors. The values given by the present model ($V_{\text{Ti-O}}=-2.64$ eV and $V_{\text{O-O}}=0.69$ eV), are therefore clearly too high (in absolute values) and no set of parameters allowed a better result. Our conclusion is that the MS-Q model, while suitable for describing the bulk properties of the perfect crystal, fails for describing defects. We think that this conclusion can be generalized to pairwise interactions models which are not relevant in the presence of broken bonds, due to their additive nature. This is a well known result already mentioned in Ref. 8. In the case of transition metals for example, the use of N-body potentials is required to obtain reliable behavior for vacancy or near surfaces.[37] The short-range energy calculated with N-body

TABLE V. Electrostatic ($E^{elec}_{V_O}$) and short-range ($E^{SR}_{V_O}$) contributions of the total formation energy of the oxygen vacancy (E_{V_O}), calculated with the MBQ model. ΔE is the difference between relaxed and unrelaxed energies.

	unrelaxed	relaxed	ΔE (eV)
$E^{elec}_{V_O}$ (eV)	+4.1	+1.5	−2.6
$E^{SR}_{V_O}$ (eV)	+1	+0.1	−0.9
E_{V_O} (eV)	+5.1	+1.6	−3.5

TABLE VI. Fitted potential parameters of the SMB-Q model for TiO_2 rutile ($r_0^{\text{Ti-O}}=1.95$Å).

	Ti-O (SM parameters)		O-O (Buckingham parameters)
A (eV)	0.112	A (eV)	540.6167
p	15.127	ρ (Å)	0.3489
ξ (eV)	2.261	C (eV)	0.0
q	1.853		

potentials is less sensitive to a change in coordination than that calculated with pair potentials. In other words, when bonds are broken, the remaining bonds are reinforced. In metals, the N-body potential is used to account for the cohesive band energy.[38] In the same manner, we shall use N-body potential in oxides for the short-range covalent part of the Ti-O bond, in place of the right term of Eq. (15).

B. The SMB-Q model

An analytical model based on the second moment approximation of the tight-binding approach, which account for the mixed ionocovalent character of the oxygen cation bond in insulating oxides has been developed few years ago.[20] In this model, assuming only nearest neighbors, the covalent energy of the bond E_{cov} is proportional to $\sqrt{Z}$, where Z is the oxygen coordination number, and to a term depending on the charge transfer $2-|q_{\text{O}x}|$. For a fixed value of the charge, which is assumed as a first approximation in this work, E_{cov} is proportional to $\sqrt{Z}$, as in transition metals.[38–40] Consequently, we use for the Ti-O bond the following form of the potential, which is similar to the one employed in our earlier works on metallic alloys:[41]

$$E^i_{\text{site}} = \sum_j A_{IJ} e^{-p_{IJ}(r_{ij}/r_0^{IJ}-1)} - \left\{ \sum_j \xi_{IJ}^2 e^{-2q_{IJ}(r_{ij}/r_0^{IJ}-1)} \right\}^{1/2}. \tag{16}$$

At each site i, the Ti-O (or O-Ti) energy is a sum of a pairwise repulsive term of the Born-Mayer type and a N-body attractive term accounting for the covalent energy of the bond. A_{IJ}, p_{IJ}, ξ_{IJ}, q_{IJ} are adjustable parameters, where I and J stand for Ti and O, respectively. r_0^{IJ} is the first neighbor Ti-O distance. Unlike for a Morse potential [Eqs. (14), (15)], r_0^{IJ} is not an additional adjustable parameter. The O-O interactions is again described by a Buckingham potential. This mixed second-moment-Buckingham-QEq model is referred as the SMB-Q model in the following.

TABLE VII. The simulated (SMB-Q model) unit cell parameters, bulk moduli, cohesive energy, and average Ti-O nearest neighbor distance for the three natural TiO_2 polymorphs compared with experimental data when available.

Phase	Parameter	Expt.	SMB-Q
Rutile			$\lvert q_{\text{O}}\rvert=1.26$
	a (Å)	4.594[a]	4.581 (−0.3%)
	c (Å)	2.959[a]	2.966 (+0.2%)
	u	0.3048	0.3025 (−0.7%)
	B (GPa)	211.0[c]	228. (+8%)
	E_{coh} (eV)	−19.9[b]	−19.9 (0%)
	$\langle d_{\text{Ti-O}}\rangle$ (Å)	1.956	1.96
Anatase			$\lvert q_{\text{O}}\rvert=1.25$
	a (Å)	3.785[d]	3.825 (+1.%)
	c (Å)	9.512[d]	9.03 (−5.%)
	u	0.2080	0.2161 (+4.6 %)
	B (GPa)	179.0[e]	220. (+23%)
	E_{coh} (eV)		−19.84
	$\langle d_{\text{Ti-O}}\rangle$ (Å)	1.947	1.947
Brookite			$\lvert q_{\text{O}}\rvert=1.26$
	a (Å)	9.174[f]	9.259 (+0.9%)
	b (Å)	5.449[f]	5.444 (+0.1%)
	c (Å)	5.138[f]	5.229 (+1.9%)
	B (GPa)		227.
	E_{coh} (eV)		−19.65
	$\langle d_{\text{Ti-O}}\rangle$ (Å)	1.955	1.973

[a] Ref. 42.
[b] Ref. 24.
[c] Ref. 34.
[d] Ref. 43.
[e] Ref. 44.
[f] Ref. 45.

As usual, we fitted the parameters of the SMB-Q model using lattice properties of TiO_2 rutile. The resulting parameters are listed in Table VI and the calculated properties using the model are listed in Table III (fourth column). Once again, the calculated properties fit the experimental data well. The transferability of the model has been checked by calculating, without fitting any parameter, the unit cell parameters and the bulk moduli of the two other natural TiO_2 polymorphs: anatase and brookite. The results reported in Table VII globally show a satisfactory agreement with experimental data, the maximum deviations being −5 and +4.6 %, respectively, for the cell parameter c and the internal coordinate of oxygen u of the anatase structure. In fact, these two parameters are not independent as the product $c\times u$ is equal to the greatest Ti-O distances (along the c axis) of the TiO_6 octahedra on which all the TiO_2 polymorph structures are built. The calculated distance is 1.96 Å, which compares very well with the experimental value (1.979 Å).What happens is that the octahedra plane perpendicular to the c axis is distorted in anatase, two opposite oxygen atoms being shifted by a distance x (in c unit) and the two other by a distance $-x$ (x and u are such that $u+x=1/4$). Experimentally, this creates an angle Ti-$\widehat{\text{O}}$-Ti of 156° (instead of 180° in an undistorded octahedra). Our calculations yield 162° (+3.8%). The conclusion is that our model is a slightly too rigid and leads to a relative smoothing of the plane. This small effect would merit thinking about but this is well beyond the scope of this work.

TABLE VIII. Electrostatic ($E_{V_O}^{\mathrm{elec}}$), short-range O-O pairs [$E_{V_O}^{\mathrm{SR}}$(O-O)] and Ti-O pairs [$E_{V_O}^{\mathrm{SR}}$ (Ti-O)] contributions to the total energy of the oxygen vacancy (E_{V_O}), calculated with the SMB-Q model. ΔE is the difference between relaxed and unrelaxed energies.

	unrelaxed	relaxed	ΔE (eV)
$E_{V_O}^{\mathrm{elec}}$ (eV)	+4.1	+2.1	−2.0
$E_{V_O}^{\mathrm{SR}}$ (O-O) (eV)	−2.25	−2.7	−0.45
$E_{V_O}^{\mathrm{SR}}$ (Ti-O) (eV)	+4.95	+5.4	+0.45
E_{V_O} (eV)	+6.8	+4.8	−2.0

Let us now come back to rutile. As before, defect properties, thermal expansion coefficients and heat capacity were calculated and are shown in Table IV, fourth column. One observes that the results concerning both the oxygen vacancy and the surfaces are really better than those obtained with the MB-Q model.

As regards the oxygen vacancy, the formation energy, although still too weak, is three times greater than it was with the MB-Q model, and the volume of formation is now slightly positive in agreement with *ab initio* calculations (note that no significant effect has been observed experimentally). The detail of the energetics reported in Table VIII shows that the loss of energy due to relaxation is reduced to 2 eV instead of 3.5 eV for the MB-Q model, and concern only the electrostatic part. The *N*-body term (for which the relaxation energy is positive) represents the major part of the formation energy of the vacancy (5.4 eV), which shows its efficiency with respect to the pair-wise interaction. The analysis of the energetics given by Eqs. (6)–(8) in the case of pair potentials must be revisited for the SMB-Q model. At first neighbors ($r_{ij}=r_0^{\mathrm{Ti\text{-}O}}$) Eq. (16) yields

$$E_{\mathrm{site}}^{\mathrm{Ti}} = 6A - \sqrt{6}\xi \tag{17}$$

and

$$E_{\mathrm{site}}^{\mathrm{O}} = 3A - \sqrt{3}\xi, \tag{18}$$

where A and ξ stand for $A_{\mathrm{Ti\text{-}O}}$ and $\xi_{\mathrm{Ti\text{-}O}}$, respectively. Then, $E_{\mathrm{coh}}^{\mathrm{SR}}$ and $E_{V_O}^{\mathrm{SR}}$ can be expressed as

$$E_{\mathrm{coh}}^{\mathrm{SR}} = E_{\mathrm{site}}^{\mathrm{Ti}} + 2E_{\mathrm{site}}^{\mathrm{O}} + 11V_{\mathrm{O\text{-}O}},$$

$$E_{\mathrm{coh}}^{\mathrm{SR}} \approx 12A - 6\xi + 11V_{\mathrm{O\text{-}O}}, \tag{19}$$

and

$$E_{V_O}^{\mathrm{SR}} = -(E_{\mathrm{site}}^{\mathrm{O}} + 11V_{\mathrm{O\text{-}O}}) + 3[(5A - \sqrt{5}\xi) - (6A - \sqrt{6}\xi)],$$

or

$$E_{V_O}^{\mathrm{SR}} \approx -6A + 2.4\xi - 11V_{\mathrm{O\text{-}O}}. \tag{20}$$

Using Eqs. (19) and (20) the following values are obtained:

$$E_{\mathrm{coh}}^{\mathrm{SR}} = -10.1 \text{ eV}, \quad E_{V_O}^{\mathrm{SR}}(\text{O-O}) = -2.1 \text{ eV},$$

$$E_{V_O}^{\mathrm{SR}}(\text{Ti-O}) = 4.75 \text{ eV}.$$

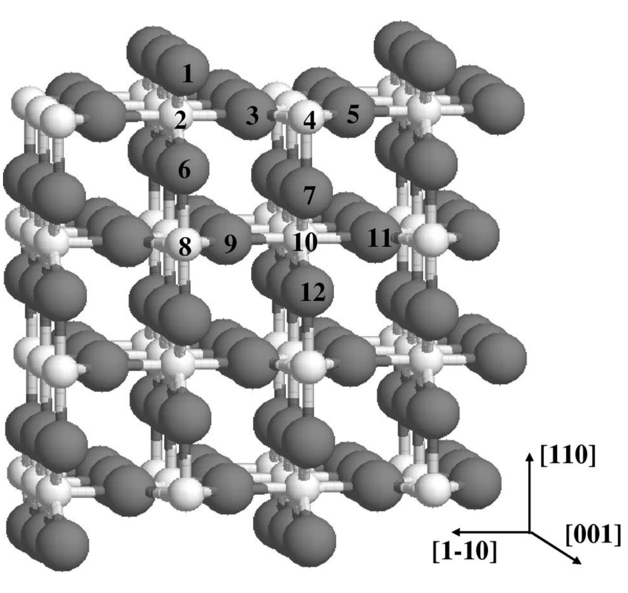


FIG. 6. The structure of the unrelaxed stoichiometric (110) surface of rutile.

The comparison with the values displayed in Tables III ($E_{\mathrm{coh}}^{\mathrm{SR}}$) and VIII ($E_{V_O}^{\mathrm{SR}}$) shows that the analysis at first neighbors is pertinent. It remains that $E_{V_O}^{\mathrm{SR}}$ (2.7 eV) is globally too small by, say, 2.8 eV in order to reach the expected value. From Eqs. (19) and (20), we obtain

$$E_{V_O}^{\mathrm{SR}} = 0.4|E_{\mathrm{coh}}^{\mathrm{SR}}| - 6.6V_{\mathrm{O\text{-}O}} - 1.2A. \tag{21}$$

Now $|E_{\mathrm{coh}}^{\mathrm{SR}}|$ is worth typically 10 ± 0.5 eV for $q_{\mathrm{Ti}} \in \{2.2, 2.8\}$. Therefore, the maximum accessible value for $E_{V_O}^{\mathrm{SR}}$ is 4.2 eV (the term 1.2 A is neglected in this estimation) unless we consider $V_{\mathrm{O\text{-}O}}<0$ which is out of the limits of the model. The conclusion is that the SMB-Q model intrinsically underestimates slightly the vacancy energy.

Let us now consider the three low index surfaces. The energies of formation calculated with the SMB-Q model, reported in Table IV (last column), fit rather well the *ab initio* results. In the case of the (110) surface (the most stable surface, shown in Fig. 6), the atomic relaxations along the (110) axis as well as the transfer of charges near the surface has been calculated and are reported in Table IX. The calculated relaxations are compared with the most complete experimental quantitative structure determinations currently available.[46,47] Significant differences are present between these two experimental studies and are analyzed in Ref. 47. Our calculations are in a very good agreement with the most recent study,[47] the major difference being for the Ti(4) and Ti(10) atoms, and satisfactorily agree with the *ab initio* results of Swamy *et al.*[32] not reported here.

As mentioned above, relaxations were calculated allowing a local charge transfer (up to 6 Å), reported in Table IX (last column) for the SMB-Q model. The charge transfer is particularly noticeable between the bridging oxygen atoms [O(1)] and the fivefold coordinated Ti atoms [Ti(4)], that is, between atoms having lost a bond. This is in qualitative agreement with tight-binding calculations,[28] though the transfer is more important.

TABLE IX. Atomic relaxations (Δw) for the (110) surface of rutile (see Fig. 6) along the [110] direction calculated with the SMB-Q model compared to the two available experimental sets of data. In the last column are reported the differences of site charges with respect to the bulk charges. The number of atoms are reported in Fig. 6.

	Δw (Å) along the [110] direction			Δq/bulk
	experimental[a]	experimental[b]	SMBQ model	
O (1)	−0.27	0.10	0.08	+0.305
Ti (2)	0.12	0.25	0.13	−0.05
O (3,5)	0.05	0.27	0.28	−0.065
Ti (4)	−0.16	−0.19	−0.02	−0.13
O (6)	0.03	0.06	0.13	−0.035
O (7)	0.00	0.00	0.07	−0.055
Ti (8)	0.07	0.14	0.10	0.03
O (9,11)	0.02	0.06	0.11	0.005
Ti (10)	−0.09	−0.09	0.06	0.02
O (12)	−0.09	0.01	0.07	+0.035

[a] Ref. 46.
[b] Ref. 47.

V. CONCLUSIONS AND FUTURE PROSPECTS

Through the example of rutile TiO_2, some atomistic models aimed at performing atomistic simulations on ionocovalent oxides were revisited, particularly the variable charge models based on the QEq formalism of Rappé and Goddard.[7] These models are very important because they are suitable to simulate heterogeneous systems such as metal/oxide or oxide/oxide interfaces. Many papers have been devoted to the subject in the literature but none of them, in our opinion, was sufficiently explanatory and critical about the choice of the parameters and the potentials used in the models and the consequence on the calculated lattice or surface properties. In this paper, we analyzed in detail each part of the formalism and of the energetics in order to render the model as transparent as possible.

In the QEq models, the electrostatic energy contribution is reduced with respect to formal charge models, first by the reduction of ionic charges and second by the shielding between charges. In absolute value, this energy is smaller than the cohesive energy (about half for TiO_2), which must be compensate by cohesive short-range interactions. Once the QEq parameters are determined, the choice of the short range interactions is of great importance and they depend on the electronic structure of the studied oxide. In the case of insulators (as TiO_2), the cation-cation interactions are expected to be small (they were neglected here) because of the lack of outer electrons on cation sites. The cation-anion interactions depends on the covalent character of the bond. In this work, we took advantage of the knowledge of the energy of formation of an oxygen vacancy (in addition to the cohesive energy) to check several type of potentials. We showed that Morse potential is not adapted to oxygen-oxygen interactions, because it introduces a non physical long-range attractive contribution. We also showed that pairwise interactions for metal-oxygen do not allow us to render an account of the defect properties of the crystal (oxygen vacancy and surfaces). On the other hand, *N*-body potential yields satisfactory results on energetics and also on atomic relaxations at surface despite of the underestimation of 1/3 of the oxygen vacancy energy. Its $\sqrt{Z}$ form, where Z is the coordination number, is in accordance with the prediction of tight-binding model for the covalent energy in insulating oxides.[20]

Nevertheless, some leads may be explored to still improve the model, particularly introducing the dependence of the covalent energy on the local charge transfer in the vicinity of defects. The role of the oxygen polarizability may be explored too. Works are in progress to exploit this model for the study on ZrO_2, $SrTiO_3$, and the interface between these two oxides.

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[21] SMASH (Simulation des MAtériaux de Structure Hétérogène) is a general Monte Carlo code developed by two of us (R. Tétot and M. Hallil) and aimed at study heterogeneous systems including oxides, as functions of temperature, and partial pressure of oxygen. A fitting procedure allows us to adjust potentials and QEq parameters on structural and physical properties of compounds. For who is interested, contact R. Tétot at the address robert.tetot@lemhe.u-psud.fr

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