



## Ab initio simulation of copper and silver adsorption on the MgO(111) surface

V.G. Zavodinsky <sup>a,\*</sup>, M.A. Kuz'menko <sup>b</sup>, A. Kiejna <sup>c</sup>

<sup>a</sup> *Institute of Materials Science of the Russian Academy of Sciences, 153 Tikhookeanskaya, 680042 Khabarovsk, Russia*

<sup>b</sup> *Khabarovsk State Technical University, 156 Tikhookeanskaya, 680042 Khabarovsk, Russia*

<sup>c</sup> *Institute of Experimental Physics, University of Wroclaw, Plac M. Borna 9, 50-204 Wroclaw, Poland*

Received 4 February 2005; accepted for publication 25 May 2005

Available online 23 June 2005

### Abstract

Density functional theory calculations using ab initio pseudopotentials and a plane wave basis are applied to study copper and silver overlayers on the unreconstructed MgO(111) surface. Each of the two adsorbates can stabilize both O- and Mg-terminations of MgO(111). We found zero charge transfer for noble metals adsorption on the Mg-terminated surface. A non-zero charge transfer, which occurs at the oxygen terminated surface, is not sufficient to induce an energy gap at the Fermi level and to convert the surface into insulating one.

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**Keywords:** Density functional theory; Copper; Silver; Magnesium oxide; Adsorption

### 1. Introduction

The metal–magnesia (MgO) interface is a principal model system to study the oxide-supported metal deposits in various experiments. The metal adsorption on the non-polar MgO(100) surface has been intensively investigated theoretically during the last decade (see for example [1–8] and the references therein) in the effort to determine metal

binding properties, which control the metal growth modes and adhesive properties. Another low-index surface, the MgO(111), is far less investigated. The MgO(111) surface is a polar, unstable surface, which shows the quasi-metallic features of electronic structure. One of the ways of achieving its stability is a  $2 \times 2$  reconstruction, which often occurs at this surface leading to the appearance of a surface forbidden gap due to the formation of atomic scale facets [9]. Another way is a microscopic faceting into neutral [100] planes upon annealing [9–11]. The MgO(111) surface can be also stabilized due to adsorption of H<sub>2</sub>O [12],

\* Corresponding author. Tel.: +7 4212719956; fax: +7 4212719598.

E-mail address: [vzavod@mail.ru](mailto:vzavod@mail.ru) (V.G. Zavodinsky).

ozone [13], oxygen [14], and presumably some other gases.

Some transition and noble metals were studied on the MgO(111) surface in Refs. [15,16] using the full-potential FP-LAPW and FP-LMTO methods, and the stable nature of this interface has been discussed there. Recently the alkali metals adsorption on the MgO(111) surface was studied theoretically by two of us [17], and it was suggested that single monolayers of alkali metals stabilize the oxygen-terminated MgO(111) surface. It has been also shown that deposition of Li monolayer leads to the transformation of the electronic structure of the MgO(111) surface from the metallic-like to an insulator-like. Copper has one s-electron above the 3d filled shell and its chemical behavior often looks like that of alkali metals. A similar electronic structure of silver (with the 5s valence-electron) makes it an interesting object to study a chemical trend of the stabilization effect for different noble metals. Such trends has been studied recently from first principles for monolayers of transition (and noble) metals on MgO(111) [16]. However, in that investigation only monolayers and bilayers were considered and the details of the noble metal interaction with the MgO(111) surface were not discussed. Another theoretical study [18] which was devoted to comparison of electronic properties of Cu/MgO(111) and Cu/MgO(100) interfaces considered even thicker Cu films, consisting of several (3–6) copper layers. Therefore, those results cannot be projected directly on the problem of monolayer and submonolayer coverages. The goal of our work is to study the energetics and electronic structure of the Cu and Ag monolayers and submonolayers on the polar unreconstructed MgO(111) surface.

## 2. Method and details of calculation

The ab initio calculations were performed using the FHI96MD program [19], employing the Perdew–Wang (PW91) form of the generalized gradient approximation for the exchange–correlation energy functional. The fully separable Troullier–Martins pseudopotentials were constructed using the FHI98PP code [20]. The parameters of

pseudopotentials for Mg and O were taken from our previous work [17] where they were verified to calculate the equilibrium lattice constant  $a_0$ , and bulk modulus  $B_0$ , in a good agreement with measured values. Pseudopotentials for Cu and Ag were optimized in the same way. The plane-wave basis with energy cut-off of 44 Ry was applied. Similarly to Ref. [17] the MgO(111) surface was represented by the Mg- and O-terminated five-layer Mg/O/Mg/O/Mg and O/Mg/O/Mg/O slabs with the  $2 \times 1$  surface unit cell. The slabs were separated from each other by the 20 Å thick vacuum space and repeated periodically.

The copper and silver atoms were adsorbed symmetrically on both sides of a slab. Both full-monolayer (1 ML) and half-monolayer (0.5 ML) coverages were studied. Similarly as in previous studies (compare [17], and references therein), relaxations of the atoms of overlayers and atoms of the first MgO surface layer were taken into account, but all other Mg and O atoms were kept fixed in their ideal bulk positions and the copper and silver atoms were positioned in three-fold coordinated sites. For the  $k$ -space integrations for slabs we used mainly a single (0.25 0.25 0.00) point. Note however, that in special cases (test calculations and calculations of the density of electronic states) larger  $k$ -point sets were implemented.

The binding energy for adsorbed atoms was determined from the following expression:

$$E_b = \frac{1}{N} \cdot (E_{M/MgO} - E_{MgO} - N \cdot E_M),$$

where  $E_{M/MgO}$  is the energy of the slab with adsorbed metal,  $E_{MgO}$  represents the energy of the clean MgO slab, and  $E_M$  is the energy of the single metal atom calculated in a large cubic cell.  $N$  is the number of metal atoms in a surface unit cell, on both sides of the slab.

## 3. Results and discussion

The calculated binding parameters for copper and silver atoms adsorbed on both Mg- and O-terminated surfaces are collected in Table 1. They are compared with the data for lithium which was

Table 1

The binding energy  $E_b$ , and the distance  $d$  from an adatom to a surface atom, for Cu and Ag overlayers deposited on the MgO(111) surface

	Mg-terminated			O-terminated		
	Cu	Ag	Li	Cu	Ag	Li
<i>0.5 ML coverage</i>						
$E_b$ (eV/atom)	-3.34 (-3.28)	-3.02 (-2.97)	-1.72	-7.13 (-7.39)	-4.87 (-5.13)	-6.78
$d$ (Å)	2.61 (2.63)	2.62 (2.64)	2.86	2.05 (2.01)	2.35 (2.32)	1.90
<i>1.0 ML coverage</i>						
$E_b$ (Ev/atom)	-3.93 (-3.94)	-3.48 (-3.94)	-2.11	-5.01 (-5.27)	-4.24 (-4.49)	-6.47
$d$ (Å)	2.51 (2.50)	2.71 (2.70)	2.74	2.20 (2.18)	2.40 (2.36)	1.85

Results for unrelaxed MgO surface (in brackets), and for Li adsorption [17] are also given for comparison.

found [17] to be the strongest bonded alkali metal at these surfaces.

For a 0.5 ML coverage, the binding of copper and silver atoms on the O-terminated surface is stronger than on the Mg-terminated one, and the Cu atoms are stronger bonded than Ag atoms. The distance  $d$  between the adsorbed and surface atom correlates with the binding energy: the larger the  $d$ , the smaller the  $E_b$ . This behavior is similar to that described in Ref. [17] for alkali metals on the MgO(111). On the Mg-terminated surface, both copper and silver are stronger bound than lithium atoms. However, on the O-terminated surface, only the binding energy of copper exceeds that of lithium. Silver atoms are bonded approximately 1.5 eV weaker than Li atoms.

For the 1.0 ML coverage, the Cu and Ag bonding is also stronger than that of Li atoms on the Mg-terminated MgO(111) surface. However, lithium is most strongly bound at the O-termination. Interestingly, the Cu and Ag bonding on the Mg-terminated surface increases with the increased coverage. This is in contrast to the O-termination, where the bonding decreases for the 1.0 ML coverage. This effect correlates with changes of the adsorbent-surface distance  $d$ , with the increasing coverage: it increases for the Mg-termination and decreases for the O-termination. In general, one can state that copper and silver adsorption on MgO(111) is characterized by a rather large bind-

ing energy of 3.5–5.0 eV per atom (in absolute value), for both surface terminations.

It is necessary to note once again, that all above calculations used a single  $k$ -point (0.25 0.25 0.0). The reliability of this single  $k$ -point representation was checked by us previously [17] by carrying out test calculations for the Li atom adsorption with 9  $k$ -points. The binding energy difference of about 0.1 eV was found. Now the same test calculations for Cu and Ag monolayers have given differences in binding energies of 0.1–0.2 eV, not larger than 5%.

Unfortunately, to the best of our knowledge, there are no experimental data on the Cu/MgO(111) and Ag/Mg(111) monolayer systems, which can be compared with our calculations. Therefore, our results are compared with those of all-electron calculations [16]. However, the latter work does not report on the binding energies but on the adhesion energies. They were determined as a difference (per metal atom) between the total Me/MgO energy and energies of a separated MgO slab and metal films. Therefore, we also have calculated adhesion energies for Cu and Ag monolayers (using a  $3 \times 3 \times 1$   $k$ -points mesh). One can see that the comparison (Table 2) with the results of Ref. [16] is rather good. The energy differences are within 0.3 eV or 11%. As one would expect, binding energies are larger (at an absolute value) than adhesion energies,

Table 2  
The adhesion energy (eV per atom) for Cu and Ag monolayers deposited on the MgO(111) surface

	Mg-terminated		O-terminated	
	Cu	Ag	Cu	Ag
This work	-1.63	-1.39	-3.13	-2.31
Ref. [16]	-1.7	-1.3	-2.8	-2.6

because the former ones contain deposits from atomic interactions within metallic film.

Our previous study of Li adsorption on the O-terminated MgO(111) surface has revealed an appearance of the energy gap around the Fermi level [17], which can be attributed to the charge transfer between adsorbed metal atoms and the MgO surface. This is in contrast to the clean MgO(111), which electronic energy spectrum does not exhibit any gap around the Fermi level. An analysis of the electronic structure for the Cu and Ag adsorbate system at 1 ML coverage on the O-terminated surface, shows that in this case there is a non-zero distance between occupied and non-occupied states at the (0.25 0.25 0.00) point. The calculated values of this distance  $\Delta E$  are 0.89 eV (Cu) and 0.84 eV (Ag) compared with 1.9 eV for Li [17]. However, in the case of Li adsorption, increasing the number of  $k$ -points (up to 16;  $4 \times 4 \times 1$  mesh) shows that the non-zero distances between occupied and non-occupied states exist not only at one  $k$ -point. Therefore, the total plot of electronic states contains a forbidden gap of 1.8 eV [17]. In the Cu/MgO(111) and Ag/MgO(111) systems the "gap" exists only at one  $k$ -point and disappears in the 16  $k$ -points scheme (see Fig. 1). Thus, the adsorption of either Cu or Ag atoms does not lead to a conversion of the metallic-like character of MgO(111) into a dielectric-like one, as the Li adsorption does. The similar features of the electronic structure were discussed for the Pd adsorption [15,16]. It seems that the reason of such properties of the Cu, Ag and Pd films is connected with an influence of d-electrons. The participation of d-electrons of Cu, Ag and Pd atoms in the metallic-like bonding of these atoms leads to the non-zero density of states at the Fermi level.

In order to compare the Cu and Ag adsorption with that of Li in details we calculated the charge

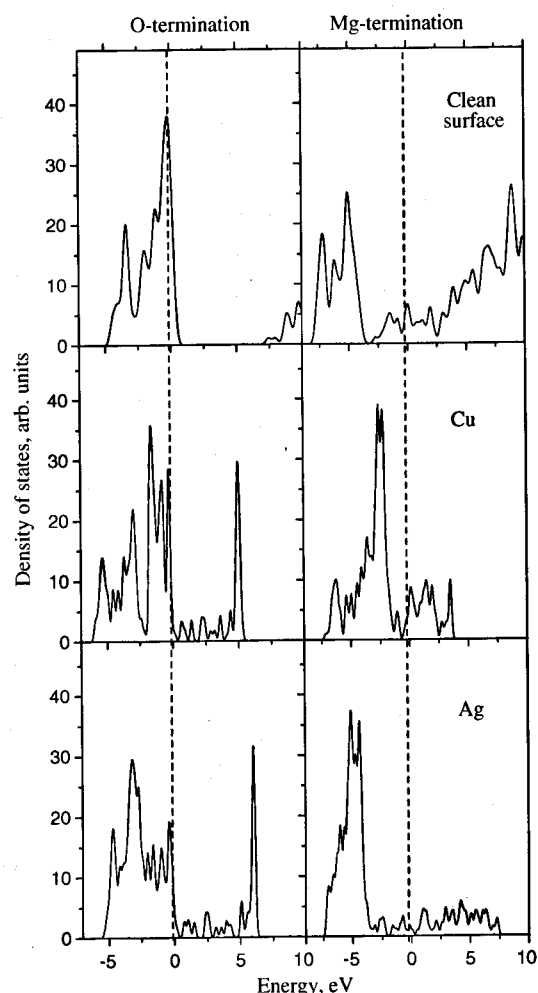


Fig. 1. Densities of states for the clean MgO(111) surface and for the 1 ML of Cu and Ag adsorption. Dashed vertical lines mark the Fermi level.

distributions for the full-monolayer of copper and silver at both terminations of the MgO(111). Electron density profiles  $n(z)$  were obtained by integration of the electron charge density distributions over the  $x$  and  $y$  space coordinates (parallel to the surface) [17]. The sum of the Gaussians, centered on the atoms, gives an average of the  $n(z)$  profile, and the areas under the Gaussians (expressed as the ratios of the total number of electrons in the system) helped to quantify the charge redistribution between the atoms of the slab (with respect to the clean surface). Fig. 2

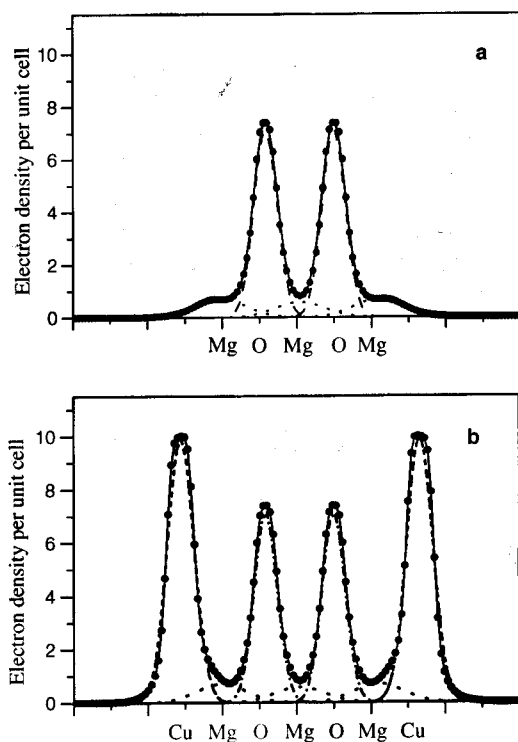


Fig. 2. The electron density profiles across the clean MgO(111) slab (a) and a slab consisting of 1.0 ML of Cu on the MgO(111) surface (b). Dashed and dotted curves represent the Gaussians used to model the densities of Mg, O and Cu atoms. A solid curve is the sum of Gaussians. Dark circles represent the electron density profiles resulting from the DFT calculations.

displays this procedure, and its quality, both for a clean surface, and for the Cu adsorbent on the Mg-terminated surface.

The analysis of electron densities shows that the Cu and Ag adsorption on the Mg-terminated surface is characterized by zero charge transfers from adsorbed atoms to MgO. The calculated magnitude of the charge localized on the particular atoms at the O-terminated surface is presented in Table 3.

One may suspect a correlation between the width of the energy distance between occupied and non-occupied states  $\Delta E$  the amount of charge transferred from the adsorbed metal  $\Delta Q$ , and the binding energy  $E_b$ . Namely, values of  $\Delta E$  and absolute values of  $E_b$  increase approximately linearly with increasing of  $\Delta Q$ .

Table 3

The calculated charge  $\Delta Q$  localized on the atoms (in units of electron per atom) in the bulk MgO, at the O-terminated MgO(111) surface, and in the MgO(111) slab Me/O<sub>s</sub>/Mg/O<sub>c</sub>/Me/O<sub>s</sub>/Me covered with a full-monolayer of metal Me (Cu, Ag)

System	Me	O <sub>s</sub>	O <sub>c</sub>	Mg
MgO-bulk			-0.90	+0.90
MgO(111)		-0.45	-0.90	+0.90
Cu/MgO(111)	+0.36	-0.81	-0.90	+0.90
Ag/MgO(111)	+0.32	-0.77	-0.90	+0.90
Li/MgO(111)	+0.45	-0.90	-0.90	+0.90

Results for Li [17] are given for comparison. O<sub>s</sub> is the surface oxygen atom; O<sub>c</sub> is the central oxygen atom of the slab.

#### 4. Summary

A first-principles study of the Cu and Ag adsorption on the MgO(111) surface is presented. Contrary to alkali-atom adsorbents, which principally may stabilize the O-terminated MgO(111) surface only, the copper and silver adsorbents can stabilize both O- and Mg-terminations of the surface. On the O-terminated surface Cu and Ag are stronger bound for the 0.5 ML coverage. On the Mg-terminated surface, their bonding is stronger for the 1.0 ML case.

We have found that the Cu and Ag adsorption on the Mg-terminated surface is followed by a zero electron transfer from metal atoms, whereas on the O-terminated surface is equal to 0.36 e/atom for Cu and 0.32 e/atom for Ag. However, this charge transfer is not large enough to form the energy gap at the Fermi level. Thus the electronic structure of the Cu/MgO(111) and Ag/MgO(111) systems preserves its metallic-like character, similar to the clean MgO(111) surface case.

An interesting, but much more difficult task is to compare directly the energetics of the MgO(111) surface, stabilized by the metallic atoms adsorption, with the clean surface, stabilized by the  $2 \times 2$  reconstruction. However, this requires much larger, and more complicated slabs than applied here, and therefore is deferred to a future work.

#### Acknowledgement

The work of A.K. was supported by the Grant 2016/IFD/2004 from the University of Wroclaw.

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