The physics behind the metallization of polar surfaces is as follows. A slab having polar surfaces is equivalent to a stack of dipole layers, which produce the bulk electric field. Since this state has an infinite surface energy, a sheet of compensating charges must be formed at the top and bottom surfaces. The system can accomplish this in two ways: either the surface is reconstructed to introduce, e.g., systematic vacancies, or a charge transfer may occur across the bulk and the surface without reconstructions. In the latter case the sheets of surplus charges imply that each surface becomes metallized.

The proposal of the metallized polar surface has long been investigated theoretically\(^1\). Specifically, the unreconstructed MgO(111) surface, which consists of a top O\(^{2-}\) surface and a bottom Mg\(^{2+}\) surface (type-III surface in the classification by Tasker\(^2\)), a quantum mechanical calculation has been performed with the discrete variational(DV)-\(X_\alpha\) method\(^3\) for a finite cluster\(^4\), a semi-empirical Hartree-Fock\(^5\), or a first-principles density functional calculation\(^6,7\) for a slab. The metallization has been confirmed in these studies.

On the other hand, the problem has a long history of experimental investigation as well, but only recently do we have definite results. Namely, various attempts to grow polar surfaces of rocksalt-structure compounds with unreconstructed polar surfaces have proved to be a difficult task. It has in fact been shown theoretically that reconstructions cannot be avoided unless we introduce hydroxylation\(^5,8\) or adsorption of metals\(^6,7,9\). If we turn to oxide surfaces, they are even more difficult to prepare than ionic crystal surfaces, because oxygen deficiencies tend to occur and hinder spectroscopy for oxide surfaces even when non-polar. Now, recent advances in fabrication techniques for ultrathin oxides\(^10,11\) is enabling us to prepare atomically-controlled oxide single crystal films\(^12\), but the unreconstructed polar surfaces remained a challenge.

Recently, however, three of the present authors\(^3\) have succeeded in growing an MgO(111) 1×1 surface by alternate adsorption of Mg and O\(_2\) on Ag(111), which has enabled them to have a unreconstructed polar surface (which turned out to be metastable, transforming to more stable ones after annealing). The electronic structure of 5 MgO layers (or 10 monolayers in another nomenclature) of MgO(111), as probed with electron energy-loss spectroscopy (EELS) and ultraviolet photoemission spectroscopy (UPS), shows that the surface is indeed un-reconstructed with a nonzero density of states at the Fermi energy (\(E_F\)) indicative of a metal.

This raises an interesting question of what should happen to the metallization when we have only few monolayers: As the film thickness decreases the macroscopic electrostatic potential due to the surface charge should decrease, so the competition between the metallic state and the insulating state accompanied by an electric field should become more subtle and interesting. The present study exactly addresses this problem.

Here we show, first experimentally, that even one layer of MgO(111) on Ag(111), as probed with EELS, is metallic. We then theoretically show with an \textit{ab-initio} calculation that the system is indeed metallic. We further predict that the nature of the surface should depend on the nature of the substrate, i.e., the surface should be
insulating for substrate with larger lattice constants. We finally show, with a spin-density functional calculation, that the surface, whose local density of states is large at the surface for thicker films, can exhibit a ferromagnetic instability.

Let us start with the experimental result. As for the sample preparation we follow Ref.\textsuperscript{13}. Namely, the MgO film was grown by alternate adsorptions of Mg and O\textsubscript{2} on the Ag substrate with temperature of 300K, where the whole experiments were performed in a ultrahigh vacuum. The formation of a clean 1×1 MgO film on the substrate is confirmed from a sharp reflection high energy electron diffraction (RHEED) pattern, while the Auger-electron spectroscopy detects no contamination.

The electronic structure is then probed \textit{in situ} with EELS. The result is displayed in Fig.1 for one layer of MgO(111) on Ag(111) as compared with MgO(100)\textsuperscript{13} of the same thickness grown on Ag(100). We can immediately see that the MgO(111) has a long and substantial tail for the energy loss $\lesssim 2.5$ eV in a marked contrast with the result for MgO(100) (while the peak around 4 eV, visible in both cases, originates from the surface plasmon of Ag substrate). The qualitative feature observed here for one layer of MgO on Ag is quite similar\textsuperscript{14} to those of five layers of MgO on Ag, reported in Ref.\textsuperscript{13}. So we conclude that one layer of MgO(111) on Ag already has, surprisingly enough, a nonzero density of states around $E_F$ suggestive of a metallic surface.

![FIG. 1. EELS result, with the primary-electron energy of 60 eV, for the one MgO(111) layer on Ag(111) as compared with that for MgO(100) on Ag(100).](image)

We have then performed a first-principles electronic structure calculation in the framework of the generalized gradient approximation (GGA) based on the density functional theory. We adopt the exchange-correlation functional introduced by Perdew et al.\textsuperscript{15} We employ ultra-soft pseudopotentials\textsuperscript{16,17} for Mg and O, and a norm-conserving soft pseudopotential for Ag, both in separable forms. The cut-off energy of the plane-wave expansion for the wave function is taken to be 25.0 Ry. The atomic configurations and the corresponding electronic ground states are obtained with the conjugate gradient scheme\textsuperscript{18}.

The optimized lattice constants in the bulk obtained in the present calculation are 4.11 (against the experimen-tal 4.09) Å for Ag and 4.22 (4.21) Å for MgO. We then introduce a slab model, where we put a (111)-directed 5 Ag layers sandwiched from top and bottom by MgO layers. The structural optimization is done as follows. We put Mg atoms on the hollow sites of the outermost Ag atoms (see Fig.2), since the total energy is found to be lower by $\sim 0.1$eV per unit cell than when we put them on the atop sites. The bulk lattice constants of Ag and MgO are slightly different (4.09 against 4.21), and we assume in the calculation that the lattice constant of the Ag substrate does not change at the interface. So we take the same unit-cell size as the bulk of Ag in the $xy$-plane, and optimize the positions of the atoms. The size of the whole slab in $z$ direction is set to be large enough (47.46 Å). Then we put oxygen atoms to have one layer of MgO(111). We repeat this for $\geq 2$ layers for multi-layer cases. While larger unit-cell sizes in $xy$ would be necessary to describe reconstructed surfaces, we take 1 × 1 unit cell here since we focus on the unreconstructed case. The reasoning is as follows. The unreconstructed surface is experimentally observed as the 1 × 1 RHEED pattern, but the state is metastable. So if we want to focus on such a state we can perform a density functional calculation in the prefixed unit cell.

![FIG. 2. Top(a) and side(b) views of the atomic configuration considered in the present study. The unit cell is indicated by white lines.](image)

Let us start with the result for three MgO layers on Ag. Figure 3 shows the band structure along with the local density of states(LDOS). The LDOS at $E_F$, plotted in Fig.3(c), is calculated by $\sum_i |\phi_i(x,y,z)|^2$, where the summation is taken over the eigenstates (labelled by $i$) having the eigenenergies $E - 0.125 < E_i < E + 0.125$ eV. The LDOS does not change significantly when the energy window (0.25 eV here) is changed to 0.5 eV. The number of sampled k points in Figs.3(b)(c) is 8 with the Monkhorst-Pack method for the integration over the Brillouin zone\textsuperscript{19}, where the bands are fitted to sinusoidal forms and the tetrahedron method is employed. The result in fact changes little when the number is increased to 18.

We can see in the energy-resolved LDOS (Fig.3(b)) that, while the LDOS at $E_F$ is small, LDOS is large around $E \approx E_F - 5$ eV, which originates from 3d levels of Ag. If we turn to the LDOS at $E_F$ in Fig.3(c), a notable
peak is seen at the outermost oxygen, which suggests that the surface is in fact metallic. This is a tail (in real space) of the bands originating from the MgO (marked in k space in Fig.3(a)). We have obtained a similar result for the case of two MgO layers (not shown). This is quite consistent with the experimental result\textsuperscript{13} that unreconstructed polar surface becomes metallic if the MgO film is \( \gtrsim 5 \) MgO layers, and also with theoretical studies\textsuperscript{4–7}.

So a small electric field may remain for the incomplete charge redistribution, but we will have to implement a theoretical method to quantify the electric field\textsuperscript{6,7}. Qualitatively, however, we can understand the incomplete charge redistribution for one MgO layer as follows. We first note in Fig.4(c) that the outermost O atoms sink deep into the Mg layer. Namely, the optimized separation, \( d \), in \( z \)-direction between the O and Mg atoms on the surface is 0.50 Å, which is much shorter than that for the case of three MgO layers (with \( d = 0.90 \) Å). This suggests that the electric field induced by the surface charge is small for one MgO layer. In other words, the energy loss due to the lattice distortion (\( \Delta_L \)) and that due to the buildup of the electric field (\( \Delta_E \)) are relatively moderate for one MgO layer, so that the energy cost due to the charge redistribution (\( \Delta_C \)) may exceed \( \Delta_L + \Delta_E \).

This observation leads us to propose here an interesting phenomenon: if we can change the value of \( d \) which dominates \( \Delta_L + \Delta_E \), we can change the relative magnitudes of \( \Delta_L + \Delta_E \) and \( \Delta_C \). This implies that we should be able to induce a metal-insulator transition for the polar surface by controlling \( d \). One of the simplest ways to change the value of \( d \) is to vary the lattice constant of the substrate. Namely, if we employ a substrate having a larger lattice constant, the separation between the hollow sites becomes larger, which in turn increases the distance between Mg atoms in xy-plane. This will make O atoms sink more deeply into the Mg layer, and a smaller \( d \) will favor an insulating surface.

To confirm that the MgO surface becomes insulating for substrates having large lattice constants, we have calculated the band structure and LDOS for the interface system where we artificially make the lattice constant larger (4.23 Å) of Ag than that in Fig.4. We can see that the larger lattice constant indeed makes the LDOS
around $E_F$ at the outermost O (Fig.5) notably smaller than in Fig.4, while the quantity becomes larger for the compressed substrate (Fig.6). This shows that the system indeed resides in the vicinity of the metal-insulator transition, so it should be feasible to control the transition.

From the behavior of the LDOS at $E_F$ we can look into an even more fascinating phenomenon, i.e., the possibility of a magnetic instability for the polar surface. As we have shown, the LDOS at $E_F$ is large for the outermost oxygen layer in thicker MgO films, where O atoms do not sink into the Mg layer. When the LDOS is large enough, we may expect a ferromagnetic instability. In fact, Goniakowski et al.\cite{6} have already shown, by means of a spin density functional calculation for a five atomic-layer slab (O/Mg/O/Mg/O with unbalanced numbers of cations and anions), that the unreconstructed polar surface of MgO has a ferromagnetic instability. However, the structure of MgO (especially the value of $d$) is not optimized in that study, so the LDOS at $E_F$ should be overestimated.

So we have performed a spin density functional calculation for one-layer and three-layer MgO(111) on Ag with the optimization for $d$ to study the magnetic instability. The result shows that the three-layer system does have a ferromagnetic ground state, although the magnetization (the difference between the numbers of opposite spins per unit cell) is small ($\sim 0.1$). Figure 7 displays the band structure and the LDOS, where an exchange splitting ($\sim 0.5$ eV) is seen for the bands lying $\sim 2$ eV below $E_F$. One MgO(111) layer is paramagnetic as expected.

One thing we have to note is that the unit cell in the present work as well as in Ref.\cite{6} is 1×1 in the $xy$-plane, so that it cannot describe other magnetic states such as antiferromagnetic ones. Thus a calculation with larger unit cells will be required to really confirm whether the ground state can become magnetic, which is an important future problem.

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