Stability of rocksalt polar surfaces: An *ab initio* study of MgO(111) and NiO(111)

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(Received 25 April 2002; revised manuscript received 3 June 2003; published 18 December 2003)

The structures of the (100) and the polar (111) surfaces of the rocksalt materials MgO and NiO have been studied using *ab initio* all electron total energy calculations, employing local basis sets, and a hybrid density functional (B3LYP). Various schemes for the stabilization of the polar surface have been examined, and we find that the hydroxylated (111) surfaces are more stable than the clean (100) surfaces. The computed energies suggest that the clean (111) surface of MgO is unstable with respect to faceting into (100) microfacets, while for the NiO(111) surface the octopolar reconstruction is favored. This distinction is due to the relatively high surface energy of the (100) surface of NiO.

DOI: 10.1103/PhysRevB.68.233405

PACS number(s): 68.35.Bs, 68.47.Gh

Oxides possessing the rocksalt structure are the most widely studied of all oxide materials. Amongst the oxides possessing this structure, MgO has been the most thoroughly investigated. MgO cleaves to produce the (100) surface, which is unambiguously the lowest energy surface in rocksalt materials. However, a cleave perpendicular to the $\langle 111 \rangle$ direction produces a crystal which has a monolayer of cations on one surface and a monolayer of anions on the other. The resulting slab of material possesses a macroscopic electrostatic field perpendicular to the surface and consequently the cleavage energy of the surface, on the basis of the ionic model, diverges with respect to slab thickness.¹

A number of mechanisms have been suggested for the stabilization of such polar surfaces. These include reconstruction of the surface, faceting, the presence of adsorbates, and changes in the surface electronic structure. These mechanisms were recently reviewed by Noguera.^{2,3} In the case of rocksalt materials, several of these mechanisms appear to be possible. Early low-energy electron-diffraction and scanning electron microscope studies of MgO(111) observed large triangular facets when attempting to form (111) surfaces.^{4,5} These facets were originally identified as (100) surfaces, but recently this interpretation has been questioned.⁶

Three stable reconstructions of the MgO(111) surface have been reported with the repeat units $(\sqrt{3} \times \sqrt{3})R30^\circ$, (2×2) , and $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$.⁷ Structure analysis based on simulation of transmission electron micrographs has led to a proposal that structures involving oxygen trimers exist on the surface.⁸

A (2×2) reconstruction is known from the (111) surface of other oxide materials that adopt the rocksalt structure. In particular, the reconstruction is observed on NiO(111) and has been studied by grazing incidence x-ray diffraction.^{9,10} Recently it has been shown that this surface consists of a structure in which $\frac{3}{4}$ of the ions in the outermost nickel layer are missing and $\frac{1}{4}$ of the oxygen ions in the second layer are missing. A similar structure is observed for the oxygen terminated surface and the two structures coexist in large domains separated by a single step.¹¹ These structures are very similar to those originally proposed by Wolf on the basis of the ionic model.¹²

In the current paper various stabilization mechanisms for

the MgO(111) and NiO(111) surfaces are investigated with *ab initio* hybrid density-functional theory. The reconstructions on these two surfaces have been compared on the basis of *ab initio* theory, although an early semiempirical study has considered similar reconstructions on MgO(111),¹³ while NiO(111) has been studied using local-density approximation+U.¹⁴ The MgO system is non-magnetic. However, for the NiO system, spin-dependent calculations have been performed.

All calculations were performed with the CRYSTAL code,¹⁵ which is based on the use of periodic *ab initio* linear combination of atomic orbitals. Triple-valence basis sets with polarization functions were used, which had been optimized in early studies of MgO and NiO.¹⁶ The estimated numerical error in the binding energy of such materials using the chosen calculation scheme is of the order of 1 mhartree and/or 0.01 mhartree in relative energies of different structures. The geometries reported here are fully relaxed in all directions consistent with the symmetry of the system.¹⁷ A hybrid exchange and correlation functional, B3LYP, was employed.^{18,19} The B3LYP functional is known to model the energetic, geometric, and electronic properties of materials with significantly greater accuracy than gradient corrected functionals and has the advantage that the ground-state energies of the simple and ferromagnetic oxides can be computed on the same footing.²⁰

The first step in the current study was the optimization of the bulk unit cell using the chosen basis set and computational parameters. This results in a lattice parameter of 4.231 Å for MgO and of 4.236 Å for NiO which are in line with the experimental values. The ground state of NiO is found to be antiferromagnetically coupled along the $\langle 111 \rangle$ direction. The energy difference between the antiferromagnetic state and a hypothetical ferromagnetic state is found to be 0.1 eV per formula unit which, as expected, is roughly three times larger than that found in Hartree-Fock calculations²¹ and in excellent agreement with recent calculations using hybrid exchange functionals.²²

The surface energy of the MgO(100) surface was found to be 1.19 J m^{-2} corresponding to a cleavage energy of 2.38 J m^{-2} , while for NiO(100) the cleavage energy is considerably higher at 5.34 J m^{-2} . The cleavage energy is de-

TABLE I. The structure of the MgO(111) and NiO(111) octopolar reconstructed surfaces. -O, -Ni, and -Mg refer to the oxygen, nickel, and magnesium terminated surfaces, respectively.

Distance	Value (Å)			
	MgO(111)-O	MgO(111)-Mg	NiO(111)-O	NiO(111)-Ni
d_{12}	1.131	0.918	1.120	0.943
d_{23}	1.197	1.231	1.214	1.232
d_{34}	1.206	1.067	1.085	1.209
Buckling in the third layer	+0.678	+0.510	0.691	0.501
d_{45}	1.171	1.235	1.224	1.116
Buckling in the fourth layer	+0.073	0.168	0.044	0.169
d_{56}	Bulk	1.112	Bulk	1.226
Buckling in the fifth layer	0.0	0.029	0.0	0.016
d_{bulk}	1.222	1.222	1.223	1.223
Pyramid closing	0.106	0.185	0.104	0.186

defined as the difference between the energy of the slab containing n formula units and n times the energy of the bulk unit cell divided by the surface area of the unit cell. For nonpolar slabs, the surface energy is simply half the cleavage energy, since the slab has two identical surfaces. For polar slabs, the two surfaces are different, and hence no unique surface energy can be defined. An earlier study has also found that the surface energy of NiO(100) is considerably higher than that of the MgO(100) surface.²³

The octopolar reconstruction of the (111) surface proposed by Wolf¹² consists of pyramids arranged in a 2×2 array. Each pyramid is analogous to the corner of a cubic rocksalt crystal and as such generates no dipole perpendicular to the surface. This structure has recently been confirmed as the basis of the reconstruction of the NiO(111) surface by grazing incidence x-ray-diffraction experiments.¹¹

In the current study the reconstruction of the cation surface has been modeled with slabs in which one surface is terminated by a $\frac{1}{4}$ monolayer of metal ions and the second layer consists of $\frac{3}{4}$ of a monolayer of oxygen ions. In order to preserve charge neutrality and stoichiometry, the other surface of the slab is terminated by a $\frac{1}{4}$ monolayer of oxygen ions with the second layer consisting of $\frac{3}{4}$ of a monolayer of metal ions. Thus, oxygen terminated cube corners on one face of the slab and metal terminated cube corners on the other face are formed. In what follows the apical atom is referred to as the first surface layer and thus the first complete layer of material is the third layer. Experimentally, both terminations are observed on the same surface separated by single height steps. However, the mean terrace size observed in the grazing incidence x-ray-diffraction measurements is 550 Å, and hence the domains can be considered as independent of each other and the current model effectively models both terminations simultaneously. In the current study the antiferromagnetic structure of NiO is preserved in the modeling of the surface, and thus each layer of Ni ions in the slab has alternating spins.

For the reconstructed (111) surfaces the geometric relaxations of the surface are converged for slabs containing 11 atomic layers. The relaxations of the metal and oxygen terminated surfaces of both MgO and NiO are very large. The

column of atoms forming the upward pointing pyramid is found to be spaced essentially at the bulk interlayer spacing with the exception of the apical atom which, in all cases, moves inward towards the surface. This inward movement is greater for the metal terminated surfaces than the oxygen terminated surfaces as the smaller ionic radius of the metal ion enables it to sink further into the hole between the three second-layer oxygen ions. Preliminary optimization of these surfaces allowed motions in only the first two layers of atoms. In this case, the three atoms in the second layer move outward to further increase the size of the hole into which the apical atom can sink. However, full relaxation of these surface structures gives rise to a different result. Instead of the pyramid opening, the pyramid actually closes, with the three second-layer ions moving towards each other. This is necessary to accommodate an enormous buckling in the third layer of the crystal. The third-layer ion which is exposed in the (2×2) unit cell moves upward by about 50% of the bulk interlayer spacing. This motion is also present in deeper layers of the crystal; it decays to zero by the fifth layer on the oxygen terminated surfaces and by the sixth layer on the metal terminated surfaces. The surface does not consist of the rather idealized cube corners anticipated but is significantly flattened. In essence, the surface can be thought of as a single buckled layer consisting of both metal ions and oxygen ions with the apical ion of the pyramid being buckled upwards and the ion that was originally in the third layer being buckled downwards. The full relaxations of the NiO and MgO surfaces are reported in Table I.

The relaxations described above produce a MgO slab with a converged cleavage energy of 3.08 J m^{-2} which is significantly larger than that of the MgO(100) surface (2.38 J m^{-2}). For NiO, the octopolar reconstructed surface is found to have a cleavage energy of 6.02 J m^{-2} . This is significantly higher than both the NiO(100) surface (5.34 J m^{-2}) and the value for the MgO(111)-octopolar surface (3.08 J m^{-2}). As the reconstruction is observed on NiO(111) but has, as yet, not been observed on MgO(111) the difference in the surface energies of the octopolar reconstruction for these two systems is surprising. However, the observation can be rationalized by considering the surface

energies of the clean (100) surfaces. For MgO the ratio of the (111) to (100) surface energy is 1.29 (3.08/2.39), while for NiO this ratio is only 1.12 (6.02/5.34). This suggests that in thermodynamic equilibrium the MgO octopolar system will be unstable with respect to microfaceting into (100) facets, while the NiO system will display the octopolar reconstruction. The driving force behind the reconstruction is therefore the relative instability of the (100) surface rather than the absolute stability of the octopolar reconstruction.

The details of these results are at variance with the surface x-ray-diffraction data for NiO.^{9,10} This study found an opening of the three atoms in the second layer of the oxide by about 0.11 Å. In addition, a smaller buckling of 0.32 Å was found in the third layer of the material. Consequently, although the theoretical and experimental studies agree that there is a significant buckling of the individual planes of this material, the detailed structure of the reconstruction does not agree. Similar discrepancies have been found between experimental x-ray-diffraction data and theoretical structure on other oxide materials and mechanisms have been proposed to explain the differences.²⁴

Various chemical mechanisms can also be imagined for the stabilization of polar rocksalt-type surfaces. The simplest is the dissociative adsorption of water. Adsorption of an OH group onto the metal terminated surface and adsorption of H onto the O terminated surface gives rise to a symmetric slab which does not give rise to a macroscopic field. Calculations have therefore also been performed on this system. For MgO, it is well known that a coverage of one monolayer provides a compensating charge that will cancel the dipole across the slab.²⁵ The geometric relaxations converge for an eight-layer slab.

For MgO the OH groups are found to have a bond length of 1.098 Å, while on NiO the OH groups have a bond length of 0.963 Å. The first to second interlayer spacing (O metal) contracts slightly, while deeper layer spacings are essentially bulklike. The relaxed geometries of the hydroxylated MgO(111) and NiO(111) surfaces are reported in Table II.

The cleavage energy of the MgO-H₂O system is computed to be 1.13 J m⁻² relative to the bulk system and a gas phase water molecule. This is more stable than the MgO(111) octopolar reconstruction and indeed is a lower cleavage energy than that of the MgO(100) surface. Hence, we may expect that periclase grown in aqueous environments will preferentially expose hydroxylated (111) surfaces,

TABLE II. The structure of the hydroxylated MgO(111) and NiO(111) surfaces.

Distance	Value (Å)	
	MgO(111)-OH	NiO(111)-OH
OH bond length	1.098	0.963
d_{12}	0.959	1.113
d_{23}	1.274	1.291
d_{34}	1.245	1.186
d_{bulk}	1.222	1.223

as is observed in practice. This finding is in line with previous calculations of the hydroxylated MgO(111) surface which have also reported surfaces energies lower than that of the (100) surface.^{13,26} For NiO the cleavage energy, again relative to the bulk system and a gas phase water molecule, is found to be 0.99 J m⁻². Similarly, this observation is consistent with the fact that naturally occurring samples of bunsenite preferentially display (111) surfaces. It has been noted that the octopolar reconstructions on NiO are stable with respect to hydroxylation²⁷ presumably due to kinetic hinderance of the dissociation mechanism.

The (111) surfaces of MgO and NiO have been studied using *ab initio* hybrid density functional theory. The (2 × 2) octopolar surfaces are stable having low cleavage energies relative to the other surfaces studied.²⁷ These surfaces display large and dramatic relaxations in which the third-layer atoms are strongly distorted away from their bulk locations. The buckling of the third layer is ≥ 50% of the bulk interlayer spacing.

For MgO, the relatively low surface energy of the (100) surface gives rise to an instability of the octopolar (111) reconstruction with respect to (100) microfacets. On NiO, the (100) surface is relatively less stable, and although the octopolar reconstructed surface also has a higher surface energy than that found on MgO, the octopolar reconstruction appears to be favored over microfaceting. The hydroxylated (111) surfaces are shown to have a lower surface energy than the corresponding (100) surface and an isolated water molecule. This is in line with the frequent observation of (111) surfaces in naturally occurring periclase and bunsenite which grow in aqueous environments.

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⁸It is not clear how the cyclic ozone reconstructions cancel the dipole field of the surface. While it is clear that these reconstructions may arise on the oxygen terminated surface of the slab, it is unclear what corresponding reconstruction would be present on the metal terminated surface. Consequently, we have not performed calculations on this system within the current study.

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