Structural, energetic and electronic properties of (100) surfaces for alkaline earth metal oxides as calculated with hybrid density functional theory

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ABSTRACT

We perform a systematic investigation of (100) surfaces for rocksalt-structured group 2 metal oxides, namely MgO, CaO, SrO and BaO, using GGA and Hybrid-DFT exchange-correlation functionals. We examine the structural, energetic and electronic properties of the surfaces, with a specific focus on the surface ionisation potential and band bending; the latter of which we quantify by examining the density of states as a function of depth from the system surface. We report structural and energetic results in-line with previous experimental work when we use the Hybrid-DFT method, and for the electronic structure we find inequivalent band bending for the valence and conduction bands, which results in reduced ionisation potentials and the closure of the band gap at the surface when compared to bulk systems. We also report downward bending of the conduction band for MgO that brings it below the vacuum potential, unlike previous theoretical investigations, and thus indicates an origin of the positive electron affinity found in the experiment.

1. Introduction

Metal oxides are of technological importance due to their applications in fields such as heterogeneous catalysis and microelectronics [1–5], where surface stability is a desirable material characteristic [5,6]. For alkaline metal oxides that form in a rocksalt (NaCl) crystal structure, the (100) surface is particularly well studied owing to its stability and ease of experimental preparation [5,7,8]. A detailed understanding of the surface properties can be used to explain observed phenomena such as their differing catalytic activities: for instance, Liu et al. analysed the reaction of H_2O with MgO and CaO (100) surfaces, finding that the latter formed a surface hydroxide at significantly lower pressures [9,10]. It was suggested that dissociation of H_2O over MgO occurs only at surface defects [11] and subsequent theoretical calculations confirm this, with preference towards corner (3-coordinate Mg) and edge (4-coordinate Mg) sites [12–15]; more recent results suggest that the reactivity found over CaO would also occur for BaO [16,17]. CaO and SrO are also known to be better catalysts for the Tishchenko reaction: the dimerisation of aldehydes to form esters [18,19]. This

superiority may be related to the basicity of the lattice oxygens, as suggested from calculations for the etherification of glycerol where the reactivity is ordered BaO > SrO > CaO > MgO [20,21].

Creating a surface on a material results in an inherent stress, due to the undercoordination of surface atoms. This stress is typically relieved by structural relaxations and, in more complicated cases, atomic rearrangement [3,22–25]. Surface relaxation mechanisms have been proposed for ionic systems, with most models describing the relaxation in terms of the electrostatic interactions and short-range repulsion between ions [3,22]. In particular, the relative shift of surface cations and anions normal to the surface, i.e. surface rumpling, is suggested as being linked to the differences in the size and polarisability for the species, though the second neighbour interactions could also be important [3,26]. These structural changes, along with the "dangling-bonds" of the surface atoms, can lead to novel surface-specific electronic properties, such as band bending [6,27]. However, generally such changes for rocksalt oxides, like MgO, are small due to the maintenance of 5-fold coordination by the surface atoms and the relatively low levels of rumpling that occurs, though the introduction of defects is understood to alter this equilibrium significantly [28–30].

Table 1 presents previous experimental data for MgO surface rumpling (d_{rum}), which is the difference in the surface protrusion between

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Table 1

Comparison of experimental (exp.) and theoretical rumpling (d_{rum}) and relaxation (d_{rel}) for (100) surfaces of MgO, along with surface energies (γ_{surf}). Method acronyms are as stated in the text; the -SIC appenditure on to LDA stands for "self-interaction correction", as applied in the specific calculation. The exchange-correlation functional is given in parentheses for theoretical results.

|	Method	[Ref]	d_{rum} (%)	d_{rel} (%)	γ_{surf} (J/m^2)
Exp.:	LEED	[31]	–	-0.3 ± 1.6	–
	LEED	[32]	0	0–2.5	–
	LEED	[33]	2 ± 2	0 ± 0.75	–
	LEED	[34]	5 ± 2.5	1 ± 2	–
	LEED	[35]	3.3 ± 1.5	-0.2 ± 0.7	–
	CAICISS	[36]	0.3 ± 0.9	-15 ± 3	–
	MEIS	[37]	0.5 ± 1.0	-1.0 ± 1.0	–
	GIXS	[38]	1.07 ± 0.5	-0.56 ± 0.35	–
	FAD	[39]	0.03 ± 0.03	–	–
		[46]	–	–	1.04
Theory:	LDA (VWN)	[23]	1.87	0.22	1.18
	LDA (PZ81)	[41]	1.8	-0.2	1.14
	LDA (LSDA)	[42]	0.95	-1.4	
	LDA-SIC (PZ81)	[43]	2.0	0.1	1.29
	GGA (PBE)	[23]	2.40	-0.43	0.90
	GGA (PBE)	[41]	2.2	-0.2	1.02
	GGA (PW91)	[44]	2.27	0.00	0.90
	GGA (PW91)	[45]	2.2	0.0	0.83
	GGA (PBE-D)	[39]	0.06	–	–
	Hybrid (B3LYP)	[47]	1.5	-2.9	–

cation and anion species relative to the bulk interlayer separation; Table 1 also gives the surface relaxation (d_{rel}), which is the separation of the surface layer from the next underlying layer when compared to the bulk lattice constant. These are illustrated in Fig. 1, and defined as [23]:

$$d_{rum} = \frac{Z_a^{(1)} - Z_c^{(1)}}{Z_0}, \tag{1}$$

$$d_{rel} = \frac{\left[\left(Z_a^{(1)} + Z_c^{(1)}\right)/2 - \left(Z_a^{(2)} + Z_c^{(2)}\right)/2\right]}{Z_0} - 1, \tag{2}$$

where the surface normal is chosen to align with the Z-Cartesian axis, and Z_a and Z_c are used to identify the Z-coordinate of the anion and cation species, respectively, and Z_0 is the bulk interlayer distance ($= a_0/2$). The superscript notations $^{(1)}$ and $^{(2)}$ denote the surface and first sub-surface layer respectively. A positive value of d_{rum} indicates that the anions protrude from the surface, farther than the cations; and a negative sign implies the inverse. For d_{rel}, a positive sign implies expansion between the surface layers, whilst a negative sign implies contraction.

Experimental measurements have mostly used low-energy electron diffraction (LEED), with a notable scatter in results such that d_{rel} could be interpreted as positive or negative [31–35]. d_{rum}, however, is
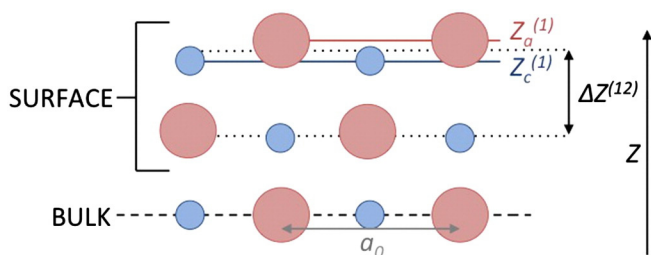
Fig. 1. Schematic representation of anions (red) and cations (blue) in a slab system, and the variables then used in the calculation of d_{rum} and d_{rel}. $Z_a^{(1)}$ and $Z_c^{(1)}$ are as defined in Eq. (1), whilst $\Delta Z^{(12)}$ is the inter-layer distance between the average position of layers $^{(1)}$ and $^{(2)}$, $[(Z_a^{(1)} + Z_c^{(1)})/2 - (Z_a^{(2)} + Z_c^{(2)})/2]$, as included in the numerator of Eq. (2). a_0 is the bulk lattice constant, and Z_0 ($= a_0/2$) is the bulk nearest neighbour distance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

unanimously positive with a range of 0 to 5%, indicating that the O^{2-} anions protrude farther from the surface than the Mg^{2+} cations, consistent with measurements using coaxial impact collision ion scattering spectroscopy (CAICISS) [36], medium energy ion scattering (MEIS) [37], grazing incidence X-ray scattering (GIXS) [38], and fast atom diffraction (FAD) [39]; the latter two methods in particular report improvements in accuracy, and reduced error bars. Complementary to these experiments have been a range of computational simulations, ranging from molecular mechanics based forcefield calculations [40], to higher-level Hartree-Fock (HF) calculations [28]. We have limited our literature data selection (Table 1) to density functional theory (DFT) calculations as we are specifically interested in these results in the context of our work; d_{rum} is positive in all cases, matching the experimental observations, but the results acquired using the local-density approximation (LDA) [23,41–43] are in general smaller than those obtained using the generalised-gradient approximation (GGA) [23,41,44, 45]. Contrastingly, d_{rel} varies between -1.4 (-0.43) and 0.22 (0.1) % for the LDA (GGA) calculations; for the Hybrid-DFT a significantly lower result of -2.9% is reported. Finally, we also give the surface energy (γ_{surf}), which for the reported calculations illustrates that the LDA (1.14–1.29 J/m^2, [23,41,43]) and GGA (0.83–1.02 J/m^2, [23,41,44,45]) methods slightly overestimate and underestimate, respectively, the energy required to create a (100) MgO surface when compared to the experimental measurement of 1.04 J/m^2, [46].

We summarise the available literature reports in Table 2 for other rocksalt structured metal oxides formed from the alkaline earth metals. The experimental literature for CaO is limited to a LEED experiment by Prutton et al. [48], though there are many DFT calculations [23,41, 43–45]: for these, d_{rum} is between -1.31 to -0.2%, which is the opposite sign to experiment in all cases (2%), whereas d_{rel} has the same sign though smaller in the experiment (-1%) than DFT (-1.12 to -2.7%). Comparing the LDA and GGA calculations, there are similar trends as for the MgO calculations: the LDA gives lower values of d_{rum} and d_{rel} compared to the GGA. However, these trends are not consistent for SrO and BaO, where the LDA and GGA results are similar. γ_{surf}, on the other hand, is consistently higher for the LDA by ~0.3 J/m^2 for CaO, SrO and BaO. In general all previous DFT calculations found that rumpling of the (100) surface becomes increasingly negative as one descends group 2 of the periodic table.

The structural and energetic changes at a surface are driven largely by the underlying electrostatic potential, which depends on factors such as the undercoordination of surface atoms and the varying polarisability of the respective constituent elements. The energy levels of electrons are also determined by the electrostatic potential [49], and typically one finds that the energy levels, particularly of the valence electrons, vary depending on the nature of a material. For an n-type material, such as ZnO, the electrostatic potential of e.g. an O^{2-} species generally decreases at a nonpolar surface, thus the energy of valence electrons rises, reducing the number of electrons occupying this spatial region [50,51]. Typically, this is referred to as depletion in the space charge region, and the opposite effect (space charge accumulation) occurs in p-type materials [49,52]. We note, however, that the space charge is often also associated with surface point defects, where for example oxide vacancies may accumulate on a surface of a metal oxide. Generally, a dynamic equilibrium should be achieved between bound and free charges on the surface determining the space charge features.

The overall increase/decrease in the energy levels of the electrons near a surface is known as the surface band bending effect, and has implicit links to properties such as the ionisation potential of a material [49,52,53]. Of the materials of interest in this study, MgO has been investigated previously in this context: the ionisation potential was calculated using embedded-cluster methods to decrease for the (100) surface when compared to the bulk [29,28], i.e. implying upward bending of the valence band maximum (VBM), which is confirmed by the experiment [54]. Upward bending for the valence band at the surface of MgO slabs has also been reported by Ochs et al., in a comparative study of