



# The adhesion nature of the Ag/MgO(100) interface: an ab initio study

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Received 25 August 1997; in final form 27 November 1997

## Abstract

The atomic and electronic structure of the Ag/MgO(100) interface are calculated by means of the ab initio Hartree–Fock approach combined with a supercell model. The electronic density distribution and the interface binding energy/distance are analyzed for different Ag adsorption positions, slabs of different thicknesses and varying Ag surface coverage. It is demonstrated that the adhesion energy arises mainly due to the electrostatic interaction of substrate atoms with a complicated charge redistribution in the metal layer(s), characterized by large quadrupole moments as well as electron density redistribution towards bridge and hollow positions between the nearest and next-nearest Ag atoms. © 1998 Elsevier Science B.V.

## 1. Introduction

Metal/oxide interfaces are known to be of considerable technological importance [1–4]. Microscopic calculations of their properties require methods able to calculate correctly delicate charge density redistribution in the interfacial region assuming no a priori type of metal/oxide bonding. In recent years some interface structures were studied experimentally by means of high resolution transmission electron microscopy, giving almost atomic resolution. In the particular case of the Ag/MgO(100) interface it was found that the Ag atoms sit directly above either O or Mg atoms rather than above the gap position between them [5,6].

Recently, three self-consistent formalisms based on the local density approximation (LDA) as incorporated into the full-potential linearized muffin-tin orbital method (FP LMTO) [7], full-potential linearized augmented-plane wave (FLAPW) [8], as well as self-consistent local-orbital (LO) method [9–11] were applied to the Ag/MgO(100) interface. It is important to go beyond these approximations using an exact non-local treatment of the exchange interaction between atoms, which could be crucial for the clarification of the nature of the metal/oxide adhesion. This became available recently after the development of an ab initio Hartree–Fock (HF) computer code Crystal, suited to the study of periodic (2D, 3D) systems [12,13]. This approach was successfully ap-

plied to numerous oxide crystals, including the MgO surface [14,15], as well as to several bulk metals including Al [16], Be [17] and Li [18]. Recently, this approach has been extended by incorporating electron-correlation corrections [19] (hereafter HF-CC method). This formalism is well suited for the quantitative analysis of the electron density redistribution in the interfacial region which is necessary for understanding the adhesion nature. In this Letter, we present results of the HF-CC study of the Ag/MgO(100) interface and compare them with previous calculations based on the LDA approximation focusing on the quantitative analysis of the electronic density distribution in the interfacial region.

The main focus of this Letter is to understand what the nature of bonding in the Ag/MgO(100) interface is and what kind of interaction could govern the interfacial structure and cause a stabilization of Ag atoms atop either O or Mg ions. No doubt, there are two contributions to the interface adsorption energy: the attractive image potential and repulsive Pauli exchange interaction. However, magnitudes of these interactions depend essentially only on the interfacial distance and are insensitive to a shift of Ag slab along the interface. To explain preferential localization of Ag above  $O^{2-}$  or  $Mg^{2+}$  on the interface, one needs to incorporate either covalent bonding of Ag atoms with underlying substrate ions, as it was proposed in Refs. [9–11], or an ionic bonding. An ionic bonding can be caused either by a charge transfer between the interface Ag atoms and substrate ions, or a nonhomogeneous charge distribution inside the Ag slab, which mimics a charge distribution of an ionic crystal. We address this spectrum of possibilities in the discussion of the results of our calculations and show that there is neither covalent bonding in the studied interface, nor charge transfer between Ag and MgO, but a small charge redistribution of the electron density from Ag atoms towards hollow and bridge positions in the Ag slab.

## 2. Model and method

The calculations were performed by means of the Crystal computer code [12] with HF-CC corrections

[19]. It gives the lattice properties – equilibrium lattice parameters  $a_0$ , bulk modulus  $B$ , along with the band structure, total and projected densities of states (DOS) and the total/difference electronic density maps. In order to reduce the computational effort, pseudopotentials were used for Ag atoms following the small-core version of Hay and Wadt [20]. This allows the reduction of the number of electrons to 19 on the Ag atom ( $4s^2 4p^6 4d^{10} 5s^1$ ). The initial guess for the Ag basis set was taken from earlier HF-CC AgCl calculations [21]. Then the outer Gaussian exponent was reoptimized in order to minimize the total HF energy per unit cell of Ag bulk at the experimental value of the lattice constant  $a_0 = 4.08$  Å. This basis set was used for test calculations of basic properties of Ag bulk and Ag(100) slabs and for further simulation of adsorption of Ag on MgO(100) substrate. The basis set of atomic orbitals (AOs) was taken for MgO from Refs. [14,15]. Mg and O are treated as all-electron atoms (8-61G and 8-51G basis sets, respectively). A posteriori electron correlation corrections to the total energies were calculated using the Perdew–Wang functional [22]. In order to extend the basis set for the Ag atoms we centered additional 1(sp)–1(d)G orbitals at the hollow positions D, between Ag atoms (see the insert in Fig. 1) where we observed electronic density concentration in our preliminary calculations [23]. Their exponents were optimized in the bulk Ag calculations and then reoptimized for Ag(100) slabs.

To avoid the effects of the boundary conditions, well-known in a quantum cluster model, the 2D *supercell model* was used in terms of which several (from one to three) Ag layers cover one to three MgO layers. Along with these calculations for 100% (1:1) surface coverage by Ag atoms, we studied also the case when only 25% of surface sites are covered by Ag atoms (1:4 coverage). The distance between outer layers in MgO three-layer slab was optimized and found to be 4.21 Å, close to the experimental bulk constant of 4.205 Å. We neglect surface relaxation of the MgO substrate which is known to be small [14] and also ignore the small ( $\approx 3\%$ ) mismatch of the lattice constants of Ag and MgO. At the same time, we simulated relaxation in a three-layer Ag(100) slab. The equilibrium interlayer distance was found to be 1.983 Å instead 2.04 Å in bulk Ag. The interfacial structure has been studied for the

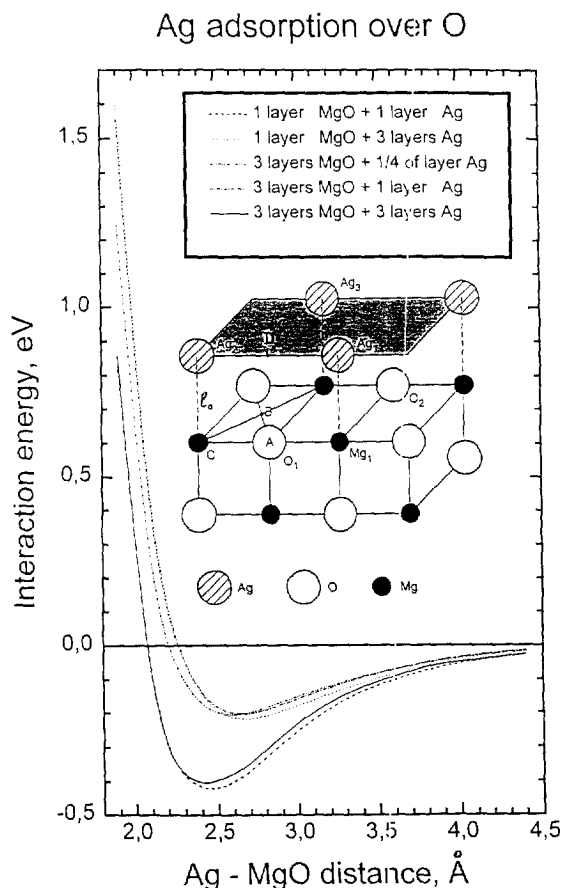


Fig. 1. The interfacial energy as a function of the distance between the Ag layer and MgO substrate; see the legend for explanations. The insert shows a schematic view of the interface with the alternative adsorption positions marked as A, B and C. Additional orbitals are centered on the *hollow* sites D between Ag atoms. The bridge position in the Ag slab corresponds to the middle point connecting two nearest Ag atoms (for instance,  $Ag_1-Ag_3$  or  $Ag_2-Ag_3$ ).

three possible adsorption sites shown in Fig. 1: over a surface O atom (A), over a gap (B) and over Mg (C). The equilibrium distance  $l_0$  between the Ag monolayer and the MgO substrate was reoptimized each time.

### 3. Results and discussion

The main results are summarized in Fig. 1 and Table 1 (the adhesion energy  $E_0$  is the total energy

difference for the interface with optimized distance and for two separated slabs). First of all, the adsorption site over the O atom is the energetically most favourable, in agreement with previous experimental data [2,5,6] and LDA-type calculations [7–11]. The Ag adhesion energy grows in this case from 0.20 eV/atom for an Ag monolayer up to 0.41 eV/atom for three Ag layers. Moreover, both Table 1 and Fig. 1 show that an increase in the number of Ag layers affects these results much more considerably than the number of MgO layers. Three LDA calculations differ by a factor of three in their estimates of the adhesion energy, varying between 0.30 and 0.95 eV. Most likely, this is a result of a different number of Ag layers used in the three simulations (Ag monolayer in FLAPW, three layers in LMTO and five layers in LO calculations). In the case of the C interfacial configuration the adhesion energy practi-

Table 1

Equilibrium distances between Ag atoms and MgO-substrate surface atoms,  $l_0$  (in Å) and the relevant adsorption energies,  $E_0$  (in eV) for three kinds of adsorption sites. HF-CC are results of the present study. The correlation corrections are incorporated using the Perdew–Wang functional [22],  $m \times n$  denotes  $m$  Ag layers atop  $n$  MgO layers. In parentheses are results obtained for interface models with additional orbitals centered on hollow positions D between Ag atoms (see Fig. 1)

Ag atom over	$l_0$	$E_0$	Method
O	2.58	0.21	HF-CC 0.25 × 3
	2.64 (2.56)	0.20 (0.26)	HF-CC 1 × 3
	2.66	0.22	HF-CC 1 × 1
	2.47	0.42	HF-CC 3 × 1
	2.45 (2.43)	0.41 (0.46)	HF-CC 3 × 3
	2.49	0.88	FP LMTO 3 × 3 [7]
	2.69	0.30	FLAPW 1 × 3 [8]
	2.35	0.95	LO 5 × 3 [9–11]
Mg	2.89	0.22	HF-CC 0.25 × 3
	3.24 (3.23)	0.06 (0.06)	HF-CC 1 × 3
	3.18	0.08	HF-CC 1 × 1
	3.18	0.08	HF-CC 3 × 1
	3.23 (3.23)	0.07 (0.07)	HF-CC 3 × 3
	2.50	0.45	FP LMTO 3 × 3 [7]
	2.81	0.60	LO 5 × 3 [9–11]
gap	2.69	0.20	HF-CC 0.25 × 3
	3.00 (2.94)	0.10 (0.15)	HF-CC 1 × 3
	2.90 (2.86)	0.13 (0.17)	HF-CC 3 × 3
	2.50	0.58	FP LMTO 3 × 3 [7]

cally does not change when the number of Ag layers increases from one to three.

Table 1 shows that the use of additional orbitals centered in the D positions of the Ag slab shortens the interfacial distance and increases the adhesion energy by  $\leq 0.06$  eV. This change is the most pronounced for the A adsorption site (over the O atom), while for the C interface configuration it is negligible. Therefore, the introduction of atomic orbitals and thus extension of the basis set for the Ag slab do not considerably affect our previous results [23]. Results for a single MgO(100) layer (especially over Mg atoms) differ from those for three MgO layers due to differences in their electrostatic fields in the interfacial region (note that ionic charges in the second MgO layer have an opposite sequence compared to those in the first layer).

Table 2 presents results of the calculations for the

Table 2

Bond populations,  $p_{X-Y}(e)$ , condensed to atoms on the Ag/MgO interface where  $a_0$  is the distance between the atoms X and Y (in Å) for an Ag monolayer atop three MgO layers. Cases A to C correspond to the Ag position over the O atom, a gap and the Mg atom, respectively. Atomic numbering is shown in Fig. 1. In parenthesis are results obtained on centering additional orbitals on the D positions in the Ag slab (numbers in parentheses in  $a_0$  column show changes in the interfacial distances due to introducing of these orbitals)

Case	Atom X	Atom Y	$a_0$	$P_{X-Y}$
A	Ag <sub>1</sub>	Ag <sub>3</sub>	2.977	0.106 (0.103)
		O <sub>1</sub>	2.640 (2.560)	-0.034 (-0.055)
		Mg <sub>1</sub>	3.376 (3.314)	0.001 (0.002)
	O <sub>1</sub>	Ag <sub>2</sub>	4.210	0.016 (0.017)
		Mg <sub>1</sub>	2.105	-0.007 (-0.008)
		O <sub>2</sub>	2.977	-0.012 (-0.012)
B	Ag <sub>1</sub>	Ag <sub>3</sub>	2.977	0.106 (0.103)
		O <sub>1</sub>	3.349 (3.295)	0.007 (0.006)
		Mg <sub>1</sub>	3.349 (3.295)	0.001 (0.001)
	O <sub>1</sub>	Ag <sub>2</sub>	4.210	0.015 (0.015)
		Mg <sub>1</sub>	2.105	-0.005 (-0.005)
		O <sub>2</sub>	2.977	-0.012 (-0.012)
C	Ag <sub>1</sub>	Ag <sub>3</sub>	2.977	0.101 (0.101)
		Mg <sub>1</sub>	3.240 (3.230)	0.002 (0.001)
		O <sub>1</sub>	3.864 (3.855)	0.003 (0.005)
	O <sub>1</sub>	Ag <sub>2</sub>	4.210	0.014 (0.014)
		Mg <sub>1</sub>	2.105	-0.006 (-0.006)
		O <sub>2</sub>	2.977	-0.012 (-0.012)

Table 3

Approximation of the interfacial energy vs. the Ag–MgO distance by the universal binding energy relation (UBER), Eq. (1) and by splines

Slab		Ads. over	UBER			Splines	
MgO	Ag	$E_0$ , eV	$l_0$ , Å	$s$ , Å	$E_0$ , eV	$l_0$ , Å	
1	1	Mg	0.0699	3.232	0.4322	0.077	3.18
		O	0.2287	2.658	0.3843	0.219	2.66
		gap	0.1177	2.949	0.4907	0.124	2.97
1	3	Mg	0.0708	3.243	0.4413	0.077	3.18
		O	0.4303	2.462	0.3865	0.420	2.47
		gap	0.1749	2.736	0.4809	0.178	2.65
3	1	Mg	0.0566	3.290	0.4309	0.061	3.23
		O	0.2119	2.641	0.3713	0.204	2.64
		gap	0.0950	2.987	0.4813	0.100	3.00
3	3	Mg	0.0580	3.287	0.4370	0.063	3.22
		O	0.4151	2.446	0.3709	0.406	2.44
		gap	0.1525	2.758	0.4765	0.156	2.64
3	1/4	Mg	0.2160	2.859	0.4241	0.228	2.88
		O	0.2176	2.588	0.3674	0.207	2.58
		gap	0.2009	2.679	0.4764	0.201	2.68

bond populations between different atoms X and Y (in terms of the Mulliken analysis) per atom:

$$p_{X-Y} = \sum_{\mu}^{(X)} \sum_{\nu}^{(Y)} P_{\mu\nu} \cdot S_{\mu\nu}, \quad (1)$$

where  $P_{\mu\nu}$  and  $S_{\mu\nu}$  are elements of the density and overlap matrices in the AO representation, respectively. The bond population between two nearest surface Ag atoms is  $\approx 0.1 e$  per atom and does not really depend on the Ag adsorption position. This is much larger than the population between the Ag and substrate atoms (Table 2). For the energetically most favourable adsorption site A (Ag over O atoms), the latter is even negative which means an effective repulsion of atoms. This demonstrates clearly that *no chemisorption* takes place in the Ag/MgO(100) interface.

In the literature the so-called *universal binding energy relation* (UBER) is often used:

$$E(l) = -E_0 \cdot (1 + (l - l_0)/l) \times \exp(-(l - l_0)/s), \quad (2)$$

where  $E_0$  is the adhesion energy,  $l_0$  the equilibrium

interfacial distance and  $s$  the scaling constant. A good fit of the interface energy to this relation was interpreted in Refs. [9–11] as evidence for a considerable covalent contribution to the metal-ceramic bonding. Table 3 also demonstrates a good fitting of our interfacial energy to Eq. (1), which, however, does not necessarily mean a considerable covalency of the metal-oxide bonding. Note that the Coulomb potential for a neutral surface of an ionic crystal decays exponentially, which could explain the successful use of the UBER relation. At short distances the UBER describes usual exchange repulsion.

These results are confirmed in Fig. 2 demonstrating the electron density plots in the cross-section perpendicular to the surface. The *difference maps* (i.e. the total self-consistent electronic density for the interface at equilibrium distance minus a superposition of the two well-separated Ag and MgO slabs) show that a considerable part of the electron density is concentrated in the *bridge* and *hollow* positions

between nearest and next-nearest Ag atoms, respectively. In contrast, the charge redistribution in the interfacial region, i.e. between the metal layer and the MgO substrate, is negligibly small.

These density maps, as well as the present population analysis, indicate a reason why Ag adsorption over O atoms is favourable: the electrostatic interaction of the electron density concentrated around the *hollow* position of the interfacial Ag layer ( $\approx 0.07 e$  for 1:1 Ag coverage) with the  $Mg^{2+}$  ion below is attractive. In contrast, for Ag adsorption over Mg atoms we have a repulsive interaction of electron density localized in the D position with the  $O^{2-}$  ion below. As to the change of the adhesion energy in the case of the *three* Ag layers for both A and C interfacial configurations when compared to the Ag monolayer, it may be explained by a more complicated electron density distribution around the interfacial Ag layer. For an A adsorption site  $\approx 0.04 e$  is localized on the corresponding *hollow* position over

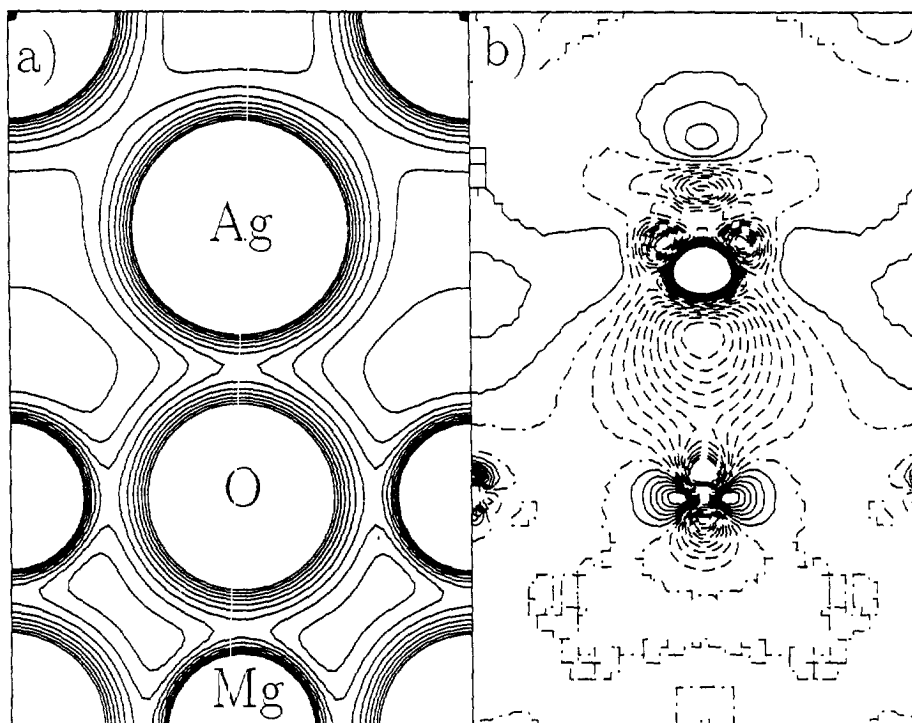


Fig. 2. The total (a) and difference (b) electronic density maps for the cross-section perpendicular to the interface plane. The difference (b) is taken with respect to a superposition of interacting and well-isolated Ag and MgO slabs. Iso-density curves for total densities are drawn from 0.01 to  $0.1 e \text{ au}^{-3}$  with an increment of  $0.01 e \text{ au}^{-3}$ , whereas the difference maps are drawn from  $-0.01$  to  $0.01 e \text{ au}^{-3}$  with an increment of  $0.001 e \text{ au}^{-3}$ . The full, dashed and chained curves show positive, negative and zero difference density, respectively.

$\text{Mg}^{2+}$ , as well as  $\approx 0.12 e$  localized on each of four side *bridge* positions above the D point. For the C adsorption site the corresponding electron density over  $\text{O}^{2-}$  is smaller ( $\approx 0.03 e$  and  $\approx 0.1 e$ , respectively) and considerably more remote from the surface oxygen ion. An analogous explanation may be suggested for an additional increase of adhesion energy when introducing atomic orbitals in the D positions of both one- and three-layer Ag slabs.

The quantitative information on the electron density distribution caused by the interface formation could be also learnt from a comparison of the calculated atomic populations in the isolated Ag(100) and MgO(100) slabs with those for Ag/MgO(100) interfaces with different Ag positions and number of Ag layers. Such an analysis shows that practically no charge transfer takes place between Ag layer and MgO substrate: only  $\approx 0.04 e$  is typically transferred from the substrate atoms to each Ag atom. In the three-layer Ag slab above MgO substrate the electron density (ca.  $0.04 e$  per atom) concentrates on the interfacial Ag layer. In fact, the effective charges of the MgO substrate atoms turn out to be close for the interface and for isolated MgO slabs. Additional information on atom deformations is available from the dipole and quadrupole moments of the surface atoms. The atomic dipole moments  $d(10)$  are matrix elements of the relevant atomic orbitals for the operator  $z$  (perpendicular to the surface). The quadrupole moments  $q(20)$  and  $q(22)$  correspond to the operators  $z^2 - x^2/2 - y^2/2$  and  $3x^2 - 3y^2$  and characterize atomic deformation in the direction perpendicular to the surface and inside the layer, respectively [13,15]. The conclusion could be drawn that the quadrupole moments of the surface Ag atoms exceed those for the surface O atoms by an order of magnitude; this clearly demonstrates a strong deformation of the surface Ag atoms.

In the case of a partial, 1:4 Ag coverage of the MgO(100) surface the mechanism of adsorption differs from the cases of both monolayer and three layer 1:1 coverages. Firstly, for such a low coverage there is no interatomic electron density concentration between Ag atoms, therefore its attraction or repulsion with the nearest substrate ion is absent as well. For a neutral MgO(100) surface, Ag adsorption over O and Mg positions is characterized by the presence of a single nearest substrate ion (either  $\text{O}^{2-}$  or

$\text{Mg}^{2+}$ ) and four next-nearest substrate ions (either  $\text{Mg}^{2+}$  or  $\text{O}^{2-}$ ). In a gap adsorption site every Ag atom has *four* nearest substrate ions (two  $\text{Mg}^{2+}$  and two  $\text{O}^{2-}$ ). Charge transfer from substrate to each isolated Ag atom ( $\approx 0.07 e$  for the A adsorption site) is twice as large as in the case of an Ag monolayer or three Ag layers atop MgO. Since adsorption energies of practically isolated Ag atoms are close for all three adsorption sites, A to C (Tables 1 and 3), it may be explained by a partial compensation of electrostatic attraction and repulsion between the charged Ag and the substrate ions. The value of dipole moment  $d(10)$  on Ag is twice as large as for the 1:4 than that for the 1:1 coverages. At the same time, the quadrupole moment  $q(20)$  for a single Ag is significantly smaller than that for the monolayer ( $-0.43 e \cdot \text{bohr}^2$  vs.  $-2.05 e \cdot \text{bohr}^2$  for A sites). This difference may be caused by a strain in a silver film after adhesion upon the MgO(100) substrate due to the above-mentioned mismatch of the corresponding lattice constants, while in the case of small coverage, Ag atoms do not really interact each with other. Nevertheless, the  $q(20)$  for these Ag atoms exceed the corresponding magnitudes for surface Mg and O atoms by at least a factor of four. Therefore, Ag atoms adsorbed on the MgO(100) surface are deformed in any case.

#### 4. Conclusions

The small adsorption energy and the negligible population of the bonds between Ag atoms and substrate atoms confirm our general conclusion [23] that the Ag/MgO interface formation is a result of *physisorption* rather than chemisorption (in agreement with Refs. [2,8]). The quantitative analysis of the electron density distribution in terms of the effective charges and quadrupole moments of the atoms shows that the Ag adhesion energy arises due to the electrostatic interaction of the surface MgO substrate ions with a complicated electronic density redistribution in the vicinity of the Ag interface atoms. This is characterized by both large quadrupole moments of Ag atoms as well as by concentration of a negative charge in the middle of the bond between two nearest Ag atoms (the *bridge* position,  $\approx 0.2 e$ ) and in the center of square formed by four nearest Ag

atoms (a *hollow* position,  $\approx 0.07 e$ ). Our conclusion about such an electron density redistribution is confirmed by inelastic He scattering studies [24,25]: only introduction of negative *pseudo-charges* in the bridge positions in metals allowed a good fit of theoretical phonon-dispersion curves to experimental data, using a minimal number of parameters in the frequency matrix. All other models need many more fitting parameters to obtain a good agreement with experiments. It should be stressed here that such pseudo-charges arise not only due to interface formation, but also exist in a pure metal where their magnitudes are smaller.

Of great importance are further *ab initio* simulations of the thin Ag film growth on MgO substrate. This is necessary for the interpretation of contradicting experimental data [26–29], as well as for a study of Ag adsorption on a realistic, *defective* surface, e.g. above an Mg-vacancy where the binding energy could be much larger than at a flat surface.

### Acknowledgements

EK thanks the Institute of Physics, Aarhus University in Denmark for the financial support of this study. Authors are indebted to M. Finnis, P.J. Møller and A.M. Stoneham for numerous stimulating discussions.

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