

Electronic Supplementary Information

Surface Core Level Binding Energy Shifts for MgO(100)

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1 Details of Calculations.

The clusters used for the SCLS presented in the main text were constructed with the logic that the atoms terminating the cluster must be the compact Mg^{2+} cations rather than more polarizable O^{2-} anions; the cluster is further embedded in an Evjen [1] field of point charges. The termination by extended cations, rather than point charges, is needed to provide a compressional effect on the anions [2] and has significant consequences for the absolute magnitude of the BE's [2,3]. The clusters used to determine the BE's for bulk and surface O atoms, including the atoms explicitly included and a representative number of embedding point charges, are shown in Fig. S.I. The $\text{OMg}_6\text{O}_{18}\text{Mg}_{38}$ cluster for the bulk contains a central O anion and its 6 nearest neighbor Mg cations; the second shell of 18 O anions insures that each of the Mg cations has 6 nearest O neighbors; and the outer shell of Mg cations insures that all the 18 O anions in the previous shell have 6 nearest neighbor Mg cations. The $\text{OMg}_5\text{O}_{13}\text{Mg}_{25}$ cluster for the (100) surface simply has the atoms in the layers above the central layer of the bulk cluster removed. The clusters used to determine the BE's for bulk and surface Mg atoms are simpler and have only three shells of atoms with $\text{MgO}_6\text{Mg}_{18}$ describing the bulk Mg BE's and $\text{MgO}_5\text{Mg}_{13}$ describing the surface BE's. The crystal structures and geometries are taken as in the bulk octahedral structure of MgO [4]. As will be discussed below, large and flexible basis sets were used to describe the orbitals of these clusters.

In addition to these specific cluster models of bulk and (100) surface MgO, we describe here the full range of embedded clusters and periodic MgO slabs that we have examined. The embedded cluster

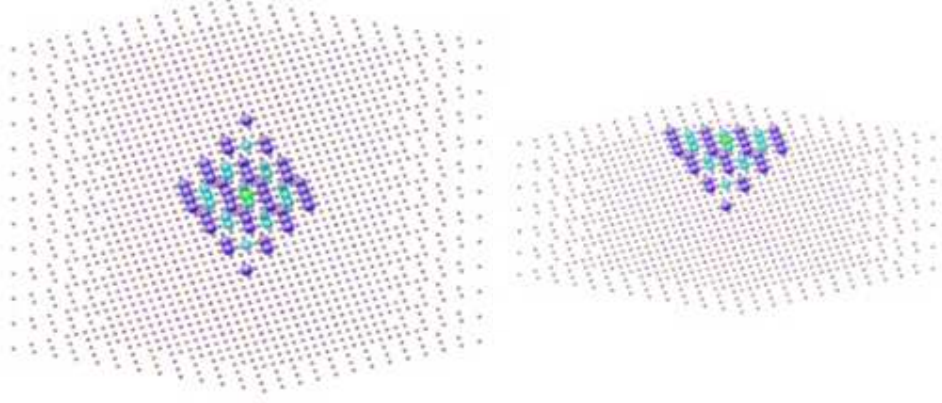
a) $\text{OMg}_6\text{O}_{18}\text{Mg}_{38}$ b) $\text{OMg}_5\text{O}_{13}\text{Mg}_{25}$ 

Figure S.I. Schematic representations of the bulk, $\text{OMg}_6\text{O}_{18}\text{Mg}_{38}$, and surface, $\text{OMg}_5\text{O}_{13}\text{Mg}_{25}$, cluster where the atoms in the clusters are shown as large spheres and a partial set of the point charges as small circles.

models consisted of a small number of atoms explicitly treated and embedded in an extended point charge field which contained ≈ 10000 point charges at the positions of the ions in an ideal MgO crystal. With the Evjen embedding [1], for a bulk MgO cluster, the point charges are within a cube, where the interior point charges are ± 2 , the face point charges are ± 1 , the edge point charges are ± 0.5 , and the corner point charges are ± 0.25 . The Evjen embedding for a surface cluster is obtained by simply removing layers above the "surface" layer. These clusters were designed in two different ways.

In the first design for "saturated" clusters, the central bulk or surface ion, either Mg^{2+} or O^{2-} , is surrounded by concentric shells of cations and anions. Like the specific clusters described above, all the saturated clusters are terminated with Mg cations. Thus, all O atoms in the cluster have the correct number of nearest neighbor Mg^{2+} ions; either 6 for bulk or 5 for surface O atoms. Representative examples of saturated clusters with a central bulk O atom are O_1Mg_6 and $\text{O}_1\text{Mg}_6\text{O}_{18}\text{Mg}_{38}$. When the surrounding point charges are chosen following the Evjen embedding [1], the total charge on the cluster including the atoms explicitly included and the point charges is zero.

In the second design, the clusters were formed in several layers, each layer being a square with either 1, 9, 25, etc. atoms. Thus a five layered cluster to model a bulk atom would have layers with 9, 9, 25, 9, and 9 atoms and the equivalent cluster for a surface atom would have three layers with 25, 9, and 9 atoms. These clusters were used in an earlier study [3] to compute accurate $\text{O}(1s)$ binding energies, BE's, for MgO. These layered clusters have almost equal numbers of Mg cations and O anions explicitly included in the cluster with the numbers of these ions differing by only 1. However, the clusters designed in this way have some O anions where the nearest neighbors include embedding point charges. In order to avoid any difficulties that might be associated with these near neighbor point charges, they were replaced with semi-empirical pseudopotentials for the Mg^{2+} core electrons [5].

For the 2D periodic calculations we used both unsupported (free) slabs of 1, 3, 5, and 7 layers of MgO and slabs of 1, 2, 3, and 5 layers supported on four layers of point charges, which were also equipped with repulsive pseudopotentials. In both cases, one can obtain the SCLS's by comparing the BEs of the inner and outer atoms. Except for the calculations of the MgO surface corrugation, described in the main text, where one of the surface atoms was displaced from its bulk position, the geometry of the clusters and slabs was taken from bulk MgO with the experimental lattice constant of 4.212 Å [4].

The Hartree-Fock, HF, cluster wavefunctions were non-relativistic and were calculated using either the Bochum suite of programs [6-9] or the CLIPS program system [10]. The coupled electron pair approximation, CEPA [11], calculations that were used to treat electron correlation effects to obtain high accuracy BE's were carried out with the Bochum suite [9]. The slab model calculations to treat the extended periodic MgO crystal were carried out with the 2D-SCF code developed at Bochum [12]. A few features of the HF calculations reported in the main text deserve mention. The initial states wavefunctions of all the clusters are closed shell. The SCF calculations for the open shell core-hole configurations were carried out using the off-diagonal Lagrange multiplier formulation to insure the orthogonality of the closed and open shell orbitals [13]. For the Mg 2p-hole HF wavefunctions an average of the $2p_x$, $2p_y$, and $2p_z$ holes was used to optimize the orbitals. For the bulk BE, this average serves to keep the O_h spatial symmetry of the hole-state wavefunctions. However, for the surface BE, where the symmetry is lower, the different 2p-holes are not exactly degenerate and the HF energy for the surface 2p-hole configuration is to an average of the configurations with a $2p\sigma$ -hole and a $2p\pi$ -hole. We have calculated the energy difference of these two configurations and find that it is 0.04 eV, too small to be of concern for the SCLS calculations; thus, the use of an average Mg 2p-hole for surface BE's is appropriate. We have used non-relativistic wavefunctions where scalar BE shifts and spin-orbit splitting of the $2p_{1/2}$ and $2p_{3/2}$ levels are neglected. However, these relativistic effects are reasonably small for the light O and Mg atoms; see, for example, Ref. [14]. More importantly, they are atomic effects that should be very similar for bulk and surface atoms. Hence neglect of these effects for the SCLS is appropriate. The HF BE's neglect electron correlation effects and, based on calculations for 10 electron atoms [14], this is expected to lead to errors in the absolute values of the core-level BE's of ≈ 1 eV. However, since the correlation effects are expected to be dominated by atomic effects, the differential effects for the BE's of bulk and surface atoms should be small. This is supported by a study of the correlation effects for bulk and surface O(1s) BE's for MgO [3] where the differential correlation contributions to bulk and surface atom BE's was found to be 0.06 eV.

Several, generally rather large, basis sets were used in these calculations. Here, we focus on the basis sets used for the HF calculations reported in the main text. These basis sets are modifications of sets used by us in previous work on MgO. The basis sets used for the O centered clusters, $OMg_6O_{18}Mg_{38}$ and $OMg_5O_{13}Mg_{25}$ are based on the basis sets used by Uhl and Staemmler [3] but with the higher

angular momentum functions added to account for electron correlation effects not included. The Mg centered basis functions contained 10s and 6p elementary Gaussian type basis functions contracted to 5s and 3p denoted (10s,6p/5s,3p). The O centered basis sets were (10s,6p,1d). For the Mg centered clusters, $\text{MgO}_6\text{Mg}_{18}$ and $\text{MgO}_5\text{Mg}_{13}$, we used basis sets modified from those used in Ref. [15]; in particular, we added diffuse d functions to both Mg and O centers to allow for polarization of the charge, especially at the surface. The basis sets were (10s,6p,2d/6s,4p,2d) for the Mg centered functions and (10s,6p,1d/5s,4p,1d) for the O centered basis functions. The exponents and contraction coefficients of these basis sets are available from the authors.

We have also performed calculations where we reduced the flexibility of the O anions to respond to the MgO environment in order to keep, as much as possible, the same spherical charge distribution for bulk and surface O anions. The variational flexibility was reduced by using a minimal basis, MB, set optimized to represent spherical Mg^{2+} and O^{2-} ions in the bulk MgO environment. The simplest pair of cluster to determine the MB SCLS are embedded OMg_6 , bulk, and OMg_5 , surface, since they contain a unique O atom. The Koopmans' Theorem, KT, MB SCLS for these clusters is -0.7 eV, close to the SCLS expected from electrostatic considerations and quite different from the ≈ 0 SCLS found when we used larger, flexible basis sets, which allow the charge distributions to be different for bulk and surface O's. The nature of this difference is investigated in the main text.

2 Details of XPS Experiments.

Experiments were performed in an ultra-high vacuum chamber equipped with standard tools for single-crystal cleaning and characterization as well as a dual-anode (Mg/Al) X-ray gun (Specs XR50) and a hemispherical electron energy analyzer (Specs Phoibos 150) for X-ray photoelectron spectroscopy measurements. The Mo(100) single-crystal used as substrate for MgO thin film growth was cleaned by repeated cycles of oxidation, Argon ion sputtering and annealing until a sharp (1×1) LEED pattern was no carbon contaminations were detected by XPS. MgO(100) films with a thickness of 30 ML (monolayers) were grown by reactive deposition of Mg in an oxygen atmosphere (1×10^{-6} mbar) while the substrate was kept at 570 K. The surface quality and crystallinity of the films was verified by LEED and XPS. Prior to XPS measurements the MgO thin film sample was annealed at 1100 K in order to remove any water/hydroxyl species accumulated on the surface during and after film growth. The bulk and surface BE's of the Mg(2p) and O(1s) peaks were measured for these 30 ML MgO(100) films with un-monochromated Al $K\alpha$ X-Rays. The measurements were made for electron exit angles of 0° , or normal exit, which is most bulk sensitive, and 80° , or grazing exit, which is most surface sensitive. Taking account of the XPS resolution and the lifetimes [16] of the O K-level, ≈ 0.15 eV, and the Mg L2/L3 levels, ≈ 0.03 eV, we estimate the broadening, full width at half maximum, FWHM, of the measured bulk and surface peaks to be ≈ 1.5 eV, which is adequate to allow us to resolve SCLS's

to within 0.2 eV. Reproducibility of our XPS BE measurements indicated that charging of the MgO film was not a problem.

After including a Shirley background [17], the experimental data were fit with Voigt-type functions in order to resolve the SCLS. The Mg(2p) XPS peaks were decomposed with two peaks where the intensity, full width at half maximum, FWHM, and the energetic position were adjusted to give the best fit to the experimental spectra. For the O(1s) XPS peaks, the spectra was sufficiently close to a single peak that two peaks could not be used for the fit and only the energy and FWHM of a single peak were fit to the spectra. The results of the fits are given in Table S.I.

Table S.I. Decomposition of the XPS of MgO films grown on Mo(001), BE's and FWHM in eV, for 0° and 80° electron exit with respect to the surface normal at 0°. For Mg(2p), the two contributions are assigned as bulk and surface peaks based on the relative intensities of the peaks at 0° and 80°. For O(1s), the single Gaussian is listed as bulk although the SCLS is sufficiently small that bulk and surface peaks could not be resolved.

		Mg(2p)		O(1s)	
Exit angle	Species	BE	FWHM	BE	FWHM
0°	Bulk	50.87	1.41	531.36	1.43
	Surface	51.52	1.59
	SCLS	0.65
80°	Bulk	50.88	1.41	531.39	1.55
	Surface	51.53	1.53
	SCLS	0.65

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