

Structural and electronic properties of the (100) surface and bulk of alkaline-earth metal oxides

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(Received 1 March 2004; revised manuscript received 12 July 2005; published 9 September 2005)

Electronic and structural properties of the (100) surfaces and bulk of MgO, CaO, SrO, and BaO have been studied using the projector augmented wave (PAW) method within the local density approximation and generalized gradient approximation. Relaxed (100) MgO shows the positive rumpling of 2.2% whereas (100) CaO, (100) SrO, and (100) BaO exhibit increasingly negative rumpling and surface contraction. (100) CaO is a border case between the two trends and the sign of the rumpling of this surface can be changed at distortion. We find that the surface structures obtained as a result of relaxation are largely determined by an increasing interaction between the cation semicore states and oxygen p states observed in the oxide series.

DOI: 10.1103/PhysRevB.72.125414

PACS number(s): 73.20.At, 71.20.Dg

I. INTRODUCTION

Alkaline-earth metal oxides are technologically important materials applied in medicine, heterogeneous catalysis and electronics. Most applications exploit the surface properties of the oxides, which accordingly attract significant attention of both experiment and theory. The detailed knowledge of surface properties can explain many observed phenomena, for example, the differences in the catalytic activity of the (100) surfaces of MgO, CaO, SrO and BaO. In particular, it is known that CaO, SrO are much better catalysts for dimerization of aldehydes to yield corresponding ester (Tishechenko reaction¹), than MgO,² however, the reason for it is not understood.

The stress created by the surface formation is compensated by structural rearrangements. Surface relaxation has intensively been studied for ionic systems and a number of mechanisms has been proposed.^{3–5} Most models describe relaxation in terms of the electrostatic interaction and short-range repulsion between ions.^{4,5} In particular, the rumpling [i.e., a relative shift of the surface cation and anion with respect to each other in the direction normal to the surface (Fig. 1)] of the (100) surface of rocksalt (NaCl) crystals, such as alkaline-earth metal monoxides, is suggested to be determined by the difference in cation and anion polarizabilities.⁵ However, it has been shown that the ratio of polarizabilities is not the only factor influencing rumpling⁶ but the second neighbor interaction could be also important.⁴

A feature generally significant for oxide properties is an intrinsic instability of O^{-2} ion, which is never observed in a free state and can only be stabilized by a crystalline environment.⁷ Prutton *et al.*⁸ have suggested that this could lead to a different bonding on oxide surfaces compared to that in bulk. The theoretical study performed by the Hartree-Fock method has suggested that the degree of covalency increases at the surface.⁹ However, another Hartree-Fock investigation done by Fowler and Tole¹⁰ has shown that the properties of oxygen ion are similar both in bulk MgO and on its (100) surface. The Madelung potential on the (100) rocksalt surface is very close to that in bulk, the correspond-

ing ratio is 0.96. Moreover, the results of the cluster calculations by Sousa *et al.*¹¹ indicate that bonding is essentially the same in MgO bulk and on the (100) surface and the degree of ionicity of both is about 99%.

(100) MgO is the most studied surface of the alkaline-earth metal oxides both experimentally and theoretically. From experiment it is known to have the energy 1.04 J/m² (Ref. 12) [1.12 J/m² (Ref. 13)], exhibit 0%–2% inward relaxation¹⁴ (i.e., a decrease of the interplane spacing in the surface as compared to that in bulk) and the positive rumpling of 0%–5% (Ref. 14) (Fig. 1). The surface energies of 0.9–1.12 J/m² (GGA) and 1.18–1.8 J/m² (LDA) have been reported from the density functional theory (DFT) calculations.^{3,15} The rumpling and relaxation obtained in DFT are within 0.9%–2.4% and –1.2%–0.7%,^{3,15} respectively. Rather large rumpling (~11%) is, however, predicted by the shell model.¹⁶ The Hartree-Fock method gives the surface energy of 1.43 J/m² (Ref. 17) and atomistic simulations produce the energies of 1.04–1.15 J/m².¹⁸ There are very few studies of (100) CaO, (100) SrO, and (100) BaO. In particular, the results of the LEED measurements⁸ suggest (100) CaO to exhibit a negative relaxation but a slightly

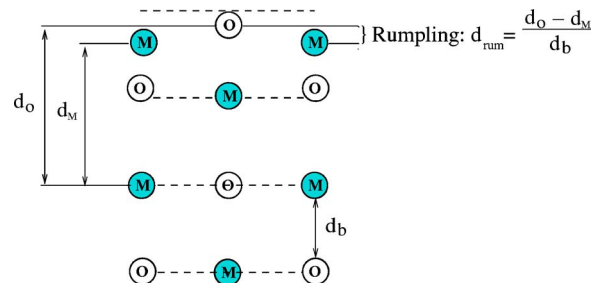


FIG. 1. (Color online) Relaxation pattern of an oxide surface showing a positive rumpling, when the oxygen ion of the top layer is shifted further towards vacuum than the metal ion. When the metal ion is shifted further towards vacuum than oxygen the rumpling is negative. Dashed lines indicate the positions of the atomic planes in an unrelaxed slab separated by bulk interlayer distances (d_b).

TABLE I. Bulk properties of alkaline-earth metal oxides, parameter of lattice a (Å), Born effective charge Z^* (in e), bulk modulus (GPa).

Oxide	a (Å)			B (GPa)		Z^* (in e)	
	GGA	LDA	Expt. (Ref. 36)	GGA	Expt.	GGA	LDA
MgO	4.25	4.16	4.21	150.7	160 (Ref. 37) [156 (Ref. 38)]	1.99	1.95
CaO	4.83	4.69	4.81	107.6	116 (Ref. 39) [110 (Ref. 40)]	2.42	2.46
SrO	5.19	5.09	5.16	85.9	91 (Ref. 41)	2.50	2.54
BaO	5.60	5.48	5.52	69.4	70 (Ref. 42)	2.72	2.85

positive rumpling, whereas the electron x-ray absorption studies suggest the relaxation of the surface to be immeasurably small.¹⁹ From DFT calculations it has been reported that (100) MgO and (100) CaO exhibit opposite rumpling, that is suggested to be determined by valence repulsion effects.³ To the best of our knowledge no detailed experimental studies of the structural properties of (100) SrO and (100) BaO have been published. In the recent work by Broqvist *et al.* the structures of the (100) and (110) surfaces of the alkaline-earth metal oxides have been studied.^{20,21} The MgO surfaces are found to exhibit positive rumpling whereas the CaO, SrO, and BaO surfaces show a negative rumpling. The origin of this phenomenon has been understood as a balance between the local O-Me bond and the minimization of the kinetic energy contributions in the electron delocalization bond (anion-anion).²¹

Based on the detailed analysis of the electronic structure of the alkaline-earth metal oxides and their (100) surfaces we show here that the observed increase of the positive rumpling of the (100) surfaces in the oxide series is determined by an increasing interaction between the cation semicore states and the p states of oxygen. The increasing electron localization around oxygen observed from MgO to BaO and consequently decreasing overlap between oxygen ions have the same origin. The paper is organized as follows: the description of the computational details is given in Sec. II, the results for the bulk and (100) surfaces of the four oxides are discussed in Sec. III and summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

The PAW method²² (as implemented in the VASP program²³) based on the density functional theory has been used. The exchange-correlation density and potential were calculated within both the local density approximation (LDA) and the generalized gradient approximation (GGA) using the Perdew-Wang parametrization.²⁴ The calculations were performed with the cutoff energy of 500 eV, treating $2p, 3s(\text{Mg}), 3s, 3p, 4s(\text{Ca}), 4s, 4p, 5s(\text{Sr}), 5s, 5p, 6s(\text{Ba}), 2s, 2p(\text{O})$ orbitals as valence states. The convergence of the total energy (~ 1 meV/atom) with respect to the number of k points had been achieved in bulk calculations, using the unit cell defined on the vectors of the primitive cubic lattice, and the obtained grid of $10 \times 10 \times 01$ k points was further employed in surface calculations.

The (100) surfaces were simulated using periodically reproduced slab supercells, consisting of 7, 9, and 11 oxide

layers infinite in the x and y directions and separated in the z direction by 15 Å of vacuum. For the studied surfaces already seven layer slabs were found to be rather adequate models. Starting from bulk interatomic distances surface slabs were allowed to fully relax under the restriction of fixed lattice parameters in the x and y directions. The surface slabs were considered to be relaxed when the forces acting on ions became smaller than 1 meV/Å. We notice that the setup of our calculations does not allow for in-plane relaxation or surface reconstruction.

The surface energies are calculated as $E_{\text{surf}} = (E_{\text{slab}} - E_{\text{bulk}})/2S$, where E_{slab} is the total energy of the supercell, and E_{bulk} is the energy of the bulk cell with the same number of atoms. S is the surface area. Changes in the surface structure due to relaxation can be characterized by two parameters, surface relaxation (d_{rel}) describing changes in the interlayer surface distances with respect to the bulk value and surface rumpling (d_{rum}) describing a relative arrangement of cation and anion in the surface layer (Fig. 1). These parameters can easily be computed from the atomic positions directly obtained in our calculations. Most often in literature we find that they are calculated using coordinates of the top-most and first subsurface layers.²¹ However, when the surface relaxation involves more than one atomic layer, as it is in the case of (100) CaO, (100) SrO, and (100) BaO, it appears to be more appropriate to use the definition of rumpling shown in Fig. 1 [$d_{\text{rum}} = (d_{\text{O}} - d_{\text{M}})/d_b$]. In this case one calculates all the distances with respect to the first undistorted surface layer, which is the third surface layer for (100) CaO, (100) SrO, and (100) BaO. Surface relaxation (d_{rel}) written as $d_{\text{rel}} = (d_{\text{O}} + d_{\text{M}} - 4d_b)/2d_b$ takes into account the changes in interplane spacing in the whole surface region affected by relaxation.

III. RESULTS AND DISCUSSION

A. Bulk properties of MgO, CaO, SrO, and BaO

Oxides of the considered group crystallize in the NaCl structure and show an increase of the lattice parameter from MgO to BaO (Table I). The bulk modulus, on the contrary, noticeably decreases indicating a weakening of interatomic bonds in the series. The electronic structure of the oxides is characterized by a relative narrowing of the valence band, mostly consisting of the p states of oxygen, 4.44 eV (MgO), 2.57 eV (CaO), 2.08 eV (SrO), 1.83 eV (BaO). The bandwidths are overestimated as compared to experimental val-

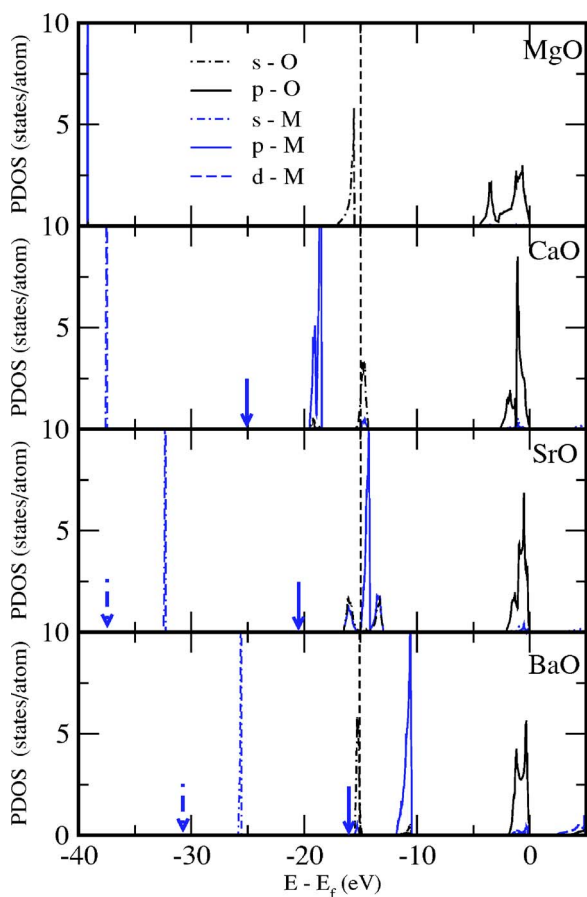


FIG. 2. (Color online) Partial densities of state for bulk MgO, CaO, SrO, and BaO. The oxygen and cation states are shown with the black and blue lines, respectively. Arrows indicate the positions of the p - M (solid blue) and s - M (dashed blue) states of the cation atoms. These values were obtained by calculating extremely expanded unit cells, where the M - O separation was about 15 Å. The corresponding atomic s - O level is shown by the dashed black line.

ues. For example, the experimentally obtained widths for MgO and CaO are just 3.3 eV (Ref. 25) and 0.9 eV (Ref. 25), respectively. Nonetheless, the tendency to the band narrowing from MgO to BaO is well reproduced in our calculations in good agreement with earlier DFT results.²¹ We notice that the Hartree-Fock method overrates the bandwidths even more [HF, 5.91 eV (MgO) 3.17 eV (CaO) (Ref. 25)] than the method used here.

The band narrowing was previously thought to originate from a weakening O-O interaction⁴ due to the increasing distance between oxygen atoms from MgO to BaO. If this assumption is indeed correct, one could expect to obtain similar bandwidths for the strontium and magnesium oxides if the latter is calculated at the SrO lattice parameter. Such calculations for MgO, however, predict $\sim 60\%$ wider p - O band than that actually obtained for SrO. At the same time, the comparison of the partial density of states (PDOS) shows that the metal semicore p states (p - M) shift towards higher energies as the atomic number of cation increases (Fig. 2). In MgO the p - M states are situated ~ 20 eV lower than the s - O states, whereas in CaO the energy interval between them is only ~ 4.8 eV. In BaO the p -Ba states are pushed ~ 3 eV

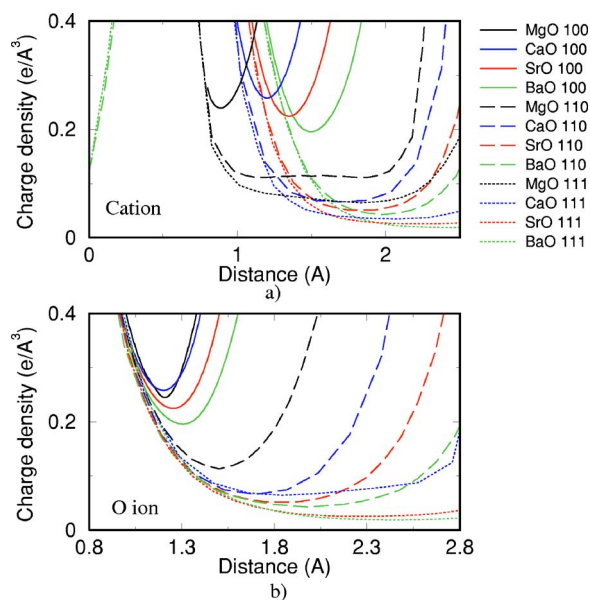


FIG. 3. (Color online) Electron densities for cation (a) and oxygen (b) ions along the [100] (M - O), [110] (O - O), and [111] (M - O) directions obtained for the bulk MgO, CaO, SrO, and BaO crystals. The cation radii are 0.9 Å (Mg), 1.19 Å (Ca), 1.35 Å (Sr), 1.5 Å (Ba).

above the s - O band being now only ~ 8 eV lower in energy than the p - O states. This increasing shift of p - M towards the p - O band and repulsive interaction between them leads to the narrowing of the valence band observed in the series. This is in accordance with earlier studies, which demonstrated an important role of metal semicore states in the stabilization of oxide structures.²⁶

The band narrowing is accompanied by a relative increase of electron localization around oxygen ions (Fig. 3). Figure 3 presents the charge density for the metal (M) [Fig. 3(a)] and oxygen (O) ions [Fig. 3(b)] along the [100], [110], and [111] directions, connecting the central ion with those in its first, second, and third coordination shells, respectively. Charge density clearly differs in these three directions. The position of the density minimum in the [100] direction can be considered as a border between the M and O ions and the ionic spheres of the corresponding radii can be used to analyze the density distribution in detail. Further we will refer to these radii as to r_c for the cation and r_a for anion spheres (Fig. 3). The size of the oxygen sphere changes from ~ 1.22 Å in MgO to ~ 1.3 in BaO. Inside the sphere electrons are spherically distributed in the following manner: 53% of the electrons are found in the sphere of radius $0.5r_a$, 90% are in the sphere of radius $0.85r_a$, and only 10% in the region closer to the ionic sphere boundary. We notice, however, that the analysis using spheres is not really sufficient for these oxides as ~ 1.5 electrons (compared to the ideal O^{2-} ion) leave the oxygen sphere for the interstitial region making the charge distribution around oxygen essentially anisotropic. The number of electrons outside the cation sphere differs from being zero in MgO to ~ 0.7 electron in BaO. The electronic distribution inside the cation sphere also changes from Mg to Ba. Whereas about 90% of Mg valence electrons are found

TABLE II. The surface properties of (100) MgO, CaO, SrO, BaO.

Oxide	$E_{\text{surf}}^{\text{unrelaxed}}(\text{J/m}^2)$		$E_{\text{surf}}^{\text{relaxed}}(\text{J/m}^2)$		$d_{\text{rel}}(\%)$		$d_{\text{rum}}(\%)$
	GGA	LDA	GGA	LDA	GGA	GGA	
MgO	0.92	1.16	0.90	1.14	0.003	2.27	
CaO	0.65	0.87	0.63	0.85	-1.12	-0.68	
SrO	0.55	0.69	0.53	0.66	-1.67	-2.26	
BaO	0.39	0.53	0.33	0.46	-2.45	-4.89	

within the sphere of radius $0.5r_c$, in the Ba sphere of the corresponding size ($0.5r_c$ of the ionic sphere radius) we find only $\sim 20\%$ of Ba electrons. At the same time, the majority of Ba electrons are located in the space limited by the spheres $0.5r_c$ and $0.9r_c$. Thus, an increasing (from Mg to Ba) electron localization at the boundary of the cation sphere is observed, suggesting an increase of cation polarizability in the series.

In order to quantitatively estimate the polarization of the ions we have calculated the displacement dipoles or the Born effective charges. As it has been shown by King-Smith and Vanderbilt²⁷ the change in polarization is related to a Berry phase²⁸ of the valence wave functions. One can calculate components of the Born effective charge tensor (Z^*) from the total difference in the polarization between distorted and undistorted structures: $\Delta P = (e/V)\sum_i Z_i^* \Delta u_i$, where u_i is a sublattice displacement. In our calculations we have used the smallest possible unit cell for the B1 structure, containing just two atoms. A shift of one atom in such a cell corresponds to a shift of the cation and anion sublattices with respect to each other. The obtained values are given in Table I. Assuming the polarizability of oxygen ion in the oxides to change insignificantly, one can attribute the enlargement of the displacement dipole observed in the series to an increasing cation polarizability.

Summing up, we find that the electronic structure of the alkaline-earth metal oxides is characterized by an increasing interaction between the metal semicore and oxygen states that causes a narrowing of the p -O band and leads to a significant increase of electron localization around oxygen observed in the oxide series.

B. MgO, CaO, SrO, and BaO (100) surfaces

The energies of the cleaved and relaxed (100) surfaces of the four alkaline-earth oxides are presented in Table II. The energies calculated using GGA are systematically lower than those from LDA calculations. Such a trend has earlier been reported for oxide surfaces^{21,29} as well as for the $4d$ metal series³⁰ and jellium model.³¹ The experimentally obtained surface energy for MgO [1.04 J/m^2 (Ref. 12), 1.12 J/m^2 (Ref. 13)] falls in between our GGA and LDA values. Unfortunately, we are not aware of experimental data on the energies of (100) CaO, (100) SrO, and (100) BaO, but our results show good agreement with earlier calculations. For example, the energies calculated for (100) CaO, 0.65 J/m^2 (GGA), 0.87 J/m^2 (LDA), are in perfect correspondence with 0.66 J/m^2 (GGA) [0.87 J/m^2 (LDA)] obtained in ear-

lier DFT calculations.³ Our results for (100) SrO [0.55 J/m^2 (GGA), 0.69 J/m^2 (LDA)] are in good agreement with 0.59 J/m^2 calculated within the Hartree-Fock scheme,⁹ but lower than the energy obtained in atomistic calculations, 0.76 J/m^2 .³² The surface energy decreases from MgO to BaO, confirming the weakening of interatomic interaction within the series already indicated by the decrease of the bulk modulus (Table I).

Surface relaxation lowers the total energy of the system by the amount $\Delta E_{\text{total}} = E_{\text{surf}}^{\text{relaxed}} - E_{\text{surf}}^{\text{unrelaxed}}$, which can be divided into the band energy term (ΔE_{band}) representing the changes in the sum over the occupied one-electron states, and the term including changes in the remaining contributions [$\Delta(E_{\text{total}} - E_{\text{band}})$, electron-electron Coulomb interaction (Hartree term), electron-core interaction, electronic exchange and correlation, core-core Coulomb energy (Ewald energy)]. The interplay between these two terms has been shown to determine equilibrium structure solids obtained³³ and, equally, it might indicate the mechanism of surface relaxation (Fig. 4). For (100) MgO the lowering of the total energy with relaxation is due to a decrease of ΔE_{band} , whereas for (100) CaO, (100) SrO, and (100) BaO it is determined by the electrostatic interactions. A small difference between ΔE_{band} and $\Delta(E_{\text{total}} - E_{\text{band}})$ observed for (100) CaO displays this oxide as a border case between the two trends.

(100) MgO shows a nearly zero relaxation (d_{rel}) and the positive rumpling of 2.27% (d_{rum}) (Table II). On the contrary, (100) CaO, (100) SrO, and (100) BaO relax inwards and show negative rumpling (Table II). Thus we observe the change of the sign of rumpling in the oxide series in agree-

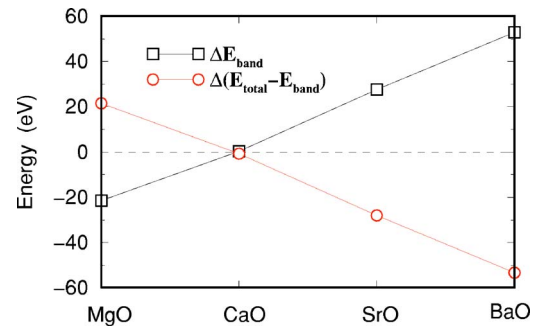


FIG. 4. (Color online) Relaxation energy terms for the (100) surfaces. ΔE_{band} is a difference between the one-electron energies of the relaxed and unrelaxed surface slabs. $\Delta(E_{\text{total}} - E_{\text{band}})$ is the sum of corresponding changes of all other energy terms constituting the total energy (the Ewald energy, the electron-electron electrostatic interaction, ion-electron, and exchange-correlation interactions).

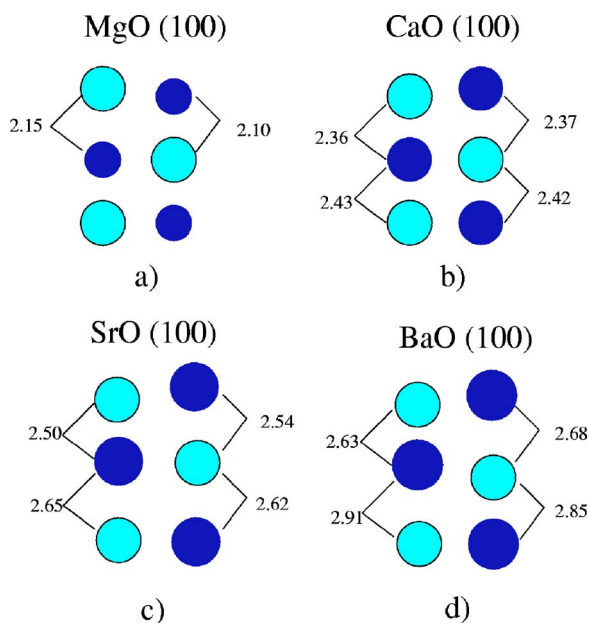


FIG. 5. (Color online) Interplane distances for the (100) surfaces of MgO, CaO, SrO, and BaO. Light circles indicate oxygen ions, dark ones stand for cations. The distances are given in Å. Only the distances different from those in bulk are shown. The corresponding bulk values are 2.13 Å for MgO, 2.42 Å for CaO, 2.6 Å for SrO, and 2.8 Å for BaO.

ment with the results by Broqvist *et al.*²¹ The relaxation patterns for the four surfaces are schematically shown in Fig. 5. They indicate that the perturbation caused by the surface involves deeper subsurface layers and leads to larger distortions when one goes from (100) MgO to (100) BaO. The relaxation of the (100) MgO surface is mostly due to an outward shift of oxygen. Mg slightly goes down whereas subsurface layers remain practically unaffected [Fig. 5(a)]. In fact, (100) MgO demonstrates rather insignificant structural rearrangement that is reflected in almost unchanged, as compared to bulk, charge distribution [Fig. 6(a)]. The surface layers of the other three surfaces show an inward relaxation,

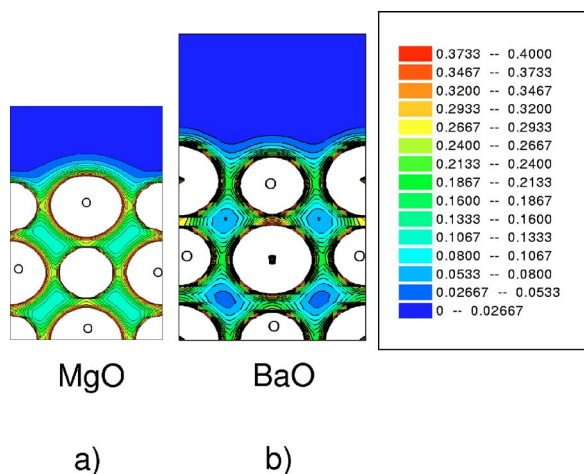


FIG. 6. (Color online) Charge density distributions for (100) MgO (a) and (100) BaO (b).

increasing from (100) CaO to (100) BaO, whereas the subsurface layers shift upwards. This effect is especially pronounced on (100) BaO, where a formation of a buckled surface consisting of two atomic layers is indicated [Fig. 5(d)]. The distance between a Ba atom in the surface layer and its closest O neighbor in the second layer is 2.68 Å, whereas the distance between an O atom in the surface layer and its Ba neighbor in the second layer is 2.63 Å. In this case a significant charge redistribution is observed and the appeared bridges of charge density between the first and second atomic layers of (100) BaO can be clearly seen [Fig. 6(b)].

The values of rumpling and relaxation presented in Table II noticeably differ from those reported by Broqvist *et al.*²¹ As we indicate in Sec. II we use a slightly different definition of rumpling and relaxation parameters (Fig. 1) from those employed by Broqvist *et al.*,²¹ who calculated them as $d_{rel} = (d_a + d_c - 2d_b)/2d_b$ and $d_{rum} = (d_a - d_c)/d_b$, where d_a and d_c are the interlayer distances for the surface anion and cation. Such a definition takes into account only the interlayer distance between the uppermost and first subsurface layers, whereas our approach allows one to consider the whole surface area distorted by relaxation, which consists of two surface layers in the case of (100) CaO, (100) SrO, and (100) BaO. In the case of (100) MgO, when only the topmost layer is affected by relaxation, the two approaches become identical and the calculated rumpling (2.27%) is in perfect agreement with the value (2.2%) by Broqvist *et al.*²¹ In order to demonstrate that the positions of the surface atoms obtained by us and those by Broqvist *et al.* should be similar we have calculated the rumpling parameters according to the definition from Ref. 21. We obtain the rumpling of -0.33% , -1.2% , and -1.78% for (100) CaO, (100) SrO, and (100) BaO, respectively. These should be compared to -0.2% , -1.3% , and -1.6% obtained by Broqvist *et al.* for the corresponding surfaces in their GGA calculations.²¹ Surface relaxation parameters (d_{rel}) calculated in the way suggested by Broqvist *et al.*²¹ are -1.9% for (100) CaO, -3.1% for (100) SrO and -5.1% for (100) BaO and they are in reasonable agreement with the corresponding data from Ref. 21.

The electronic structure of the cleaved surfaces is characterized by a downward shift of the semicore p -states of surface cations. It has, however, little impact on (100) MgO as in this oxide the p -Mg states lie sufficiently low in energy not crucially affecting the oxygen p band (Fig. 2). Oxygen electrons spill out into the vacuum region that causes the narrowing of the p -O band on the surface (4.29 eV) compared to that in bulk MgO (4.42 eV) [Fig. 7(a)] and leads to an upward shift of the semicore s -O states. On the contrary, the p band of oxygen on the unrelaxed (100) CaO, SrO, and BaO surfaces becomes wider than that in bulk as the cation semicore p states shift towards lower energies [Fig. 7(b)].

Surface relaxation leads to an insignificant increase of the p -O bandwidth in the case of (100) MgO. For the other oxide surfaces it results in a noticeable decrease of the p -O widths almost down to their bulk values and in the corresponding equilibration of the p -M positions as illustrated for (100) BaO in Fig. 7(b). This behavior demonstrates that the p -O bandwidth and the position of p -M in the spectrum are largely correlated in CaO, SrO, and BaO. The increasing electron localization around oxygen, accompanying the band

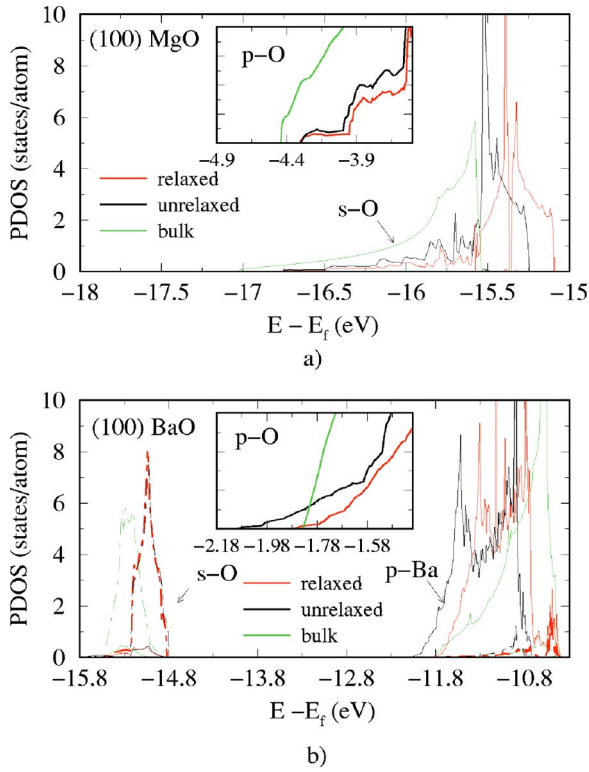


FIG. 7. (Color online) Partial density of states for the surface atoms on the relaxed and unrelaxed (100) MgO (a) and (100) BaO (b) surfaces. The main figures show the semicore states and the insets show the left edge of the p -O band indicating its width. Results for the relaxed, unrelaxed surfaces and bulk are given in red, black, and green, respectively.

narrowing, is clearly displayed by the electron localization function (ELF)^{34,35} calculated for the relaxed (100) oxide surfaces (Fig. 8). The vacuum region occupied by delocalized oxygen electrons appears to noticeably shrink from (100) MgO to (100) BaO. We notice that the increase of electron localization from (100) MgO to (100) BaO has also been observed by Broqvist *et al.*,²¹ who studied the Kohn-Sham orbital densities for the oxide surfaces.

The performed here analysis indicates that the mechanism of surface relaxation in the alkaline-earth metal oxides is essentially determined by the p - M - p -O interaction causing the increasing localization of oxygen electrons in the series that, in turn, leads to increasing Coulomb interaction be-

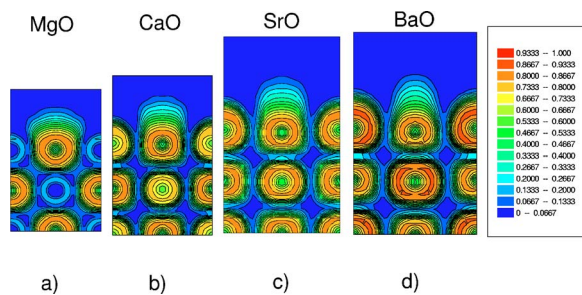


FIG. 8. (Color online) Electron localization function for (100) MgO, CaO, SrO, and BaO. The values 0.5 and 1 correspond to complete delocalization and localization, respectively.

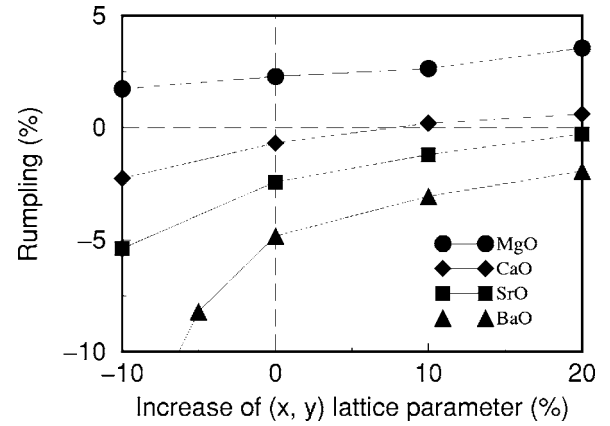


FIG. 9. Rumpling of the (100) surface of MgO, CaO, SrO, and BaO for slabs with different in-plane (x, y) lattice parameters. The percents correspond to the changes of the x and y parameters with respect to the bulk values.

tween cations and anions. Consequently, it results in a more pronounced surface contraction for (100) CaO, (100) SrO, and (100) BaO that is also reflected in a decrease of the electrostatic energy [$\Delta(E_{\text{total}} - E_{\text{band}})$] (Fig. 4). A local adjustment of the surface atoms, leading to a surface rumpling, should allow further equilibration of the p - M position. Cations tend to surround the surface oxygen, thus pushing it downwards and establishing a positive rumpling on (100) CaO, (100) SrO, (100) BaO. The decisive role of the semicore states for the character of rumpling is further confirmed by the calculation of the slabs with artificially increased by 10%, 20% and decreased by 5%, 10% in-surface-plane lattice constants (Fig. 9). Our results show that for (100) MgO rumpling is always positive and it is always negative for the (100) surfaces of SrO and BaO. (100) CaO is a border case, showing a negative rumpling for the compressed and undistorted slabs but a small positive rumpling at extension. We notice that our results on artificially distorted (100) CaO are in good agreement with those obtained by Alfonso *et al.*,³ who showed that the 5% decrease of the in-surface-plane lattice constant increases the negative value of rumpling (-1.65%) and its 15% increase results in the positive (0.37%) rumpling of (100) CaO. The common feature for all the surfaces is that the lattice stretching promotes positive rumpling, whereas compression suppresses it. Extension results in a decrease of the number of the nearest cation neighbors leading to a downward shift of the p - M band. This facilitates the delocalization of oxygen electrons and oxygen outward relaxation. Compression has an opposite effect reducing the oxygen outward relaxation. In the case of CaO the p -Ca band is situated relatively low in energy already in bulk (~ 5 eV lower than the s -O band). A surface extension, causing further downward shift of this band, alters the rumpling of (100) CaO from positive to negative.

IV. SUMMARY

The electronic structure and charge distribution in bulk and on the (100) surfaces of the alkaline-earth metal mono-

oxides are found to be determined by an increasing interaction between the cation semicore and oxygen states, that causes a narrowing of the p -O band from MgO, where oxygen electrons are most delocalized, to CaO, SrO, and BaO, where an increasing electron localization around oxygen ions is observed. Differences in the relaxation patterns obtained for (100) MgO and (100) CaO, (100) SrO, (100) BaO are largely determined by this interaction. In the case of (100) MgO, where its role is insignificant, the relaxation results in a negative rumpling and a slight surface expansion. For the

other three oxides, where the p - M - p -O interaction is important, an increasing surface contraction and positive rumpling of the (100) surface is observed.

ACKNOWLEDGMENTS

The financial support from The Swedish Natural Science Research Council and The Royal Swedish Academy of Sciences is acknowledged. Valuable discussions with L. Vitos are highly appreciated.

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