Opposite rumpling of the MgO and CaO (100) surfaces:
A density-functional theory study

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Density-functional theory calculations using the periodic slab approach are carried out to investigate the relaxed structures of the regular MgO and CaO(100) surfaces. Both local density and gradient corrected approximations to the exchange-correlation energy are employed and slab orbitals are expanded in Gaussian atom-centered orbitals as well as in plane waves. For MgO, the cations are displaced downwards towards the bulk relative to the oxygens with surface rumpling of ca. 2%. The vertical displacements of the atoms in CaO are in the opposite direction, producing a rumple of ca. −0.5%. It is suggested that the opposite rumpling is driven by steric effects, i.e., by the larger size of calcium cations relative to magnesium cations.

I. INTRODUCTION

MgO and CaO cleave easily along the (100) plane.[1] In the case of MgO(100), earlier work established that the surface is almost an exact termination of the bulk crystal structure. The accepted model of the surface corresponds to an inward relaxation of the surface plane (i.e., a decrease in the spacing between the surface plane and the second plane compared to the bulk value) of no more than a few percent and a rumpling of the surface (i.e., the motion of one type of ion relative to other types in a direction normal to the surface) of less than 2% of the interplanar spacing, with the positive sign corresponding to the O ions moving away from the bulk relative to the cations.[1,2] However, results on the extent of surface rumpling are somewhat scattered. Various low-energy electron diffraction (LEED) studies of air-cleaved/vacuum-annealed samples produced values ranging from 0% to 5%.[3–6] Medium energy ion scattering study (MEIS) reported a 0.5% ± 1.0% rumpling.[7] Theoretical studies based on shell-model approximations, semiempirical tight-binding, Hartree-Fock, and pseudopotential density functional theory (DFT) predicted values ranging from 0% to 11%.[7–12] A recent theoretical effort using the Car-Parinello scheme reported only a 1.5% rumpling.[13]

Investigations based upon empirical and first-principles calculations, MEIS, LEED, and reflection high-energy electron diffraction (RHEED) measurement yielded values for the relaxation of MgO(100) of no more than ± 3%.[3–15] On the other hand, impact collision ion scattering spectroscopy (ICISS) and surface extended energy-loss fine-structure (SEELFS) analyses deduced a larger surface plane relaxation of −15 to −17%.[16,17]

There are only a few studies on the characterization of the corresponding CaO(100) surface in comparison with MgO(100). Based on LEED measurement, this surface resembles MgO(100) in the sense that it is likewise an exact termination of the bulk crystal structure with small and positive rumpling, i.e., with the O ions relaxing towards the vacuum relative to the Ca ions.[18] The measured surface rum-

pling and reduction of interlayer spacing are no more than 2% and 1%, respectively. A prediction from a shell-model approximation yielded a rumple of 5% and surface contraction of 3%.[18]

This direction of surface rumpling, according to shell-model calculations, is primarily controlled by polarizabilities of the cations and anions.[2,8,9] De Wette *et al.* reported a systematic feature that the ion with smaller polarizability relaxes inward from the ion with the larger polarizability. However, some exceptions have been reported even within the shell model.[9] For example, a negative rumpling for LiCl and KBr was found even though the anions were assumed to be more polarizable than the cations. As was suggested by de Wette *et al.*, the rumpling is not solely a function of the ratio of polarizabilities but is, to some extent, determined by other model properties as well.

The polarizabilites of ions in solids are different from polarizabilites of gas-phase ions and they depend on the nature of the crystal environment. Therefore, the rule about the direction of rumpling based on ionic polarizabilites may be inconclusive for systems which display similar anionic and cationic polarizabilites. In this work we study the surface relaxation of the MgO and CaO (100) surfaces using modern density-functional methodology. We have chosen these two model systems because the ratio of anionic to cationic polarizability is 41 for MgO but only 8 for CaO (according to the Pauling scale[19]). Even though anionic polarizabilities are larger in both systems, our results expose an *opposite* rumpling of MgO(100) and CaO(100). To our knowledge, this is the first comparative study of the structural aspects of the MgO and CaO surfaces using a rigorous first-principles approach.

II. COMPUTATIONAL DETAILS

Ab initio total-energy calculations were carried out using primarily the GAPSS code.[20,21] The description of electron correlation is accomplished via the local-density approximation (LDA), using the parametrized functional of Vosko, Wilk, and Nusair (VWN).[22] The LDA is well established to

be reliable in predicting geometries for a variety of materials as the errors in bond lengths are typically a few hundredths of an Å.[20] However, the LDA performs less effectively in predicting energetics due to the inherent limitation of this approximation.[23] Hence, in some cases where reliable information about energetics is needed, we decided to resort to the generalized gradient approximation (GGA) [here we adopt the Perdew-Burke-Enzerhof functional (PBE96) (Ref. 24)].

In the GAPSS code, the Kohn-Sham equations are solved self-consistently using an efficient, modified Broyden-based convergence accelerator scheme.[25] The core and valence electron states are explicitly represented by localized Gaussian-type basis functions. The electronic charge density is represented in a similar manner in order to avoid the computation of expensive four-center integrals. The basis functions are adapted from standard molecular DFT basis sets and are of DZVP (double zeta valence plus polarization) quality.[26] Notice that d functions are included in the description of the wavefunctions and the charge density. The outermost s, p, and d orbital basis functions of Mg and Ca were readjusted in order to minimize the total energy of bulk MgO and CaO, respectively.

The GAPSS results indicated that the MgO and CaO (100) surfaces rumple in opposite directions but the magnitude of rumpling is only $\sim 2\%$ for MgO and -0.5% for CaO. To further verify these small but opposite rumplings, additional calculations were performed with the Vienna Ab initio Simulation Package (VASP).[27] An exhaustive discussion of this state-of-the-art plane-wave method is presented in Ref. 27. The electron-core interactions are represented in this approach using ultrasoft pseudopotentials.[28] This enables us to use a relatively small cutoff of E_{cut} of about 396 eV for both systems considered here. An important technical point is that in addition to the 4s state, 3p was included in the valence set for Ca since it is only slightly lower in energy than the O 2s. We did not find significant variation in the computed structural parameters with respect to the increase in E_{cut}. The plane-wave basis set with a cutoff of 930 eV was used to expand the augmentation charges. The calculations were done using the LDA exchange-correlation functional of Perdew and Zunger (PZ).[29] For comparison, we also performed calculations at the level of GGA as formulated by Perdew and Wang (PW).[30]

III. RESULTS AND DISCUSSION

A. Tests on MgO and CaO crystals

In order to assess the accuracy of the density-functional approach for the system under investigation, we initially calculated the properties of bulk MgO and CaO in the rocksalt structure. These preliminary verifications were performed at both LDA and GGA levels. Total energies at various lattice parameters are determined and fitted to the Murnaghan equation of state to obtain the bulk modulus and other crystal properties. The smallest unit cells (fcc primitive cells) were used. In calculations with the GAPSS code, the $13 \times 13 \times 13$ Monkhorst-Pack k-point sampling was employed.[31] For MgO, the LDA predicted lattice constant and bulk modulus are 4.162 Å and 1.86 Mbar, respectively, whereas the PBE96 values are 4.247 Å and 1.69 Mbar. Experiments produced

4.205 Å (Ref. 32) and 1.55 Mbar.[33] In the case of CaO, the LDA calculated lattice constant and bulk modulus are 4.768 Å and 1.16 Mbar, respectively. Using PBE96, we find 4.886 Å and 1.17 Mbar. The experimental values are 4.811 Å (Ref. 34) and 1.15 Mbar.[35] The lattice constants obtained with the VASP code differ from the GAPSS predictions by less than 0.005 Å for MgO and 0.07 Å for CaO. Overall, the agreement of theoretical results with experiments is satisfactory.

B. MgO and CaO (100) surfaces

In calculations of the surface energy, σ, the geometrical relaxation of surface atoms was initially neglected. For this calculation, the bulk is modeled by an eight-atom cubic supercell. In the GAPSS calculations, periodicity normal to the (100) plane is removed to generate a slab model for the surface. This resulting slab contains two atomic layers with two pairs of (cation-O) per layer. The unrelaxed surface energy is then calculated by subtracting from the total energy of the bulk the total energy of the slab and dividing it by twice the surface area. Our results together with those from previous theoretical works are tabulated in Table I. We verified that calculations based on a three-layer slab yield essentially the same result.

Our GAPSS estimate for the surface energy of MgO at the LDA level is 1.39 J/m^2. Values from previous efforts are rather scattered. Empirical model based studies produced values of 1.07–1.16 J/m^2.[36] Simple ionic models using experimental ionization energies and bulk and surface Madelung constants yield values ranging from 1.04 to 1.2 J/m^2.[37] A somewhat high value of 1.8 J/m^2 was obtained from full-potential linear muffin-tin orbital (FP-LMTO) calculations.[38] Periodic Hartree-Fock calculations yield 1.43 J/m^2.[11] Our value is close but not identical to other LDA results of 1.03–1.04 J/m^2 which were obtained from calculations which used plane-wave basis sets and pseudopotentials.[12,13] Interestingly, the VASP LDA results, which are also reported in Table I, are intermediate between the GAPSS results and the earlier plane-wave results.[12,13] The differences in lattice constants are too small to be responsible for discrepancies among different LDA studies. Therefore, the difference between the GAPSS and the plane-wave LDA value of surface energy must be attributed to different approximations in the calculations: (i) we did not employ pseudopotentials to represent the core states of the atoms; (ii) finite basis-set artifacts.

In view of the fact that LDA usually gives too large cohesive and binding energies, we repeated the calculations using the GAPSS-PBE96 and VASP-PW exchange-correlation functional and lattice constants reoptimized at this level of approximations. A significantly lower value of 1.12 (PBE96) and 0.90 (PW) J/m^2 is obtained. This effect also emerged from the recent work of Musolino et al. on MgO,[13] and in other works involving SnO$_2$ and TiO$_2$ surfaces.[39]

Our computed surface energy for CaO is lower than that for MgO, see Table I. Within the LDA, we get a value of 1.05 (GAPSS) and 0.87 (VASP) J/m^2 whereas gradient corrected exchange-correlation functionals yield a lower value of 0.87 (GAPSS-PBE96) and 0.66 (VASP-PW) J/m^2, as expected. Results from theoretical calculations at various levels of sophistication suggest that MgO and CaO have compa-

TABLE I. Experimental and computed surface energy σ, surface rumpling, d_{rum} and change in the topmost interplanar spacing, d_{rel}. The last two parameters are defined in the text. CP stands for Car-Parinello.

	Method	Ref.	σ (J/m^2)	d_{rum}(%)	d_{rel}(%)
MgO	LEED	3			-0.3 ± 1.6
	LEED	4		~2	~0
	LEED	5		~0	~2.5
	LEED	6		5 ± 2.5	1 ± 2
	RHEED	14		~6	
	RHEED	15			$0-3$
	ICISS	16		-0.3 ± 0.9	-15
	SEELFS	17			-17
	MEIS	7		0.5 ± 1.0	-1.0 ± 1.0
	Shell model	8,9		$0-11$	$-0.2--0.7$
	Tight-binding	10		2.4	-1.5
	Empirical	37	1.04-1.20		
	LDA(FP-LMTO)	38	1.80		
	Hartree-Fock	11	1.43	0.9	0
	LDA(CP)	12	1.03	1.7	0.7
	LDA(CP)	13	1.04	1.5	-1.2
	GGA(CP)	13	0.86		
	LDA(GAPSS)^a		1.39	2.2	~0
	GGA(GAPSS)^a		1.12		
	LDA(VASP)^a			1.86	0.25
	LDA(VASP)^b		1.18	1.87	0.22
	GGA(VASP)^a			2.40	-0.14
	GGA(VASP)^b		0.90	2.40	-0.43
CaO	LDA(GAPSS)^a		1.05	-0.6	~0
	GGA(GAPSS)^a		0.87		
	LDA(VASP)^a			-0.98	-1.81
	LDA(VASP)^b		0.87	-1.31	-2.25
	GGA(VASP)^a			-0.42	-1.36
	GGA(VASP)^b		0.66	-0.55	-1.69
	LEED	18		2	-1
	Shell model	18		5	-3

^{a}Results based on a three-layer model slab.
^{b}Results based on a four-layer model slab.

rable ionicities.[40] The CaO lattice constant is larger than that for MgO and we expect a lower Madelung contribution to the surface energy in the former.[41] This qualitatively explains why the surface energy for CaO is lower than for MgO.

Next, we allowed for geometrical relaxation of the surface ions. The MgO and CaO (100) surfaces are represented by three-atomic-layer periodic slabs in the rocksalt structure, with each layer containing four atoms in the unit cell. Additional calculations were performed with a four-layer slab with the VASP code. The equilibrium structure of the simulation systems was obtained by relaxing the atoms, except those in the bottom layer, using the steepest-descent technique[42] (GAPSS) and damped dynamics method (VASP) until the forces decreased below ~0.01 eV/Å (GAPSS) or ~0.04 eV/Å (VASP). We employed a grid of 5×5 (GAPSS) and 7×7 (VASP) special k points derived from the Monkhorst-Pack scheme to sample the two-dimensional electronic Brillouin zone of the supercells. We employed two

commonly used parameters to describe surface relaxation: surface rumpling (d_{rum}) and change in the first interlayer spacing (d_{rel}). These are defined as

$$d_{rum}=\frac{\delta Z_{ac}}{Z_o}, \qquad (1)$$

$$d_{rel}=\frac{\delta Z_{12}}{Z_o}, \qquad (2)$$

where $\delta Z_{ac}=\Delta Z_a^{(1)}-\Delta Z_c^{(1)}$ refers to the spacing of the top layer cation and anion planes, $\delta Z_{12}=[(\Delta Z_c^{(1)}+\Delta Z_a^{(1)})/2]-[\Delta Z_c^{(2)}+\Delta Z_a^{(2)})/2]$ refers to the relaxed surface top- to second-layer spacing, and Z_o represents the bulk interlayer spacing.

The relaxation effects for MgO(100) are found to be small in agreement with previous works.[43] The resulting surface energy based on the relaxed structure went down by only ~0.01 J/m^2. We find a slight rumpling of the top layer of the surface, without a noticeable change in the first interlayer spacing. The outward and inward displacements of the oxygen and magnesium atoms, respectively, are nearly identical and gave rise to d_{rum} of 2.2% (GAPSS) and 1.9% (VASP) at the LDA level. The rumpling is slightly larger for the PW functional and amounts to 2.4%. Moreover, the magnitude of rumpling is insensitive to the increase of the slab thickness to four layers. These observables are tabulated in Table I together with other results from past works.

The small value for the MgO(100) rumpling obtained in the present investigation agrees well with most of the previous experimental and theoretical works. Except for the LEED study of Blanchard et al.[6] and the RHEED measurement of Murata et al.,[14] experimenters agree upon a value of about 2% or less. Various first-principles calculations predict values from 0.9% to 1.7%,[11–13] in reasonable accord with our findings. The predicted numbers from shell-model approximations are somewhat scattered (0–11%).[8,9] This is not surprising because that type of calculation is based on empirical potentials whose parameters are fitted to existing bulk data. Virtually all the previous investigations reported a small or no contraction of the topmost interlayer spacing with the exception of the ICISS and SEELFS studies.[16,17] In particular, the LEED study of Welton-Cook and Berndt and periodic Hartree-Fock and LDA calculations produced a value of ~0, similar to our prediction.[4,11,7]

In the case of CaO(100), the rumpling is in the opposite direction of that for MgO(100), i.e., the oxygens are displaced downwards to the bulk with respect to the cations (Fig. 1). To our knowledge, this is the first time information about the relaxation of this surface from a first-principles standpoint has been reported. The magnitude of the rumpling is even smaller than for MgO(100) and the surface energy based on the relaxed structure went down by only ~0.01 J/m^2. Hence, CaO(100) can also be viewed as a slightly modified version of the bulk-terminated surface. The cations move outward and the anions move inward from their bulk positions producing the LDA value of d_{rum} for a three-layer slab of about -0.6% (GAPSS) and -1.0% (VASP). The VASP-PW result for a three-layer slab is -0.4%. The increase of the slab thickness to four layers leads to a more pronounced rumpling: -1.3% (VASP-PZ) and -0.6%
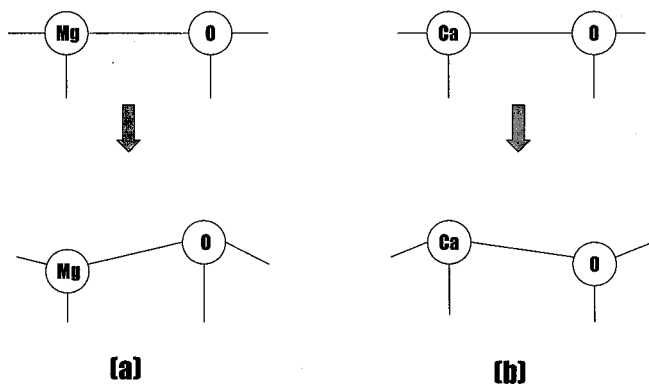
FIG. 1. Relaxation pattern for MgO and CaO(100) surfaces. (a) Positive rumpling of MgO(100) substrate; (b) negative rumpling of CaO(100) substrate.

(VASP-PW). There is virtually no contraction of the top interlayer spacing in GAPSS calculations, whereas the VASP results indicate a small contraction of about 2%.

A *negative* rumpling of CaO(100), predicted here at the DFT level of theory using two different DFT methodologies, both LDA and GGA functionals, and relatively thick slabs, is intriguing because oxide anions are assumed to be more polarizable than calcium cations.[19] The experimental findings for CaO(100) suggest a *positive* rumpling of 2% and a small relaxation of -1%.[18] The former is opposite and the latter consistent with our finding. However, the experimental results[18] were ambiguous as discussed below. The shell-model calculations yield values of 5% for d_{rum} and -3% for d_{rel}.[18]

For both MgO and CaO surfaces, we noted very slight relaxation of the atoms in the second layer giving rise to rumpling whose sign is opposite to that of the top-layer atoms. Previous works indicate that this occurs in the (100) surface of oxides with rocksalt structure.[1] The atoms below the two top atomic planes of MgO and CaO(100) did not significantly relax from their bulk positions. This implies that increasing the slab thickness would have a negligible effect on our calculated relaxed positions. Thus, our four-layer slab models are already excellent representations of the semi-infinite alkaline earth metal surfaces. A spot check on a six-layer CaO(100) slab further confirms this conclusion. The VASP GGA results yield d_{rum} and d_{rel} of $\sim -1\%$ and -2%, respectively.

In their LEED study from 1979, Prutton *et al.* speculated that the surface relaxation in CaO(100) may not resemble that of the MgO(100).[18] In fact, they had problems to fully explain their data by a positively rumpled CaO(100) surface. There were some features in the experimental LEED intensity energy spectra which were not properly resolved if the interpretation was based on this model. They suggested that the data may be more consistent with a negatively rumpled surface model but this possibility was not explored. A simulation using an empirical shell model was also attempted and the calculations yielded a positive rumple of 5%.[18] It is well established that the success of shell models is dependent on how reliably they account for important aspects of short-range overlap forces and long-range Coulomb interactions.[9] The potential used in Ref. 18 may be deficient in this respect since it predicts an unphysical negative anion-anion force

constant. There are two important parameters of shell model, named A and B in Ref. 18, that are related to elastic constants. The correctness of these parameters was not established in Ref. 18 as evidenced by the lack of data that would indicate how well the potential describes the dynamical properties of the CaO lattice.

We now attempt to provide an explanation for the opposite rumpling of the CaO and MgO (100) surfaces. It was postulated for moderately polarizable compounds that, in general, the larger the cation polarizability, the less positively rumpled the surface becomes.[1,9] De Wette *et al.* concluded that the ratio of polarizabilities is not the only factor that dictates rumpling.[9] For example, systems like LiCl and KBr(100) exhibit a negative rumpling despite the fact that the anions are more polarizable than the cations.

For the purpose of interpretation, it is convenient to separate the total interaction potential for ions in the crystalline environment into the first-order electrostatic term, which is usually approximated by the Madelung potential, the polarization term, which is dominated by the interactions between permanent monopoles and induced dipoles, and the short-range valence repulsion term. If the mode of rumpling was controlled by the first-order electrostatic term, then we would observe the same sign of d_{rum} for MgO and CaO (100). The opposite holds, hence the mode of rumpling is controlled by either the polarization or the valence repulsion term, or both.

More insight may by gained by monitoring relaxation of artificial slabs of MgO and CaO with lattice constants suitably modified to expose the role to the two remaining terms. The calculations were done for a four-layer slab and the GGA exchange-correlation functional. We performed calculations for the CaO slab with the in-surface-plane lattice constants artificially increased by 15% and decreased by 5%. On the basis of Mulliken population analysis, we find that the ionicity of the artificial structures is very similar to the ionicity of the undistored CaO slab. Therefore, the polarizabilities of the constituting ions remain approximately constant. We observed, however, a positive (0.37%) and negative (-1.65%) rumpling for the expanded and contracted structure, respectively. In fact, the negative rumpling for the contracted structure was even larger than for the undistorted CaO slab (-1.65% versus -0.55%). Therefore, we conclude that the negative rumpling of CaO(100) is primarily caused by the valence repulsion effect, not by the polarization term that is related to ionic polarizabilities.

We suggest that the opposite rumpling of the MgO and CaO (100) surfaces is driven by valence repulsion effects and is related to the difference in cationic radii, 0.65 and 0.94 Å for Mg^{2+} and Ca^{2+}, respectively.[44] It is interesting that our interpretation of the opposite rumpling does not contradict the well established rule that a negative rumpling may occur for highly polarizable cations.[1] In fact, for a fixed ionic charge, ionic polarizabilities are related to ionic radii. Therefore, our interpretation is consistent with the rule based on ionic polarizabilites, even though we emphasize the role of steric effects.

IV. SUMMARY

The rumpling of the MgO and CaO (100) surfaces was studied at the density-functional level of theory using peri-

odic boundary conditions. The exchange-correlation effects were described in the local-density approximation and using gradient corrected functionals. Results were obtained for three- and four-layer atomic slabs. The theoretical models provide accurate lattice constants and bulk moduli for MgO and CaO crystals.

We found opposite rumpling for the MgO and CaO (100) surfaces. For CaO(100), the cations are displaced away from the slab relative to the anions with the surface rumpling of $\sim -0.5\%$. For MgO(100), the anions are displaced away from the slab relative to the cations with the surface rumpling of $\sim 2\%$. The surface energy for MgO and CaO of 0.9–1.1 and 0.7–0.9 J/m^2, respectively, is sensitive to the choice of computational methodology and exchange-correlation functional.

It is common in the literature to relate the direction of rumpling to the ratio of cationic and anionic polarizabilites. The larger the cation polarizability, the less positively rumpled the surface becomes. Our results indicate, however, that the opposite rumpling of the MgO and CaO (100) surfaces is driven by valence repulsion effects and is related to the difference in cationic radii. The rule based on ionic polarizabilities may still hold because, for a fixed ionic charge, the polarizability and the ionic radius are related. We emphasize, however, the role of steric effects in rumpling of metal oxide surfaces.

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