

# OXIDATION OF Mg(0001): A COMBINED EXPERIMENTAL AND THEORETICAL STUDY

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The oxidation of magnesium proceeds in several stages, beginning with the oxygen dissociation process and ending with the formation of magnesium oxides. Our focus is on the intermediate oxidation state at the Mg(0001) surface, whose geometrical structure is an unsettled problem. By combining the results of high-accuracy electronic structure calculations with angle-scanned x-ray photoelectron diffraction measurements we are able to unambiguously determine the structure of the Mg(0001) surface upon oxidation. In contrast to previous studies of Mg(0001) oxidation and unlike the case of aluminum oxidation we find a rather unanticipated surface oxide structure, consisting of two mixed oxygen-magnesium layers on top of an almost undisturbed Mg(0001) surface. This unusual surface oxide structure is locally formed already at very low coverages of 0.1 monolayer and grows laterally with increasing oxygen coverage up to 2 monolayers.

## Introduction

The oxidation of metallic surfaces is an important but complicated process. The oxidation proceeds in several stages, beginning with the dissociation of the oxygen molecule above or at the surface and ending with the correctly restructured oxide. In the complex intermediate stage the oxygen atoms may adsorb onto the surface or into the metal layers immediately below the surface. The aluminum and magnesium surfaces are particularly interesting as they belong to the group of simple metals and are considered to be model systems for studies of oxidation of transition metals.

Our focus is on the adsorption of oxygen at the Mg(0001) surface at low ( $\leq 2$  monolayers (ML)) coverages. The structure of the Mg(0001) surface after uptake of a low dose of oxygen is still an unsettled problem [1, 2]. We study the atomic structure of the slightly oxidized Mg(0001) surface by X-ray photoelectron diffraction (XPD) experiments and first-principles density functional theory (DFT) calculations. By combining the XPD measurements and the DFT calculations we are able to solve the atomic structure of the Mg(0001) surface upon initial oxidation to a high degree of accuracy.

## Experiment

The XPD experiments were carried out for O<sub>2</sub> exposures between 0.2 and 12 Langmuir, corresponding to oxygen coverages between 0.1 and 1.7 ML. Our measurements clearly show that oxygen is adsorbed into sites below the surface already at the lowest coverages. Furthermore, the evolution of the O 1s diffraction features with coverage indicates that the local atomic geometry is the same over the entire coverage range. Single-scattering cluster (SSC) calculations for oxygen atoms adsorbed in single sites are not able to reproduce the experimentally observed XPD patterns, indicating that oxygen atoms take more than one inequivalent site.

## Theory

Using DFT calculations in the Generalized Gradient Approximation (GGA) with plane waves and ultrasoft pseudopotentials [3] we calculated the adsorption energy of a large number of relaxed Mg(0001) structures for various low (1/16 to 2 monolayers) local coverages. Our results show that the initial oxygen atoms are adsorbed directly into subsurface octahedral adsorption sites without first forming an oxygen layer on top of the metal surface, in contrast to the corresponding initial processes in aluminum oxidation. Further, our results indicate that after incorporation of the very first oxygen atoms the following oxygen atoms are adsorbed as close neighbors to already occupied sites, thereby starting the formation of oxygen sub-surface

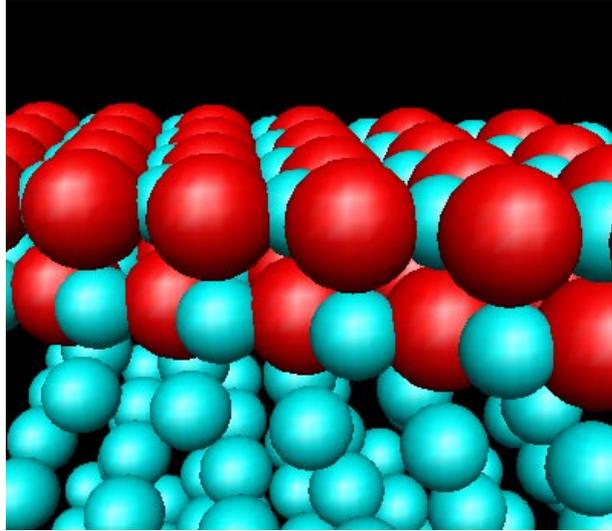


Figure 1: A sketch of the upper layers of the  $Mg(0001)$  surface after adsorption of two monolayers of oxygen. The atomic positions are as found by combined XPD measurements and DFT calculations. The figure shows a side view of the surface. Blue spheres illustrate the positions of the magnesium atoms, red spheres those of the oxygen atoms.

clustering.

With the DFT calculations we searched for the atomic structures yielding the largest adsorption energies, and extracted four atomic structures with approximately equal adsorption energies. Three of the structures are a  $Mg(0001)$  surface with slightly changed atomic positions to accommodate oxygen uptake within the topmost and within the second layer of magnesium atoms, whereas the fourth structure is a restructuring into a thin rock-salt  $MgO$  structure on top of a  $Mg(0001)$  surface. Due to the very small differences of adsorption energy between these structures DFT calculations alone cannot determine the structure of  $Mg(0001)$  at such low oxidation.

### Combining Experiment and Theory

Neither the XPD measurements nor the DFT calculations alone thus are able to unequivocally determine the atomic structure of the slightly oxidized  $Mg(0001)$  surface. However, by simulating the XPD images of the structures extracted from the DFT calculations one single structure, among the four structures with largest adsorption energy, was found to fit excellently to the experimental XPD images, whereas the simulated signal from the other three structures fit poorly to the experiment. We have thus determined the physically correct structure of the disturbed  $Mg(0001)$  surface into which two monolayers of oxygen are adsorbed.

In this structure the magnesium atoms were only slightly displaced to give space for uptake of oxygen within the topmost magnesium layer and within the Mg-layer below, yielding a double-layer of mixed oxygen-magnesium on top of an almost undisturbed  $Mg(0001)$  surface (Fig. 1). Thus the energetics of the conversion of the oxidized  $Mg(0001)$  structure into a two-layer  $MgO(111)$  rock-salt structure is presented for the first time.

### Conclusion

By combining the results of high-accuracy electronic structure calculations of the slightly oxidized  $Mg(0001)$  surface with XPD measurements we were able to unambiguously determine the atomic positions of magnesium and oxygen atoms of the  $Mg(0001)$  surface upon oxidation. In contrast to previous studies of the initial oxidation of  $Mg(0001)$  and unlike in the case of the oxidation of aluminum we find a rather unanticipated surface oxide structure, consisting of two mixed oxygen-magnesium layers on top of an almost undisturbed  $Mg(0001)$  surface.

### References

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