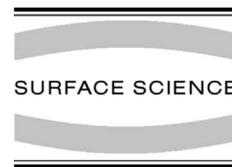




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Hartree–Fock study of adhesion and charge redistribution on the Ag/MgO(001) interface

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Abstract

Ab initio study of the Ag/MgO(001) interfaces based on a quantitative analysis of the bonding in the interfacial region is provided in the framework of Hartree–Fock approach. We are describing the way interfacial electronic and other properties evolve as a function of metal coverage. General conclusion that could be drawn from our calculations is that chemical bond formation is not important for the Ag/MgO(001) perfect interface. Physisorption of Ag atoms over surface O²⁻ ions associated with atomic polarization and charge redistribution in the metal planes are the dominant effects. The adhesion energy is enhanced by the interaction of the substrate Mg²⁺ ions with the surplus of electron density accumulated near the interatomic positions of the interfacial silver monolayer. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Despite the existence of numerous theoretical studies of the adhesion of noble and transition metals on MgO substrates, a full understanding of interface formation and of properties on an atomic scale is still lacking even at the level of idealized

models [1–16]. Partly this is because of some very sensitive balances between contributions to the energy of interfacial interaction [2,3]. Meanwhile, there is a substantial gap between the basic science of idealized metal–ceramic interfaces considered in theoretical and the formulations for these technologically important materials, which can be used by engineers [1]. Such a gap could be particularly bridged using both phenomenological *image interaction model* (IIM) [2,3] and atomistic *shell model* (SM) [4]. At any case, the best verification of our results may be provided when linking them to numerous experimental data, in particular to high

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resolution electron microscopy measurements, which give high resolution for a few metal/oxide (e.g. Ag/MgO) interfaces [17,18] at near-atomic resolution.

Explicit first principles calculations on electronic structure still belong to the most spread techniques for theoretical description of metal–ceramic interface. To perform these calculations, *cluster* models [5–8] and *slab* models (periodic in two dimensions) [9–14] have been mainly used. An ab initio Hartree–Fock formalism has been used in cluster calculations of some Me/MgO interfaces [5,6]. The density functional theory approximation (DFT), as implemented in a full-potential linearized muffin-tin orbital method (FP LMTO), has been applied in a slab model for metal adhesion on the MgO surfaces [9–11], as have full-potential linearized augmented plane waves (FP LAPW) [12], and self-consistent local orbitals [7,13,14]. In order to go beyond the DFT approach for the metal/oxide interfaces, we recently made Hartree–Fock calculations for the Ag/MgO (1 0 0) interface using a slab model [15,16].

In this paper, we give the ab initio study of the Ag/MgO(0 0 1) interfaces based on a quantitative analysis of the bonding in the interfacial region. We shall describe the way interfacial electronic and other properties evolve as a function of metal coverage. This ab initio supercell calculations of metal/oxide interfaces for metal superstructures with low surface coverages should be a basis for the development of a thermodynamic formalism, which could be applied to the given system and permits to predict conditions when metal distribution is random, or metal atoms aggregate into clusters, and to estimate metal density in such clusters.

2. Theoretical

2.1. Computational details

We have used the ab initio Hartree–Fock computer code *CRYSTAL95* for periodic systems [19], which incorporates electron correlation corrections (hereafter, HF-CC method). These corrections were implemented in last versions of

CRYSTAL code using DFT approach [20]. Such terms are necessary, since standard Hartree–Fock calculations usually underestimate binding energies and overestimates bond lengths [21]. For HF-CC calculations, we have used mainly Perdew–Wang a posteriori corrections in the framework of generalized gradient approximation [22]. The basis set for MgO, optimized elsewhere [23], consists of all-electron 8-61G and 8-51G functions (s and sp shells) for Mg and O atoms, respectively. To reduce computational efforts, we employed the small-core Hay–Wadt pseudopotentials for Ag atoms [24], thus reducing the total number of electrons per Ag atom to 19 ($4s^2 4p^6 4d^{10} 5s^1$). An initial guess for the basis set of bulk silver (311-31G for sp and d shells) was taken from AgCl calculations [25], and the outer exponents were reoptimized [15,16]. Calculations for the Ag $4d^9 5s^2$ configuration give essentially the same results.

In Table 1 we present equilibrium geometries of several interface configurations described in next subsection, adhesion energies, Mulliken charges and bond populations as well as projections of dipole and quadrupole moments for adsorbed silver atoms normal to the surface (along z -axis) (see more in Ref. [16]). To define an optimal value of adhesion energy E_{adh} according to the so-called universal binding energy relation (similar to the potential energy curve for diatomic molecule) [13], we use the potential binding energy curve $E_b(z)$ obtained from calculated total energy of the interface:

$$E_b(z) = E_{\text{adh}} \left(1 + \frac{z - z^{(0)}}{z} \right) e^{-(z - z^{(0)})/s}, \quad (1)$$

where $z^{(0)}$ is the equilibrium interfacial distance, and s a scaling constant. Note that for well-separated MgO and Ag slabs $\lim_{z \rightarrow \infty} E_b(z) = 0$. Both change of electronic charge on Ag atoms $e(00)_{\text{Ag}}$ and interatomic bond populations are obtained using the Mulliken population analysis. The atomic dipole moments $d(10)_{\text{Ag}}$ are calculated as matrix elements of the atomic orbitals with the operator z (its direction pointing outwards from the surface) [19]. They characterize a shift of

Table 1

Optimized parameters for the Ag/MgO(001) interface the relevant adsorption positions are shown in Fig. 1

Ag atom over	Coverage	Distance $z^{(0)}$ (Å)	Adhesion E_{adh}^a (eV)	Charge ^b $e(00)_{\text{Ag}}$ (e)	Dipole $d(10)_{\text{Ag}}$ (e au)	Quadrupole $q(20)_{\text{Ag}}$ (e au ²)
O atom (A)	1/4 Layer	2.58	0.23	0.063	0.251	-0.433
	Monolayer	2.56	0.26	0.037	0.198	-2.232
	Three layers	2.43	0.46	0.053 ^c	0.418 ^c	-1.971 ^c
	SM ^d	2.60	0.11	–	–	–
Interatomic gap (B)	1/4 Layer	2.69	0.20	0.052	-0.007	0.140
	Monolayer	2.94	0.15	0.035	-0.034	-1.597
	Three layers	2.86	0.17	0.050 ^c	0.182 ^c	-0.963 ^c
Mg atom (C)	1/4 Layer	2.89	0.22	0.038	-0.170	0.414
	Monolayer	3.23	0.06	0.027	-0.071	-1.288
	Three layers	3.23	0.07	0.042 ^c	0.116 ^c	-0.686 ^c
	SM ^d	3.20	0.02	–	–	–

^a Value of adhesion energy is given in the units of eV/interface Ag atom.^b Positive sign means excess of the electron density as compared to a neutral atom.^c For the interfacial silver layer.^d The shell model calculations [4] for 10 Ag layers atop 31 MgO planes.

electron density along the z -axis. As expected from the IIM, the dipoles have opposite signs above O and above Mg, corresponding to electrons being repelled by the anion or attracted by the cation [2,3]. The quadrupole moments $q(20)_{\text{Ag}}$ are matrix elements with the operator $z^2 - (x^2 + y^2)/2$, and also characterize atomic deformation. Their negative value means that atom is contracted along z direction being expanded in the interface xy plane and vice versa.

2.2. The model of the Ag/MgO(001) interface

The CRYSTAL95 computer code allows the calculation finite-thickness slabs as two-dimensional periodic systems. We have simulated the Ag/MgO(001) interface (Fig. 1) with either one Ag monolayer or three Ag layers atop three layers of the oxide substrate. This is a model of the so-called one-side adsorption. For the monolayer, we have considered both full (1:1) coverage and partial (1:4) Ag coverage. In the latter case we have used a supercell model of the interface with 2×2 extension of the corresponding slab unit cell considered in both models for (1:1) coverage. We have obtained results in this way for all three the most likely sites for Ag adsorption: above surface Mg^{2+}

and O^{2-} ions, as well as in the interatomic gaps between them shown in Fig. 1 – in the case of the

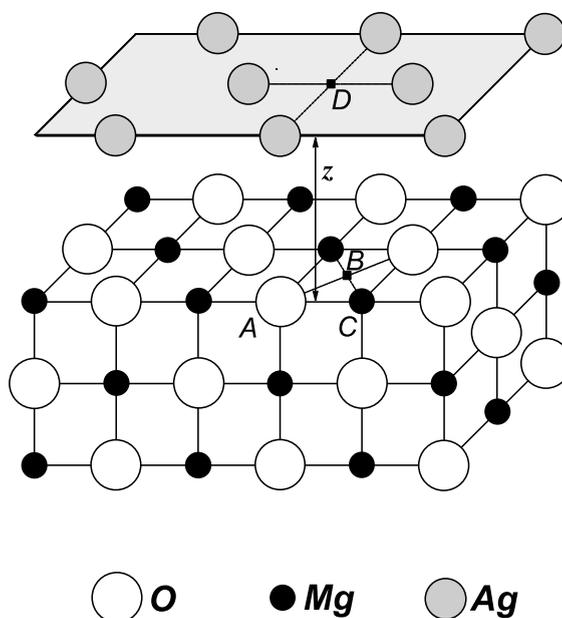


Fig. 1. Fragment of the Ag/MgO(001) interface with monolayer coverage of substrate, where Ag atoms are placed at the distance z above surface O^{2-} ions (A configuration). Two other possible adsorption positions are above the gap (B) and Mg^{2+} ions (C) of the same substrate. Enhanced electron densities inside silver monolayer are centered in its hollow sites D.

monolayer of silver atoms positioned over surface oxygen ions on the MgO(001) substrate.

In line with all previous calculations, we ignore the small (3%) mismatch in the lattice constants of fcc Ag (4.08 Å [26]) and MgO (4.205 Å [23]), although we recognize that this leads to misfit dislocations when we compare with experiment. In our slab model, we fix the lattice constant along the surface xy plane at earlier optimized value of 4.21 Å, and also neglect surface relaxation inside substrate slab, which is known to be small [23]. On the other hand, the distances between different silver planes within the metal slab are free to change: for three-layer Ag(001) slab they have been optimized to be 1.98 Å [16].

3. Silver adhesion on the MgO(001) surface

3.1. Full (1:1) substrate coverage

We distinguish the cases of full and partial silver coverages due to some differences in their adsorption nature described below. Both three- and one-layer Ag models give marked energetical preference for Ag adsorption over surface O^{2-} ions (Table 1). This agrees with recent experiments [1,17,18] and with previous DFT-type calculations [9–14] but contradicts the IIM results [2,3]. The difference in predicted optimal Ag adsorption sites observed for microscopic and the image model stems mainly from the different treatments of long-range dispersion (van der Waals) interactions. SM calculations [4] also predict preferential adsorption over oxygen ions, but with adhesion energy of only 0.11 eV – smaller than our HF predictions. All microscopic calculations are reasonably close in calculations to equilibrium interface distances for the favored Ag atoms position over O^{2-} ions. These data are falling into narrow range between 2.5 and 2.7 Å; the *image model* also agrees, giving 2.53 Å. Our HF-CC value of 2.43 Å for three metal layers coincides with the recent experimental data [27]. Monolayer adhesion energy of 0.26 eV estimated using Eq. (1) is close to the value of 0.30 eV obtained for the same structure in the FP LAPW calculations [9]. On the other hand, an increase of a number of Ag planes to three in-

creases the HF-CC adhesion energy over O^{2-} ions to 0.46 eV, but does not affect much the adhesion for Ag over a gap or over a Mg^{2+} ion. Nevertheless, our value of 0.46 eV is smaller than the adhesion energy of 0.88 eV found in FP LMTO calculations of the same interfacial structure (three Ag layers) [12]. The relevant experimental estimate is 0.26 eV [17,18], which is probably underestimated due to presence of misfit dislocations caused by the mentioned 3% difference in lattice parameters of Ag and MgO.

Chemical bonding across the interface between metal and oxide substrate is negligible: the adhesion is physical in its origin. The calculated Mulliken charges on Ag atoms indicate negligible charge transfer from MgO to Ag (Table 1). The bond populations across the interface (between silver atoms and substrate ions) are also practically zero. We remark that the existence of a good fit [13,14] of the interfacial energy versus interface distance to the universal binding energy relation written as Eq. (1) does not necessarily imply chemisorption between metal and substrate. On the other hand, there is redistribution of charge *within* the metal. We observe considerable bond populations between nearest Ag atoms (0.1e per atom) within the metal planes parallel to the interface. This population is not sensitive to the adsorption site. The concentration of the electron density in the Ag at the *bridge position* between nearest metal atoms has been confirmed in inelastic He scattering studies [28].

The bond population analysis gives a reason for Ag adsorption over O^{2-} ions to be favored. This preference is related to electrostatic attraction involving the enhanced Ag electron density concentrated around the hollow position in the interfacial Ag layer (0.07e for the (1:1) Ag coverage). The extra electron charge concentrated in the vicinity of hollow D position inside silver monolayer (Fig. 1) has an attractive interaction with the substrate Mg^{2+} ion below it. On the other hand, for the Ag adsorption over the Mg^{2+} ions, there is instead repulsion between this interatomic electron density and the substrate O^{2-} ion below it. The twice larger adhesion energy for three Ag layers, as compared to an Ag monolayer, can be attributed to a more complicated electron density distribution in the

interfacial Ag layer for both the A and C interfacial configurations. For the A adsorption site, a charge of $0.04e$ is localized on the corresponding hollow position over Mg^{2+} , whereas $0.12e$ is localized on each of the four side bridge positions in the plane above the D point. For the C adsorption site, the corresponding electron densities over O^{2-} ions are smaller (0.03 and $0.1e$, respectively) and more remote from the surface oxygen. Difference electron density maps discussed by us earlier for the cases of one [15] and three [16] Ag layers above the $\text{MgO}(001)$ substrate clearly confirm this reasoning.

For the monolayer coverage, $d(20)_{\text{Ag}}$ projection of the dipole moment is markedly larger for Ag over the oxygen site (Table 1), thus confirming aforementioned conclusion about their preference when analyzing other interface characteristics. The same belongs to $q(20)_{\text{Ag}}$ projection of quadrupole moments affected significantly by Ag 4d–5s orbital mixing. As mentioned above, its negative value for all the configurations of the interface (1:1) substrate coverage means contraction of the Ag electronic shell perpendicularly to surface and expansion along the substrate plane. For all adsorption positions, magnitudes for Ag atoms are at least a factor 4 larger than the corresponding magnitudes for surface Mg^{2+} and O^{2-} ions. Thus, Ag atoms adsorbed on the $\text{MgO}(001)$ surface are markedly deformed due to their electrostatic polarization by the substrate.

3.2. Partial (1:4) substrate coverage

In the case of low substrate coverage by metal atoms there is practically no interatomic electron density concentration between Ag atoms, therefore its interaction or repulsion with the nearest substrate atom plays no role here. For separated Ag adsorption over O^{2-} or Mg^{2+} ions, there is a single nearest substrate neighbor (either O^{2-} or Mg^{2+} ion) and four next-nearest substrate ions of the opposite type (either Mg^{2+} or O^{2-} sites). However, for the gap adsorption site, every Ag atom has four equally remote neighbors (two Mg^{2+} and two O^{2-} ions). Unlike models of full substrate coverage considered above, adsorption energies of these relatively isolated Ag atoms are close for all three

adsorption sites (Table 1). This difference may be explained by a partial compensation of electrostatic attraction and repulsion of polarized slightly charged Ag adatoms with surrounding surface ions in the case of (1:4) coverage.

The charge transfer from the substrate to each isolated Ag atom is small ($0.06e$), yet it is still twice as large as for the Ag monolayer or for three Ag layers atop MgO . The value of the dipole moment for the Ag atom is also twice as large for (1:4) than it is for (1:1) coverage. The isolated Ag atom charge density is deformed along the z -axis as expected in the *image model*. On the other hand, the quadrupole moment is significantly smaller for a single Ag than that for monolayer which shows that its non-spherical deformation due to the field gradient of the MgO ions is small (Table 1). Moreover, $q(20)_{\text{Ag}}$ is negative for Ag atoms adsorbed over O^{2-} ions and positive in other cases, therefore deformations of Ag electronic shells are noticeably different.

This may be clearly illustrated in Fig. 2, which shows the difference electron density maps for Ag positioned over oxygen and magnesium ions. Both maps are drawn with respect to a superposition of interacting and isolated silver and magnesia slabs. Their comparison indicates that Ag atoms are more distorted above O substrate ions where the charge transfer from the substrate is also greater. The same belongs to a noticeable polarization of both nearest and next-nearest interacting O^{2-} ions, while electronic shells of Mg^{2+} ions are not affected too much from deposited silver atoms. Meanwhile, participation of the subsurface substrate ions in interfacial bonding is quite negligible. Thus, difference electron charge distributions shown in Fig. 2 give the most convincing argument in favor of decisive role of the interaction between Ag atoms and surface O^{2-} ions in the mechanism of silver adhesion on the magnesia interfaces. Probably, a smaller value of the adhesion energy in the case of *shell model* (Table 1) may result from the neglect of the electron density redistribution in the interface. We suspect that an important part of the differences in detail between full electronic structure calculations and these simpler approaches stems from the relatively subtle shifts in charge density in the Ag slab.

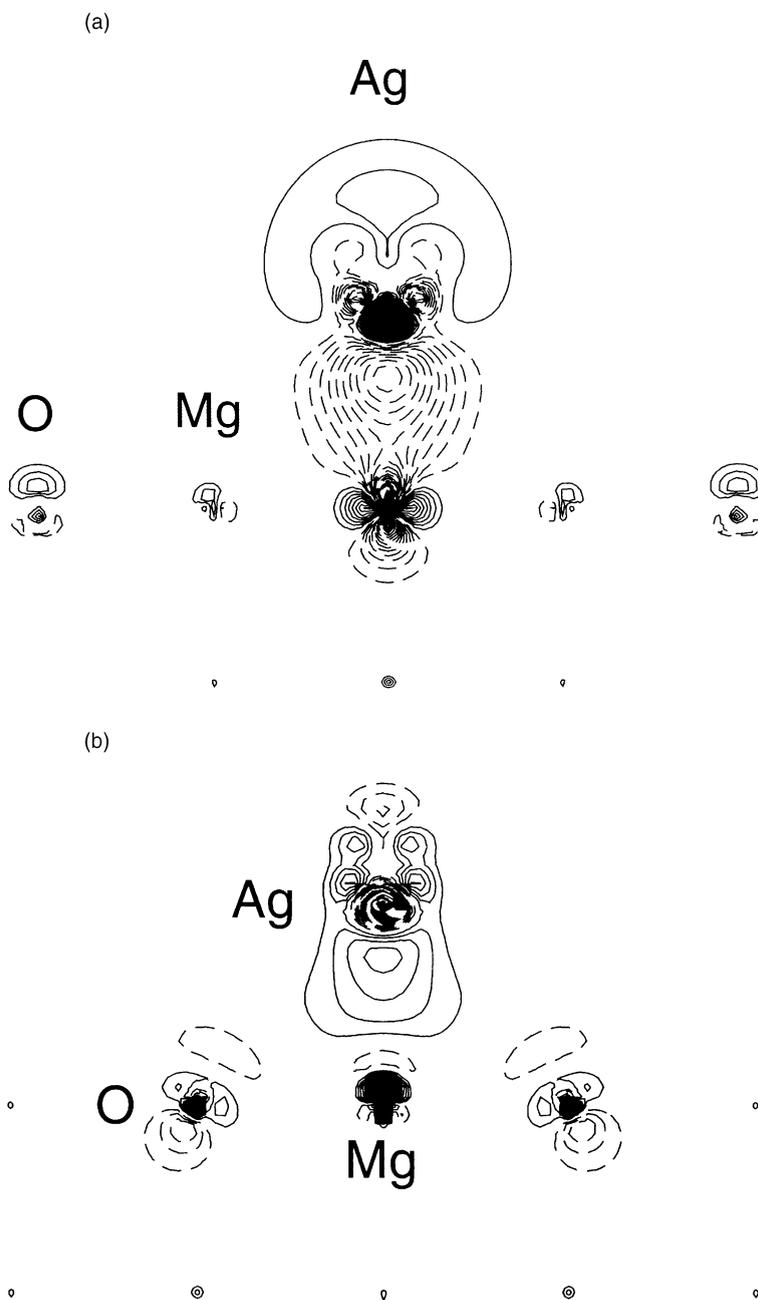


Fig. 2. Two different charge distribution maps for 1/4 silver coverage (the total electron density for the Ag/MgO(001) interface minus superposition of the same densities for isolated Ag and MgO slabs) along the (100) cross-section perpendicular to interface: (a) for Ag atoms over O^{2-} ions (Fig. 1) and (b) for Ag atoms over Mg^{2+} ions. Density isolines are drawn from $-1e$ to $1e \text{ au}^{-3}$ with an increment of $0.02e \text{ au}^{-3}$. The full, dashed and chained curves show positive, negative and zero difference densities, respectively. Note that Ag atoms are strongly polarized: above oxygen ions (a) the electron density is shifted in the direction outwards from the surface, whereas above magnesium ions (b) it is shifted towards the surface.

4. Summary

One general conclusion to be drawn from the ab initio Hartree–Fock calculations with correlation corrections is that chemical bond formation is not important for the Ag/MgO(001) perfect interface. Physical adhesion associated with polarization and charge redistribution is the dominant effect. The adhesion energy is enhanced by the interaction of the substrate ions with the extra electron density accumulated near the interatomic positions of the interfacial Ag layer. This favors silver atoms position above the surface O^{2-} ions on the (001) substrate. Our approach in a combination with thermodynamics analysis could be applied to many metal/oxide systems, which would permit the prediction of the conditions for a random metal atom distribution, or for metal atoms to aggregate into clusters, as well as to estimate the metal density in such clusters.

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