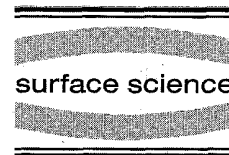




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Surface Science 364 (1996) 1–16



Oxygen vacancies on MgO(100)

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Received 22 September 1995; accepted for publication 9 January 1996

Abstract

The electronic and atomic structures of non-stoichiometric MgO{100} surfaces, with several densities of neutral oxygen vacancies, have been studied using a semi-empirical Hartree–Fock method associated with a geometry optimization code. The oxygen vacancies are periodically repeated in the surface top layer with equal spacings. Strong electron redistributions take place on the magnesiums which surround the vacancies and localized electron states appear in the gap below the conduction band minimum. Their positions shift towards lower and lower energies as the vacancy density increases. The energy of formation of a vacancy is found to be close to 10 eV at low densities. It strongly decreases as the oxygen deficiency grows, due to electrostatic interactions. The mechanisms responsible for the displacements of the magnesiums which surround the vacancy are analysed.

Keywords: Green's function methods; Magnesium oxide; Semi-empirical models; Surface defects; Surface electronic phenomena; Surface relaxation

1. Introduction

Insulating oxides have attracted much interest due to their importance in various fields of applications such as catalysis, electrochemistry or as supports for metallic thin films or clusters. In most cases, the oxide surfaces are not perfectly stoichiometric, and the presence of oxygen vacancies is recognized as inducing electronic structure modifications and structural distortions, as well as enhanced reactivity. In some cases, it may also drastically change the surface conductivity, for example in substoichiometric TiO_{2-x} oxides, or yield dramatic effects such as dielectric breakdown.

Studies performed on well characterized oxide surfaces have stressed several features associated with the presence of oxygen vacancies [1], in

particular in the electronic spectrum. On MgO{100}, an electronic excitation has been recorded at 2.3 eV, i.e. at an energy much lower than the bulk gap width (7.8 eV). This transition was assigned to the presence of a surface F center, associated with an oxygen vacancy [2,3], despite a disagreement with theoretical predictions [4,5]. It was assigned by other authors to a magnesium vacancy, inducing a surface V centre [6]. On TiO_2 {110} surfaces, which have a small amount of oxygen vacancies, an occupied state at about 0.8 eV below the bottom of the conduction band was found by ultra-violet photoemission [7]. When the sub-stoichiometry increases, this state broadens and finally overlaps the conduction band. An analysis using the STM in the spectroscopic mode proved that the absence of bridging oxygens is associated with a partial occupancy of Ti 3d orbitals [8]. The electronic characteristics associ-

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ated with oxygen vacancies were analysed by XPS, Auger and electron energy loss spectroscopies [9]. It was found that the cation core levels are raised while the oxygen core levels are lowered on reduced surfaces, that the intensity of non-bonding O 2p states in the valence band decreases while the intensity of bonding states increases. A model was proposed in which the oxygen vacancies induce the presence of an occupied state 0.3 eV below the bottom of the conduction band, i.e. about 0.8 eV below the first peak in the unoccupied part of the density of states. More recently, the strength of anion–cation hybridization in the valence band was estimated by resonant photoemission [10], and shown to increase on reduced surfaces. Information on the local electronic structure of reduced surfaces was obtained by means of STM operating in the spectroscopic mode [8,11]. Although the TiO_2 and $\text{SnO}_2(110)$ surface structures are similar, their electronic characteristics are quite different in the presence of oxygen vacancies. In particular, the gap state which lies about 1 eV below Fermi level on $\text{TiO}_2(110)$ is located close to the top of the valence band in $\text{SnO}_2(110)$ [12].

The {100} face of SrTiO_3 also presents low-lying states in the gap at 1 and 1.5 eV below the conduction band minimum, which were assigned to oxygen vacancies and to defects resulting from surface preparation [7,13–15]. The electronic structure of oxygen vacancies on the polar {111} face of SrTiO_3 was also studied [16].

The under-stoichiometric (001) face of V_2O_5 presents a gap state and a charge-transfer towards the vanadiums [17]. An increase in covalent character of the zirconium–oxygen bond was found in sub-stoichiometric $\text{ZrO}_2(100)$ surfaces [18].

The electronic structure of non-stoichiometric α -alumina surfaces has been studied by electron energy losses and photoemission [19,20]. The reduction of the (0001) face induces a gap narrowing – from 8.3 eV on the stoichiometric surface to 7 eV on the reconstructed $(\sqrt{31} \times \sqrt{31})\text{R}9^\circ$ face. In the valence band density of states, weight is transferred from non-bonding to bonding states on the non-stoichiometric surfaces.

The electronic structure of non-stoichiometric α -quartz surfaces was studied by LEED, XANES and electron energy loss spectroscopy [22,23].

Transitions at energies equal to 5.2 and 7.4 eV – lower than the bulk gap – have been observed. They have been related to models of vacancies in the quartz lattice.

Oxygen-deficient oxide surfaces have been the subject of various theoretical investigations. Atomistic approaches have been used to model charged vacancies on $\text{MgO}\{100\}$, taking into account relaxation effects around the vacancy [24,25]. Quantum non-self-consistent approaches have also been used in the case of TiO_2 [26] and SrTiO_3 [27], but, as will become clear in the following, only self-consistent treatments yield reliable results because the vacancies induce large electrostatic potentials and strong charge redistributions. Several self-consistent quantum approaches, representing the surface by small clusters involving very few atoms and neglecting the atomic relaxation, have been performed in the past [4,28–30]. Ab initio self-consistent total energy calculations, in which the atomic geometry has been relaxed to equilibrium, have only been carried out in very few cases, such as the study of high densities of oxygen vacancies on $\text{TiO}_2(110)$ [31], the analysis of steps and oxygen vacancies on $\text{MgO}(100)$ [32] and the modelling of relaxed under-stoichiometric $\text{SnO}_2(110)$ faces [33].

All these studies stress some systematic characteristics associated with oxygen vacancies: (1) on most surfaces, a localized state appears in the gap; (2) when this state is occupied, it pins the Fermi level; (3) a decrease in the neighbouring cation charge results, which shifts the core levels; (4) the density of states in the valence band is distorted. Non-bonding states transfer weight to bonding states at the bottom of the band; (5) a gap reduction may occur. In addition, the presence of a large density of vacancies on several oxide surfaces lead to changes in the size of the surface unit cells, recognized as reconstruction effects.

It is the goal of this paper to analyse the electronic and geometric modifications induced by neutral oxygen vacancies, on oxide surfaces, as a function of their density. Although it has not been the subject of as detailed systematic experimental investigations as, for example, non-stoichiometric α - Al_2O_3 surfaces, we have chosen to work on $\text{MgO}\{100\}$ because the properties of the ideal

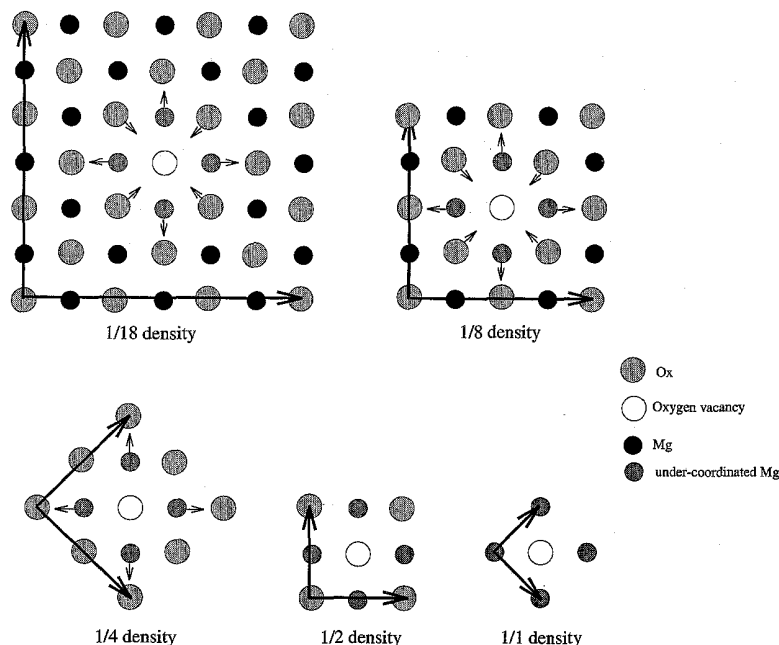


Fig. 1. Surface cells for sub-stoichiometric MgO{100} surfaces with various densities of oxygen vacancies. The magnesiums located close to a vacancy are specified and an arrow indicates their displacement in the surface plane.

surface are better known both from an experimental and a theoretical point of view and because the structure is simpler. We have modelled increasing densities of neutral vacancies: 1/18, 1/8, 1/4, 1/2 and 1/1 in the surface top layer, and, as far as this study is concerned, we have assumed that the vacancies are equally spaced on the surface. This assumption will be released in a following paper, which will study the relative stability of various reconstructed MgO{100} surfaces at constant vacancy densities [34]. To determine the surface electronic structure and the structural distortions, we have performed a self-consistent quantum calculation associated with a geometry optimization, which is described in Section 2. We present the main results of the study in Section 3 and we discuss them, in the light of analytical models, in Section 4.

2. Method

The numerical method relies on the resolution of the Schrödinger equation for the valence

electrons in an Hartree–Fock approximation. The Slater determinant is expanded on an atomic orbital basis set, including the 2s and 2p orbitals for oxygens and 3s and 3p orbitals for magnesiums. The resulting Hartree–Fock–Roothaan equations are solved self-consistently within a CNDO-like assumption (CNDO = Complete Neglect of Differential Overlap). Some parameters are required to calculate the matrix elements, such as intra-atomic electron–electron integrals, atomic energies of the neutral atoms, etc. They have been adjusted, in previous studies, to reproduce the bulk electronic and atomic characteristics of MgO. The details concerning the Hamiltonian matrix and the parametrization are presented elsewhere [35].

We assume that the oxygen vacancies are periodically repeated in the surface top layer, with a constant spacing. We consider five densities: 1/18, 1/8, 1/4, 1/2 and 1/1. In the last case, only magnesium atoms are present in the top layer. The calculations are performed in the slab geometry, with four atomic layers. The surface cells are represented in Fig. 1. A single special point [36] is used for the summations in reciprocal space for

1/18 and 1/8 densities, because of the large size of the two-dimensional unit cells. For 1/4, 1/2 and 1/1 densities, four special points are used. We have checked that increasing the number of k points up to 17 only modifies the energies by 10^{-3} eV and the charges by 10^{-3} of an electron. We have also checked that the results obtained for the lowest density (1/18) are identical to those obtained when a single vacancy is put on an MgO cluster, made of three layers of 36 atoms, embedded in an infinite array of self-consistent point charges. Since lateral interactions between cells are absent in this latter geometry, the agreement between both calculations proves that the vacancy–vacancy interactions are negligible when the vacancy density is equal to 1/18.

We have associated a geometry optimization code to the electronic structure calculation, in order to determine the structural distortions around the vacancies at 0 K. Starting from an assumed atomic configuration, the quantum ground state energy and the Hellmann–Feynman forces are calculated and used to derive the new atomic positions. The whole procedure is repeated until the energy minimum is found. In order to save computing time, we have only optimized the structural degrees of freedom of the atoms located in the closest vicinity of the vacancies. We have considered the horizontal and vertical displacements δL and δZ of the four magnesiums which surround each vacancy, the horizontal and vertical displacements $\delta L'$ and $\delta Z'$ of the four oxygens located in the second coordination shell of the vacancy and the vertical displacements $\delta Z''$ of the oxygens in the following shell (for the 1/18, 1/8 and 1/4 densities). The directions of the horizontal displacements, which obey symmetry constraints, are represented by arrows in Fig. 1. In some cases, due to symmetry reasons, atomic displacements are forbidden. This is the case for δL at 1/2 and 1/1 densities, and for $\delta L'$ at 1/4, 1/2 and 1/1 densities. We will not focus much on the values found for $\delta L'$, which present a large uncertainty due to the flatness of the energy curves in the vicinity of the energy minimum. We will only discuss the displacements whose values are beyond the error bar of the method (a few hundredths Ångströms).

We have already used the optimization procedure to determine the relaxation and rumpling amplitudes on various clean and hydroxylated oxide surfaces [37,38]. Aside from Refs. [31–33], which consider large densities of oxygen vacancies (i.e. small surface unit cells), this is the first time, to our knowledge, that a self-consistent electronic structure calculation has been associated with a geometry optimization code to study surface oxygen vacancies over a large range of densities. It should be noted that semi-empirical methods, although less accurate than *ab initio* calculations, are useful when the unit cells involve a large number of atoms (low vacancy densities), or when various surface reconstructions have to be considered [34].

3. Results

The main results of this study are presented in Table 1 and Figs. 2a–f. We will first give the characteristics of the 1/18, 1/8, 1/4 and 1/2 surfaces and then describe the 1/1 surface at the end of this section. To rationalize the trends in the electronic and geometric structures as a function of the density of oxygen vacancies, we introduce the integer Z_{vac} , which denotes the number of vacancies located close to an under-coordinated surface magnesium. The value of Z_{vac} is equal to 1 for the 1/18, 1/8 and 1/4 densities, to 2 for the 1/2 density, and to 4 for the 1/1 density. In this latter case, no oxygen is left in the surface plane.

For the stoichiometric MgO{100} surface and the five under-stoichiometric surfaces, we have represented on Figs. 2a–f, the local densities of states (LDOS), projected on an under-coordinated surface magnesium, and on a surface oxygen located in the second coordination shell of the vacancy. The local densities of states on the other atoms of the slabs are not significantly modified compared to the stoichiometric case.

A comparison between Fig. 2a and Figs. 2b–f shows that the presence of oxygen vacancies induces a qualitative change in the shape of the conduction band. While, on the stoichiometric surface, it presents a single large peak, mainly built up from 3s and 3p magnesium states, on non-

Table 1

Characteristics of non-stoichiometric MgO{100} surfaces: the position of the Fermi level ϵ_F (in eV), the vacancy formation energy E_{vf} (in eV), the number of vacancies located close to an under-coordinated surface magnesium Z_{vac} , the electron number N_C and level positions ϵ_s (in eV) and ϵ_p (in eV) of an under-coordinated surface magnesium^a; the lower part of the table gives the horizontal and vertical atomic displacement of the atoms in the first, second and third coordination shells of the vacancy, in Å. δZ , $\delta Z'$ and $\delta Z''$ are positive when the atoms move towards vacuum; the directions of the horizontal displacements are indicated on Fig. 1 by arrows

	MgO	1/18	1/8	1/4	1/2	1/1
ϵ_F	—	−2.80	−3.20	−3.03	−4.12	−7.50
E_{vf}	—	9.95	8.75	8.71	7.41	3.48
Z_{vac}	0	1	1	1	2	4
N_C	0.76	1.00	0.84 (1.02)	1.09	1.43	2.0
ϵ_s	−2.53	−3.66	−2.68 (−3.78)	−3.45	−5.53	−7.5
ϵ_p	−0.24	0.89	0.16 (1.93)	2.03	4.47	8.0
δL	—	0.15	0.16	0.16	—	—
δZ	—	0.03	0.02	0.06	0.22	∞
$\delta L'$	—	0.07	0.31	—	—	—
$\delta Z'$	—	—	—	—	0.18	—
$\delta Z''$	—	—	0.06	0.18	—	—

^a In the case of the 1/8 density, we have also given in parenthesis the values of these quantities for the surface magnesium in the fourth coordination shell of the vacancy; see text.

stoichiometric surfaces it is split into two parts. Considering the degeneracy of the peaks, one can assign the lower one to the magnesium 3s state and the higher one to the magnesium 3p states, although, of course, each of these orbitals is hybridized with oxygen orbitals. The s–p splitting is of the order of 4–5 eV for 1/18, 1/8 and 1/4 densities ($Z_{vac} = 1$), and 8.5 eV for 1/2 density ($Z_{vac} = 2$). The higher peak is located above the bulk conduction band for high vacancy densities and the s peak lies in the bulk gap. This state is four-fold degenerate when $Z_{vac} = 1$ and two-fold degenerate when $Z_{vac} = 2$. It presents a small dispersion as a function of the two-dimensional Bloch vector.

The Fermi level is pinned by this gap state. For a surface with a $1/n$ density of oxygen vacancies, there are $n - 1$ oxygens and n magnesiums in the surface unit cell. Each oxygen brings 4p electrons and each magnesium 2s electrons, i.e. there are $6n - 4$ electrons to be placed in the surface bands; $6n - 6$ electrons are accommodated in the surface valence band and 2 electrons fill the gap state. This latter, of anti-bonding character, is thus only 1/4 filled when $n = 18, 8$ and 4, and half-filled when $n = 2$. The corresponding surfaces are metallic. The Fermi level is located at the gap state energy. Table 1 shows a lowering of ϵ_F as the vacancy

density increases, which is correlated with the lowering of the gap state energy in Fig. 2.

Several types of electronic excitations may take place on non-stoichiometric surfaces. Since the surfaces are metallic, there are low energy excitations, within the range of the gap state width (about 1.5 eV). Electrons may also be excited from the filled part of the gap state to the empty states in the conduction band: the energy difference between ϵ_F and the lowest peak in the conduction band is of the order of 2.5 eV when $Z_{vac} = 1$, and 3.2 eV when $Z_{vac} = 2$. Similarly, electronic excitations between the valence band and the empty part of the gap state may take place. The energy difference between the highest peak in the valence band and ϵ_F is of the order of 6.5 eV when $Z_{vac} = 1$, and 5.7 eV when $Z_{vac} = 2$. The 2.3 eV excitation measured by EELS [2,3,6] could thus represent an electronic transition between the gap state and the conduction band at low vacancy density. The transition between the valence band and the gap state around 6.5 eV, which has not been mentioned in the literature, is nearly degenerate with the exciton and with the surface gap in the stoichiometric part of the surface [39].

The vacancy formation energy E_{vf} is given in Table 1. It is equal to the energy difference between

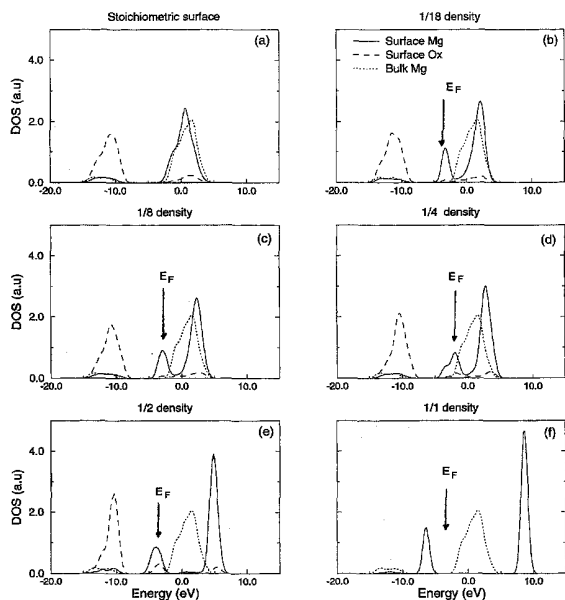


Fig. 2. Local densities of states (LDOS) on magnesiums and oxygens on the stoichiometric $\text{MgO}\{100\}$ surface and on oxygen deficient surfaces. The LDOS on magnesiums located close to a vacancy are represented by plain lines; LDOS on oxygens, second neighbours to a vacancy, are displayed with dashed lines, except for the 1/1 density where no oxygen is left in the surface plane; bulk magnesium LDOS are shown for comparison as dotted lines. In the special case of the relaxed surface with a 1/8 density of vacancy, the LDOS indicated in (c) by a plain line corresponds to the magnesiums in the third coordination shell of the vacancy (see text). The calculated LDOS have been convoluted by a 0.7 eV wide Gaussian function.

the non-stoichiometric slab plus neutral oxygens located at infinity, and the stoichiometric slab, normalized to one vacancy. It should be noted that our method does not give a good estimate of the energy of the neutral oxygen atom, because it does not take into account the multiplet structure of its ground state. The same problem occurs when an LDA method is used [32], and we have applied the same correction of 1.97 eV as the authors of Ref. [32]. The vacancy formation energy E_{vf} is large, of the order of 10 eV at low densities, in good agreement with the value 9.8 eV given in Ref. [32]. It strongly decreases as the oxygen deficiency grows. This can be interpreted as the sign of an effective attraction between vacancies. We will see in the next section that the electrostatic

interactions in the surface plane are responsible for the variations of E_{vf} .

We specify in Table 1 some electronic characteristics of the under-coordinated surface magnesiums: their outer electron numbers N_{C} (i.e. the integral over the valence band of the local density of states projected on the Magnesium 3s and 3p orbitals) and the positions ϵ_{s} and ϵ_{p} of their effective 3s and 3p levels (i.e. the diagonal terms of the Hamiltonian matrix on the magnesium 3s and 3p atomic orbitals). One of the most striking features concerns the reduction of the magnesium charge in the series. There is an increase δN_{C} of about 0.25 electron on the magnesiums which have one vacancy in their first coordination shell ($Z_{\text{vac}} = 1$), and 0.66 electrons when $Z_{\text{vac}} = 2$. The change of the magnesium electron number concerns mostly the 3s orbital: $\delta N_{\text{s}} = 0.36, 0.35, 0.42$ and 0.99 in the series. The 3p orbital, on the other hand, loses electrons: $\delta N_{\text{p}} = -0.11, -0.10, -0.08$ and -0.31 . The charge modifications on the other atoms – magnesiums below the vacancy or other surface atoms – never exceed 0.03 electrons and we will not discuss them here. In the case of the 1/8 density, nevertheless, the description which has just been given actually applies only in the absence of horizontal displacements $\delta L'$ of the oxygens. When the relaxation of the oxygens in the surface plane takes place, there is a transfer of electrons from the under-coordinated magnesiums to the magnesiums located on the cell edges (atoms located in the fourth coordination shell of the vacancy, represented as black circles in Fig. 1). As a consequence, $\delta N_{\text{C}} = 0.07$ on the former and 0.26 on the latter (values given in parenthesis in Table 1). It should be noted that the electron redistributions that we find correspond to the largest possible electron localization around the vacancy that can be achieved in a tight-binding approach. The *ab initio* method used in Ref. [32] yields an even stronger localization, with a maximum of the electron density near the centre of the vacancy.

The positions ϵ_{s} and ϵ_{p} of the magnesium effective levels are also greatly modified by the presence of the vacancies. Table 1 shows that ϵ_{s} shifts towards lower energies by 1–1.5 eV on surfaces with $Z_{\text{vac}} = 1$ and by 3 eV when $Z_{\text{vac}} = 2$, while ϵ_{p} shifts in the opposite direction by an increasing

amount as the vacancy density grows. The gap state in the LDOS shown in Figs. 2b–f is located about 1.5 eV above ϵ_s for all densities. The energy difference $\epsilon_p - \epsilon_s$ is close to the peak splitting in the conduction band. This confirms the peak assignment made above. On the 1/8 density surface, this description applies when $\delta L' = 0$. Otherwise, the level shift takes place on the remote magnesiums, rather than on the under-coordinated ones.

The horizontal and vertical displacements δL and δZ of the four magnesiums which surround each vacancy, the horizontal and vertical displacements $\delta L'$ and $\delta Z'$ of the four oxygens located in the second coordination shell of the vacancy, and the vertical displacements $\delta Z''$ of the oxygens in the following shell are given in the lower part of Table 1. When $Z_{\text{vac}} = 1$, the magnesium relaxation mainly takes place in the surface plane. The atoms move about 0.15 Å away from the vacancy and only a few hundredths Å towards vacuum in the direction perpendicular to the surface. One in-plane oxygen–magnesium bond length, denoted d_1 in the following, is thus shortened. This result is qualitatively consistent with those obtained in Ref. [32], as far as δZ is concerned. The horizontal displacements that we find, however, are much larger, both for the magnesiums and for the surface oxygens when the vacancy density is equal to 1/8. The horizontal displacement δL of 0.15 Å yields a shortening of d_1 . It is approximately equal to the contraction of distance that we had found [43] for atoms in a similar environment (the distance between a step atom and a terrace atom) on MgO vicinal surfaces, and which is in good agreement with *ab initio* results [45,46]. For the two highest densities of vacancies, displacements in the surface plane are forbidden by symmetry. The outward vertical displacement, which is equal to 0.22 Å for the 1/2 density, increases the interplane oxygen–magnesium distance, d_2 . In the case of 1/4 and 1/2 densities, an outward displacement $\delta Z' = 0.19$ Å of the oxygens is found.

For the 1/1 density, we find that there is no equilibrium position for the surface magnesiums at finite distance ($d_2 = \infty$). Calculations predict a desorption of these atoms, in a neutral state ($\delta N_C = 1.24$). The non-stoichiometric slab is thus equivalent to a stoichiometric slab, with only three layers

instead of four, and neutral magnesiums located at infinity. The local density of states on the magnesiums, shown in Fig. 2f, displays two peaks, associated with the 3s and 3p atomic levels, located respectively at –7.5 eV and 8 eV. The magnesium 3s peak is located close in energy to the top of the valence band of the underlying plane. It is singly degenerate per unit cell, and two electrons fill it. This is why the magnesiums are neutral, and why the surface maintains an insulating character. The formation energy per vacancy is lower than on the other surfaces: it is equal to 3.84 eV.

To summarize, we have found that the presence of oxygen vacancies induces changes in the electronic structure of the surfaces. Strong electron redistributions take place on the magnesiums which are located close to the vacancies. Their effective atomic levels are shifted towards low energies (3s levels) or high energies (3p levels), inducing a splitting of the conduction band and the presence of a gap state. The Fermi level is pinned on this gap state, which is partly filled except when all oxygens have left the surface. Except in this latter case, the under-stoichiometric surfaces present a metallic character. The energy of vacancy formation is large at low densities and decreases by about a factor of 2 in the series. Qualitatively, it is found that the charge redistributions, the level shifts and the vacancy formation energies do not vary monotonously with the vacancy density, but rather with the number Z_{vac} of vacancies in the first coordination shell of the under-coordinated surface magnesiums.

4. Discussion

Here we will discuss the main features of the electronic and atomic structures: the charge redistribution, the positions of the effective atomic levels, the modifications of the anion–cation bonding in the sub-stoichiometric surfaces, the oxygen vacancy formation energy and the surface relaxation, in the light of simple theoretical models.

4.1. First approach to the charge redistribution

According to Table 1, the changes δN_C in the electron number N_C of the under-coordinated sur-

face magnesiums are roughly proportional to the number of neighbouring vacancies, Z_{vac} . A simple model accounts for this result. When a neutral vacancy is formed, the oxygen leaves an excess of electrons on the surface which is equal and opposite to its charge; $\delta N_{\text{O}} = 1.24$ in the present calculation. This electron excess is shared between the four magnesiums which surround the vacancy in the surface plane. Considering that each under-coordinated magnesium has Z_{vac} vacancies in its neighbourhood, this leads to a variation of N_{C} equal to:

$$\delta N_{\text{C}} = \frac{\delta N_{\text{O}}}{4} Z_{\text{vac}}, \quad (1)$$

i.e. to 0.31 ($N_{\text{C}} = 1.05$), 0.62 ($N_{\text{C}} = 1.36$) and 1.24 ($N_{\text{C}} = 2$) electrons respectively for $Z_{\text{vac}} = 1, 2$ and 4. Such numbers compare well with the results obtained in the absence of structural relaxation: $N_{\text{C}} = 1.05, 1.06, 1.09, 1.42$ and 2.03 respectively for the five vacancy densities. The structural distortions in the vicinity of the vacancy modify the values of N_{C} by less than 0.05 electrons, except for the $1/8$ density, on which the electron excess is shared between the magnesiums in the fourth coordination shell of the vacancy, rather than between those in the second shell. Yet, in this case, on these atoms, δN_{C} is also close to 0.31 of an electron.

4.2. Atomic level positions

As seen in Section 3, the positions ϵ_{s} and ϵ_{p} of the magnesium effective levels are greatly modified by the presence of the vacancies. To discuss this effect, we shall use the expressions of ϵ_{l} ($\text{l} = \text{s}, \text{p}$) in the simplest Hartree–Fock approximation (in atomic units):

$$\epsilon_{\text{l}} = \epsilon_{\text{l}}^{00} - V_{\text{Mad}} + U \left(N_{\text{C}} - \frac{N_{\text{l}}}{2} \right). \quad (2)$$

In this equation, ϵ_{l}^{00} is related to the energy ϵ_{l}^0 of the atomic orbital l in the neutral atom by: $\epsilon_{\text{l}}^{00} = \epsilon_{\text{l}}^0 - U(N^0 - 1)$ where N^0 is the outer electron number in the neutral atom. V_{Mad} is the Madelung potential exerted on the atom by all the surrounding ions and U is the magnesium intra-atomic

electron–electron repulsion integral. Compared to the level positions on the stoichiometric surface, two corrections take place in the presence of oxygen vacancies: one is due to intra-atomic effects associated with the changes δN_{C} , δN_{s} and δN_{p} in the electron numbers. The second correction, which is the same on s and p orbitals, comes from the modification of the Madelung potential V_{Mad} , as a consequence of the disappearance of one oxygen and of the modification of the surrounding magnesium charges.

Intra-atomic effects: The level shift due to intra-atomic effects amounts to $U(\delta N_{\text{C}} - \delta N_{\text{l}}/2)$. It contains a Hartree positive contribution, $U\delta N_{\text{C}}$, which shifts both the s and p levels towards higher energies. The Fock contribution, however, is different on the different orbitals. Since, qualitatively, δN_{s} is close to δN_{C} , and since δN_{p} is small, the Fock term cancels nearly half of the Hartree term in ϵ_{s} and vanishes for ϵ_{p} . A strong splitting of the levels results, of the order of $U\delta N_{\text{C}}/2$. Since δN_{C} is roughly proportional to Z_{vac} , the same is true for the conduction band splitting, which is in agreement with the numerical results given in Table 1.

Madelung potentials: The Madelung potential exerted on the surface ions is modified in the presence of oxygen vacancies, due to the disappearance of the oxygen charge at the location of the vacancy and to the modification of the surrounding magnesium charges. Despite the fact that electrostatic interactions are long range, we find that noticeable variations of the Madelung potential take place only on the magnesiums which surround the vacancy. The term δV_{Mad} amounts to about 3 V when $Z_{\text{vac}} = 1$, 5.5 V when $Z_{\text{vac}} = 2$ and 10 V when $Z_{\text{vac}} = 4$. It is roughly proportional to Z_{vac} .

To account for this result, we first consider the case $Z_{\text{vac}} = 1$ and recall that the electrons left behind by the missing oxygen are nearly exactly shared between the four surface magnesiums which surround the vacancy. Compared to the stoichiometric surface, the charge variation at the vacancy position δN_{O} is thus exactly balanced by the charge modification $-\delta N_{\text{O}}/4$ on the four neighbouring magnesiums. The entity, which involves the five sites and which is schematized in Fig. 3, exerts a very weak potential on all atoms which do not

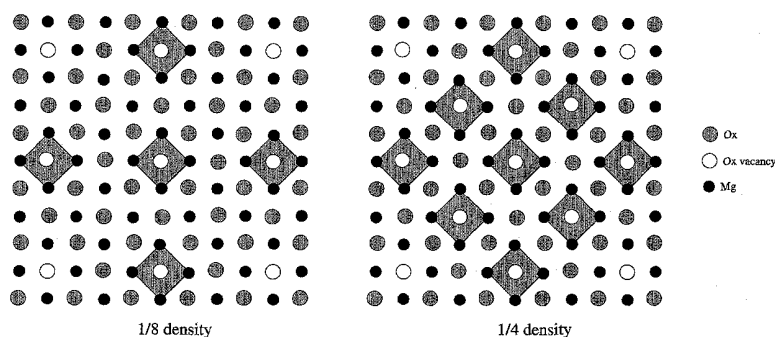


Fig. 3. Representation of the neutral entities used to estimate the modifications of the Madelung potential: the centre of the entity is the location of the vacancy with an effective positive charge δN_0 and four magnesiums surround it with charge variations equal to $-\delta N_0/4$. When n entities overlap, the charge variation on a magnesium belonging to these entities is $-n\delta N_0/4$.

belong to it, because it has no charge and no dipole moment. Conversely, on a magnesium inside the unit, one can estimate that δV_{Mad} is equal to 3.3 V. On all surfaces on which the surface magnesiums have $Z_{\text{vac}} = 1$, this is the only contribution to δV_{Mad} . On the surface with a 1/2 vacancy density, each magnesium belongs to two units and thus feels a potential change equal to twice 3.3 V. An additional doubling takes place when $Z_{\text{vac}} = 4$.

According to Eq. (2), the reduction of V_{Mad} on under-coordinated magnesiums shifts their levels towards lower energies. It competes with the intra-atomic correction which has the opposite effect. As far as the 3s levels are concerned, the Madelung term is larger and a global shift towards lower energies results. However, the 3p levels are pushed towards higher energies, because the intra-atomic term prevails.

4.3. Modifications of the anion–cation bonding

The above energy shift is responsible for a change in the degree of anion–cation hybridization, that was not considered in the simple estimate of the charge redistribution made in Section 4.1. The latter was not satisfactory, because it neglects several aspects of the problem: (1) it does not treat explicitly the bond breaking processes; (2) it is not clearly related to the filling of the gap state; and

(3) it neglects the shifts of the magnesium electronic levels in the vicinity of the vacancy. To take into account these effects, and describe non-stoichiometric surfaces in which there exist inequivalent magnesiums with different effective atomic energies, we propose an extension of the theoretical model that we developed in the case of clean oxide surfaces in order to interpret their electronic and structural properties [40].

We consider the general system, described by a Hamiltonian H , whose matrix elements on an atomic orbital basis set are of two types: the diagonal terms, equal to the effective atomic orbital energies ϵ_i , and the non-diagonal terms which are non-zero when orbitals on two neighbouring sites are involved (resonance integrals β_{ij}). H may thus be written as the sum of a diagonal operator H_D and a non-diagonal one H_{ND} . Unlike the treatment made in Ref. [40], no hypothesis is made at this stage concerning ϵ_i . The operators G_0^+ and G^+ are to be the advanced Green's operators associated, respectively, with H_D and H . G_0^+ is diagonal on the atomic orbital basis set, and its matrix elements are equal to:

$$\langle i | G_0^+ | i \rangle = \frac{1}{E - \epsilon_i + i\eta}. \quad (3)$$

The density of states, proportional to the trace of the imaginary part of G_0^+ is a sum of delta peaks

located at the energies ϵ_i of the atomic orbitals. To estimate G^+ , Dyson's equation is used:

$$G^+ = G_0^+ + G_0^+ H_{\text{ND}} G_0^+ + G_0^+ H_{\text{ND}} G_0^+ H_{\text{ND}} G_0^+ + \dots \quad (4)$$

The different terms of Eq. (4) may be represented by diagrams, the simplest of which are given in Fig. 4. To obtain a tractable expression for the electron numbers, only "bubble" diagrams are retained but their summation to infinite order is performed. These diagrams represent hopping processes along closed paths, in which an electron, located on a given atomic orbital i , hops on a neighbouring atom and then comes back to i . They provide a correct description to the local anion-cation hybridization inside a small cluster which includes the central atomic orbital i and all the first neighbours. Long range band effects, however, are neglected, but the first and second moments of the local densities of states are exactly obtained.

Within this self-energy approximation, the G^+

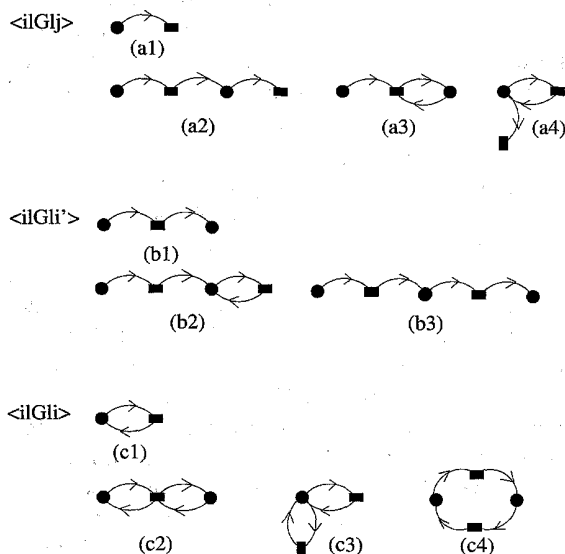


Fig. 4. Lowest order diagrams associated with cation-anion orbital hybridization. Unlike the representations used in the many body problem, the diagram vertices – a dot for an anion and a rectangle for a cation – here symbolize the matrix elements of G_0^+ , while the arrowed lines indicate hopping processes associated with H_{ND} . Only "bubble" diagrams of the c_1 - and c_3 -types are kept to derive the local charge transfer.

operator is diagonal on the atomic orbital basis set. Its matrix elements are equal to:

$$\begin{aligned} \langle i|G^+|i\rangle &= \frac{1}{E - \epsilon_i - i\eta} + \frac{1}{E - \epsilon_i - i\eta} \\ &\times \sum_j \frac{\beta_{ij}^2}{(E - \epsilon_i + i\eta)(E - \epsilon_j + i\eta)} \\ &+ \frac{1}{E - \epsilon_i + i\eta} \\ &\times \left(\sum_j \frac{\beta_{ij}^2}{(E - \epsilon_i + i\eta)(E - \epsilon_j + i\eta)} \right)^2 \dots \quad (5) \end{aligned}$$

$$\langle i|G^+|i\rangle = \frac{1}{E - \epsilon_i + i\eta - \sum_j \frac{\beta_{ij}^2}{E - \epsilon_j + i\eta}} \quad (6)$$

In order to be definite, we will consider, in the following, that $|i\rangle$ is a surface magnesium s orbital, that we will denote $|C\rangle$, and we will only take into account its hybridization with the oxygen 2p levels. When the Z_C neighbours have the same atomic energy ϵ_O , as happens in the bulk for example, $\langle C|G^+|C\rangle$ reads:

$$\langle C|G^+|C\rangle = \frac{1}{E - \epsilon_C + i\eta - \frac{Z_C \beta^2}{E - \epsilon_O + i\eta}} \quad (7)$$

The Green's matrix element has then two poles, equal to:

$$E_{\pm} = \frac{(\epsilon_C + \epsilon_O)}{2} \pm \frac{1}{2} \sqrt{(\epsilon_C - \epsilon_O)^2 + 4Z_C \beta^2} \quad (8)$$

The minus sign is associated with a bonding state, whose energy belongs to the valence band. The plus sign corresponds to an anti-bonding state. The weights of the poles give the local densities of states and an integration on all valence band states yields an electron number on the magnesiums equal to:

$$N_C = \left(1 - \frac{(\epsilon_C - \epsilon_O)}{\sqrt{(\epsilon_C - \epsilon_O)^2 + 4Z_C \beta^2}} \right) \quad (9)$$

When the anion (cation) orbitals are degenerate, the self-energy approximation derived here is thus equivalent to writing the local density of states as

the sum of two delta functions, in a way which reproduces exactly its first and second moments, as was done in Ref. [40].

However, Eq. (6) is more general and allows one to treat a geometry in which the $(4 - Z_{\text{vac}})$ oxygen neighbours located in the surface plane and the oxygen located in the sub-surface layer have different effective atomic energies, ϵ_{O1} and ϵ_{O2} . Thus, $\langle C|G^+|C \rangle$ is equal to:

$$\langle C|G^+|C \rangle = \frac{1}{E - \epsilon_C + i\eta - \frac{(4 - Z_{\text{vac}})\beta^2}{E - \epsilon_{\text{O1}} + i\eta} - \frac{\beta^2}{E - \epsilon_{\text{O2}} + i\eta}}. \quad (10)$$

The poles of $\langle C|G^+|C \rangle$ have no longer a simple expression, and the same is true for the ionic charges. Yet, a qualitative estimate is still feasible. Up to second order in the energy difference $(\epsilon_{\text{O1}} - \epsilon_{\text{O2}})$, the pole equation may be approximated by:

$$E - \epsilon_C - \frac{(5 - Z_{\text{vac}})\beta^2}{E - \bar{\epsilon}_\text{O}} = 0, \quad (11)$$

with an average oxygen atomic energy $\bar{\epsilon}_\text{O}$ defined by:

$$\bar{\epsilon}_\text{O} = \frac{(4 - Z_{\text{vac}})\epsilon_{\text{O1}} + \epsilon_{\text{O2}}}{5 - Z_{\text{vac}}}. \quad (12)$$

Similar expressions may be written for all other magnesiums present in the slab, taking into account their own effective levels and local environments.

On a non-stoichiometric MgO surface, for a given vacancy density, there are several inequivalent magnesium in the unit cell. The $4/Z_{\text{vac}}$ magnesiums close to vacancy per unit cell have $(5 - Z_{\text{vac}})$ oxygen neighbours. The magnesiums located below a vacancy or in the surface plane far from the vacancy have five neighbours, and all other magnesiums in the slab are six-fold coordinated. All the bonding states are filled, and a single anti-bonding state is filled with two electrons. It is the gap state which is found in the numerical calculations. The

anti-bonding state with the lowest energy

$$(\epsilon_C + \bar{\epsilon}_\text{O})/2 + \frac{1}{2}\sqrt{(\epsilon_C - \bar{\epsilon}_\text{O})^2 + 4Z_C\beta^2}$$

is found when ϵ_C is the smallest and/or when Z_C is smallest. Both criteria are fulfilled for the 3s orbital on the surface magnesiums located close to a vacancy. This expression accounts for the fact that the gap state is associated with the most under-coordinated magnesium 3s orbitals, and that it decreases in the gap as the vacancy density increases.

The number of 3s electrons on a surface magnesium close to a vacancy is obtained from the integration of its local density of states up to the Fermi level. One finds:

$$N_C = \left(1 - \frac{(\epsilon_C - \bar{\epsilon}_\text{O})}{\sqrt{(\epsilon_C - \bar{\epsilon}_\text{O})^2 + 4(5 - Z_{\text{vac}})\beta^2}} \right) + \frac{Z_{\text{vac}}}{4} \left(1 + \frac{(\epsilon_C - \bar{\epsilon}_\text{O})}{\sqrt{(\epsilon_C - \bar{\epsilon}_\text{O})^2 + 4(5 - Z_{\text{vac}})\beta^2}} \right). \quad (13)$$

The two terms correspond respectively to the filling of the valence band and of the gap state. For all other magnesiums in the slab, the expression of the electron number only involves the first term, with the appropriate effective atomic levels and coordination numbers. It was found in a study of perfect planar surfaces [42], as well as in the presence of steps and kinks [43], that the electron numbers on under-coordinated atoms are roughly equal to those found on bulk atoms, because, in the first term of Eq. (13), the modifications of $(\epsilon_C - \bar{\epsilon}_\text{O})$ roughly balance those of Z_C . This statement holds as long as only valence band states are filled. It also applies here and explains why there is no significant charge variation on the atoms, except on the magnesiums close to a vacancy.

On these latter, the first term in Eq. (13) also yields a contribution equal to the magnesium electron number N_C^0 on the stoichiometric surface. But, in addition, an increase in the electron number δN_C takes place, due to the presence of the second

term in Eq. (13). δN_C is equal to:

$$\delta N_C = \frac{Z_{\text{vac}}}{4} \left(1 + \frac{(\epsilon_C - \bar{\epsilon}_O)}{\sqrt{(\epsilon_C - \bar{\epsilon}_O)^2 + 4(5 - Z_{\text{vac}})\beta^2}} \right). \quad (14)$$

It may be rewritten as a function of N_C^0 in the following way:

$$\delta N_C = \frac{Z_{\text{vac}}}{4} (2 - N_C^0) \quad (15)$$

which is similar to Eq. (1), $2 - N_C^0$ being the excess of electrons δN_O left behind by the missing oxygen.

The theoretical model proposed in this section thus supports the first approach described in Section 4.1. In addition, it allows a microscopic understanding of the charge redistribution due the bond breaking, the change in the anion–cation bonding and the filling of anti-bonding states.

4.4. Oxygen vacancy formation energy

The energies of formation of a neutral oxygen vacancy are given in Table 2, for various vacancy densities. For non-interacting vacancies, at low density, E_{vf} is of the order of 10 eV. When the density increases, E_{vf} gets smaller. Its variations

Table 2
Breakdown of the vacancy formation energy on MgO{100} surfaces, into short range repulsion (rep), covalent (cov), internal (int) and Madelung (Mad) contributions, for various surface oxygen content^a

MgO	1/18	1/8	1/4	1/2	1/1
Rigid					
E_{vf}	10.4	9.79	9.55	7.64	4.26
$E_{\text{vf}}^{\text{rep}}$	−6.77	−6.77	−6.77	−6.77	−6.77
$E_{\text{vf}}^{\text{cov}}$	19.59	19.12	19.10	20.21	18.87
$E_{\text{vf}}^{\text{int}}$	−23.3	−24.93	−23.93	−23.79	−20.74
$E_{\text{vf}}^{\text{Mad}}$	20.88	22.37	21.17	17.99	12.90
Relaxed					
E_{vf}	9.95	8.75	8.71	7.41	3.84
$E_{\text{vf}}^{\text{rep}}$	−5.04	−2.38	−5.30	−8.50	−8.12
$E_{\text{vf}}^{\text{cov}}$	17.37	13.84	17.32	22.20	20.64
$E_{\text{vf}}^{\text{int}}$	−22.98	−25.15	−23.62	−24.44	−21.41
$E_{\text{vf}}^{\text{Mad}}$	20.60	22.44	20.31	18.15	12.73

^a The top and lower parts of the table give the values, respectively, in the absence and in the presence of surface relaxation.

are not driven by the vacancy density, but rather by the value of the integer Z_{vac} , as are all the other electronic characteristics already discussed.

In order to understand the variations of the vacancy formation energy and, more specifically, the respective weights of electrostatic and covalent forces, in Table 2 we give a breakdown of E_{vf} into four contributions: the short-range repulsion between atoms, which prevents the atoms from coming too close to each other; the covalent energy associated with electron sharing between atoms; the internal energy which involves the filling of atomic orbitals and the intra-atomic electron–electron interactions; and finally the Madelung energy which describes the charge–charge interactions in the system. Such a breakdown, whose principles were detailed in [41], has turned out to be very useful in a number of instances, such as the study of clean planar [42] or stepped [43] surfaces, hydroxylated surfaces [38,44] and adsorption processes [35,41].

According to Table 2, E_{vf} is the result of a competition between terms of similar magnitude. Three of them remain roughly constant in the series: the short range repulsion, covalent and internal terms. The Madelung contribution, however, shows a large decrease of 7 eV in the series, which derives the total variation of E_{vf} . We will first discuss the different terms in the absence of relaxation (top part of Table 2):

The *short-range repulsion term* comes from the breaking of five oxygen–magnesium bonds. Its contribution to the vacancy formation, in a rigid geometry, is independent on the vacancy density.

The *covalent term* is associated with the change in the anion–cation bonding. It is roughly constant in the series, and amounts to about 19 eV. It involves four terms: (1) the breaking of five bonds when the oxygen atom leaves the surface. This is the largest term, equal to 18.5 eV in a rigid geometry. It remains constant in the series; (2) the modification of the magnesium–oxygen hybridization along the remaining bonds in the surface plane. As already said, due to the lowering of the magnesium 3s levels, the hybridization is increased, which yields a negative contribution to E_{vf} of the order of −1 eV per magnesium. This energy has to be multiplied by $4/Z_{\text{vac}}$ in order to obtain the

contribution per oxygen vacancy; (3) the filling of the anti-bonding state always corresponds to a destabilization in the covalent energy. It thus yields a positive contribution to E_{vf} . This contribution is also roughly proportional to $1/Z_{vac}$. It decreases from about 7 eV when $Z_{vac}=1$ and 2, to 2 eV when $Z_{vac}=4$; (4) finally, there is a small contribution arising from the small shift of the levels for the magnesium located below the vacancy. It favours the electron delocalization and thus yields a negative contribution to E_{vf} of the order of -1 eV.

The *internal contribution* stems from the changes in the atomic orbital filling and in the intra-atomic electron–electron repulsion. It contains two terms: (1) the change in the charge of the oxygen, which leaves the surface. This term is very small, of the order of 0.5 eV. It is independent of the vacancy density; (2) the change in the magnesium charge which yields a negative contribution, which is a function of Z_{vac} : for each magnesium, it amounts to -4 to -5 eV when $Z_{vac}=1$, -9 eV when $Z_{vac}=2$ and -15 eV when $Z_{vac}=4$. To obtain the total contribution to E_{vf} , one has to multiply these numbers by $4/Z_{vac}$, the number of under-coordinated magnesiums per unit cell. As a whole, this contribution is equal to -20 , -18 and -15 eV, respectively, in the series.

The *Madelung contribution* is the change in the ion–ion electrostatic interactions, when vacancies are formed and electron redistributions take place. To express this we start from the most general expression of the Madelung energy, for charges Q_i interacting at relative distances R_{ij} :

$$E = \frac{1}{2} \sum_i Q_i V_i. \quad (16)$$

In this equation,

$$V_i = \sum_j Q_j / R_{ij}$$

denotes the Madelung potential acting on an atom i . The modification of the Madelung energy when a charge perturbation affects the system may be formally written:

$$\delta E = \frac{1}{2} \sum_i \delta Q_i V_i^0 + \frac{1}{2} \sum_i Q_i^0 \delta V_i + \frac{1}{2} \sum_i \delta Q_i \delta V_i. \quad (17)$$

The superscript 0 indicates the charge and potential values on the stoichiometric surface. The two first terms are equal to each other and, when the energy variation *per vacancy* is estimated, they yield a value independent on the vacancy density: this value includes the charge variation on the missing surface oxygen ($\delta Q_O = |Q_O^0|$) and on the under-coordinated surface magnesiums. For the latter, $V_{Mg}^0 = -V_O^0$. Since the surface unit cell is neutral:

$$\sum_{Mg_i} \delta Q_{Mg_i} = -\delta Q_O = -|Q_O^0|,$$

and the first two terms in Eq. (17) are equal to:

$$\frac{1}{2} \sum_i \delta Q_i V_i^0 + \frac{1}{2} \sum_i Q_i^0 \delta V_i = 2|Q_O^0| V_O^0. \quad (18)$$

In the present study, this quantity amounts to 25.8 eV per oxygen vacancy. It is large, but since it is constant in the series, it cannot explain the variations of E_{vf}^{Mad} . The third term in Eq. (17) is negative and contains only contributions from atoms whose charge *and* potential vary. These are:

(1) The $4/Z_{vac}$ magnesiums for which $\delta Q_{Mg_i} = -|Q_O^0| Z_{vac}/4$ (Section 4.1) and whose δV_{Mg_i} is roughly proportional to Z_{vac} and $|Q_O^0|$ (Section 4.2). δV_{Mg_i} can be written as $W Z_{vac} |Q_O^0|$, with $W > 0$.

(2) The missing lattice oxygen for which $\delta Q_O = |Q_O^0|$ and whose electrostatic potential change, estimated inside the neutral units defined in Section 4.2, is equal to

$$\delta V_O = 4\delta Q_{Mg}/R = -|Q_O^0| Z_{vac}/R$$

(R the smallest Mg–O distance).

The third term in Eq. (17) is thus equal to:

$$\frac{1}{2} \sum_i \delta Q_i \delta V_i = -\frac{1}{2} |Q_O^0|^2 Z_{vac} \left(\frac{1}{R} + W \right). \quad (19)$$

It is negative and its absolute value increases with Z_{vac} . The Madelung contribution to E_{vf} thus reads:

$$E_{vf}^{Mad} = 2|Q_O^0| V_O^0 - \frac{1}{2} |Q_O^0|^2 Z_{vac} \left(\frac{1}{R} + W \right). \quad (20)$$

It decreases when Z_{vac} grows, in agreement with the results of the numerical calculations.

To summarize, we have shown that the energy cost to create an oxygen vacancy is the result of a competition between terms of similar magnitude.

The variations of E_{vf} , when the vacancy density increases, however, are induced by electrostatic interactions associated with the electron redistribution around the vacancies.

4.5. Relaxation

When relaxation effects are considered, the above discussion remains qualitatively correct, both for the orders of magnitude and for the origin of the variations in the series. A careful comparison between the top and the lower parts of Table 2 shows that the covalent energy and short-range repulsion are the two contributions that the relaxation modifies the most soundly. This is similar to what occurs on planar or stepped surfaces [37,43]. We have developed in previous papers a theoretical model which accounts qualitatively for the distance contractions around under-coordinated atoms, as a result of a competition between these two energy terms. This model may also be used for understanding the horizontal displacements of the under-coordinated magnesiums on a non-stoichiometric surface. We will only focus here on the vertical displacements δZ , and especially on the fact that a desorption of the magnesiums takes place when the vacancy density reaches 1/1.

We assume that the modifications of the inter-atomic distances are independent of each other, so that only the part of the energy which depends upon $d = d_0 + \delta Z$ needs to be considered. It includes a short-range repulsion part, $E_{\text{rep}} = A/d^n$, written in a Lennard-Jones form, as in the numerical calculation, and a covalent term. The latter is obtained by integrating $EN_{\text{Mg}}(E)$ in the filled part of the electronic spectrum, with $N_{\text{Mg}}(E)$ representing the local density of states on a magnesium located close to a vacancy. The $N_{\text{Mg}}(E)$ term is proportional to the imaginary part of the Green's matrix element. Using the general expression given in Eq. (10) and the approximation shown in Eq. (11), one finds:

$$E_{\text{cov}} = - \left(1 - \frac{Z_{\text{vac}}}{4} \right) \times \frac{4((4 - Z_{\text{vac}})\beta_0^2 + \beta^2)}{\sqrt{(\epsilon_{\text{C}} - \epsilon_{\text{O}})^2 + 4((4 - Z_{\text{vac}})\beta_0^2 + \beta^2)}}, \quad (21)$$

an expression in which the resonance integrals β_0 , associated with the inter-atomic distance d_0 in the surface plane and β along the normal bond, have been discriminated. This expression may also be written:

$$E_{\text{cov}} = - \left(1 - \frac{Z_{\text{vac}}}{4} \right) \sqrt{(4 - Z_{\text{vac}})\beta_0^2 + \beta^2} \times \sqrt{N_{\text{C}}^0(2 - N_{\text{C}}^0)} \quad (22)$$

as a function of the electron number N_{C}^0 on a magnesium in the bulk or on a perfect surface. Such factorization was shown in Refs. [37] and [43] to be relevant when studying relaxation effects. Assuming that the resonance integrals vary as $1/d^m$ with respect to the inter-atomic distance d , the minimization of $E_{\text{cov}} + E_{\text{rep}}$ leads to the result that the Mg–O inter-atomic distance d_2 at equilibrium obeys the relationship:

$$\frac{d_2^{n-m}}{\sqrt{(4 - Z_{\text{vac}})\left(\frac{d_2}{d_0}\right)^{2m} + 1}} \propto \frac{1}{1 - \frac{Z_{\text{vac}}}{4}} \quad (23)$$

Because of the right hand side of Eq. (22), d_2 increases as a function of Z_{vac} . More specifically, when only magnesiums are left in the surface plane (vacancy density 1/1; $Z_{\text{vac}} = 4$), this simple model predicts that d_2 goes to infinity, in agreement with the numerical results. This happens because the number of filled bonding and anti-bonding states are equal and consequently the part of the covalent energy associated with the magnesium 3s states vanishes.

5. Conclusion

Using a self-consistent quantum electronic structure calculation, associated with a geometry optimization code, we have studied the atomic and electronic structures of sub-stoichiometric MgO{100} faces with different densities of neutral oxygen vacancies.

We have shown that strong electron redistributions take place on the surface magnesiums which surround the vacancies, as a result of the filling of an anti-bonding state located in the gap. This state

may be associated with the effective 3s magnesium levels, pushed down in energy by the modification of the Madelung potential, which is induced by the disappearance of one negatively charged oxygen from the surface plane. Aside from the shift of the 3s level, the local density of states on the surface magnesiums presents an s–p splitting, due to an unequal repartition of the additional electrons on the two levels. The electron redistribution has been interpreted within the framework of a theoretical model, which is able to account for inequivalent magnesiums in the surface cell, and for the filling of a conduction band state.

The energy of formation of a neutral oxygen vacancy is found to be close to 10 eV at low vacancy densities. It decreases down to 3.8 eV when more and more vacancies are present in the surface layer. Madelung interactions have been shown to be responsible for this effect. The variation of the vacancy formation energy as a function of the vacancy density may be interpreted as arising from an effective *attraction* between the vacancies. The consequences of this attraction on the equilibrium distribution of vacancies in the surface layer will be presented in the following paper.

The magnesiums in the vicinity of a vacancy are submitted to forces which shift them from the positions that they occupy on the stoichiometric surface. In particular, at high densities of vacancies, strong outward displacements perpendicular to the surface take place, leading to a desorption of the surface magnesiums in a neutral state. We have assigned these effects to a competition between covalent and short-range processes, in which the anti-bonding state filling has to be taken into account.

This study only represents a first step in the study of non-stoichiometric MgO surfaces, for several reasons. First, the use of a semi-empirical method is expected to give the trends in the physical phenomena, rather than to yield a quantitative description of the effects. This is already clear here, as regards the localization of the charge redistribution around a vacancy. *Ab initio* methods, when their use are extended to larger scale systems, will undoubtedly help in refining the picture obtained here. In addition, the present study relies upon the assumption that the ground

state configuration for the vacancies maximizes their separation. In a subsequent paper, we will consider other configurations, and we will analyse the microscopic mechanisms responsible for the effective vacancy–vacancy interactions.

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