Hartree–Fock simulation of the Ag/MgO interface structure

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Abstract. The atomic and electronic structure of the Ag/MgO interface are calculated using an *ab initio* Hartree–Fock computer code and a supercell model of a silver monolayer atop three layers of MgO substrate. The band structure, electronic density distribution and densities of states are analysed in detail for isolated and interacting slabs of a metal and MgO. The energetically most favoured adsorption position for Ag atoms is found to be above the O atoms, with the binding energy of 0.20 eV and the equilibrium Ag–O distance of 2.64 Å. Neither appreciable charge transfer in the interfacial region, nor considerable population of bonds between the silver monolayer and the insulating substrate take place. The adhesion energy arises mainly due to the electrostatic interaction of substrate atoms with a complicated charge redistribution in the metal monolayer, characterized by large quadrupole moments and electron density redistribution towards the gap position in the middle of the nearest Ag atoms. This could be a reason for the disagreement of all three SCF theories with the phenomenological image interaction model.

1. Introduction

Interfaces between oxide ceramics and noble metals are of great technological importance [1, 2, 3, 4]. For microscopic calculations of their properties, methods have to be able to reproduce correctly the electronic structure of both metal slabs and oxide substrates as well as the electronic charge redistribution in the interfacial region. Solution of this difficult problem imposes high demands on the method to be used. This is the more so because in recent years some interface structures (in particular, Ag/MgO) were studied experimentally by means of the high-resolution transmission electron microscopy giving almost atomic resolution [5] (see also [6]). This suggests a good test for theoretical calculations.

Recently, two self-consistent formalisms based on the *local density approximation* (LDA) as incorporated into the full-potential linearized muffin-tin orbital method (FLMTO) [7] and full-potential linearized augmented-plane-wave (FLAPW) [8] method were applied to the Ag/MgO interface. Additionally, a phenomenological treatment of the electrostatic interactions between oxide substrate ions and their images in a metal, the so-called *image interaction model*, has been developed [9, 10]. It is important to go beyond these approximations using 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. Such an opportunity became available recently after the development of the *ab initio* Hartree–Fock (HF) computer code CRYSTAL suited for the study of periodic (2D, 3D) systems [11]. This approach was successfully applied to numerous oxide crystals, including MgO surfaces [12],

as well as to several bulk metals including Be, Li, Al [13]. Recently this approach has been extended by incorporating the electron correlation corrections [14, 15] (hereafter the 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 nature of the adhesion. In this paper, we present results of an HF-CC study of the Ag/MgO interface and compare them with previous calculations based on the LDA approximation or using the image interaction model.

2. The model and method

The calculations were performed by means of the above-mentioned CRYSTAL computer code [11]. It gives the lattice properties—equilibrium lattice parameters a, 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 computational efforts, pseudopotentials were used for Ag atoms following the small-core version of Hay and Wadt [16]. This allows one to reduce greatly the number of electrons in the calculations: it is 19 now on the Ag atom ($4s^2 4p^6 4d^{10} 5s^1$). The initial guess for the Ag basis set was taken from AgCl calculations [17]. Then the outer Gaussian exponent was reoptimized in order to minimize the total HF energy per unit cell of the 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 the adsorption of Ag on MgO substrate which we discuss in this paper. The basis set of atomic orbitals (AOs) was taken for MgO from reference [12]. Mg and O are treated as all-electron atoms.

Table 1. Equilibrium distances between Ag atoms and MgO substrate surface atoms, l (in Å) and the relevant adsorption energies, AE (in eV), for three kinds of adsorption site. HF-CC indicates results of the present study. The correlation corrections are incorporated following [15].

Ag atom adsorption over	l	AE	Method
O	2.64	0.20	HF-CC
	2.49	0.88	FP LMTO [7]
	2.69	0.30[a]	FLAPW[8]
	2.52	0.32	Image model [10]
		0.25	Experiment [5]
Mg	3.24	0.06	HF-CC
	2.50	0.45	FP LMTO
	2.52	0.60	Image model
Gap[a]	3.00	0.10	HF-CC
	2.50	0.58	FP LMTO
	2.73	0.48	Image model

[a]Energetically the most favourable position.

To avoid the effects of the boundary conditions well known in a quantum cluster model, the *supercell model* was used in terms of which a single Ag monolayer covering three layers of MgO was studied. The distance between different layers in the MgO substrate was optimized and found to be 4.21 Å, very close to the experimental bulk value of 4.205 Å. We neglect surface relaxation of the MgO substrate which is known to be small [12], and ignore also the small (three per cent) mismatch of the lattice constants of Ag and MgO.
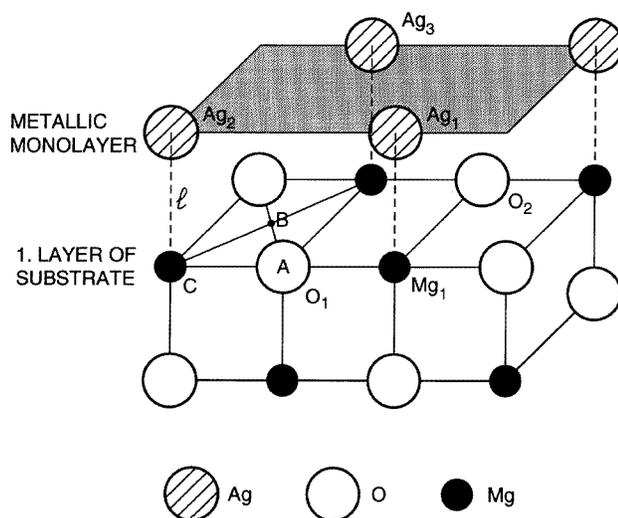
Figure 1. A schematic view of the interface when Ag atoms are positioned at the distance l above the surface Mg atoms (marked C) of the MgO substrate. The other two alternative positions are above O atoms (A) and the gap (B).
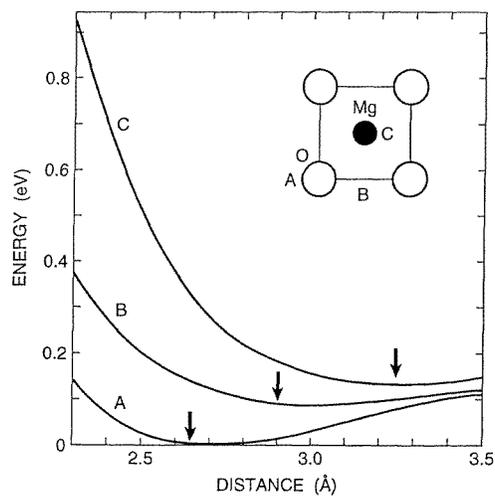

Figure 2. The interfacial energy as a function of the distance l between the Ag atoms and surface atoms which are: O (A), a gap (B) or Mg (C). Arrows indicate the calculated equilibrium distances.

3. Results

The interfacial structure has been studied for the three possible adsorption sites shown in figure 1: over a surface O atom (A), over a gap (B) and over Mg (C) [5, 6, 7]. The main geometric parameter l (the distance between the Ag monolayer and the MgO substrate) was reoptimized each time. The main results are plotted in figure 2 and summarized in table 1. We established that the adsorption site over the O atom is the energetically most favourable.

This is in agreement with previous LDA-type calculations [7, 8] but contradicts the image interaction model conclusion which suggests a position over an Mg atom [10].

The adsorption energy (AE) of 0.20 eV/atom is close to the experimental estimate of 0.25 eV [5]: the agreement seems to be the more satisfactory keeping in mind that our (commonly accepted) oversimplified model neglects misfit dislocations, which play an important role here [5, 6]. The two other LDA calculations differ considerably in their estimates of the AE (0.30 and 0.88 eV). This could result from the different numbers of Ag layers used in these simulations (a monolayer in the FLAPW method and three layers in the LMTO method).
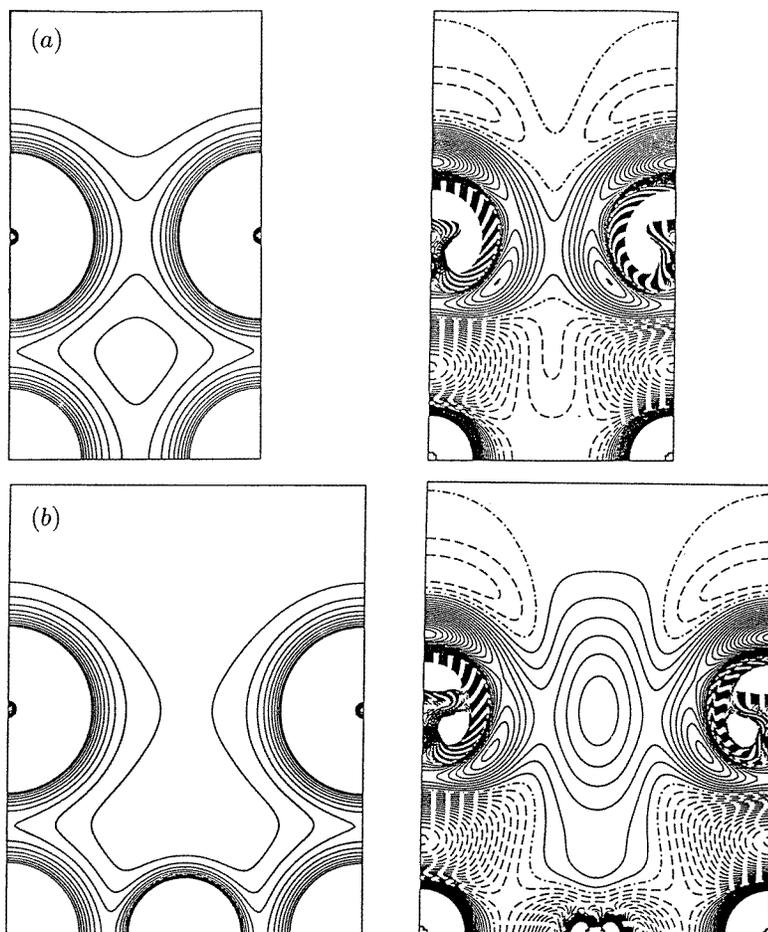
Figure 3. Total (left) and difference (right) electronic density maps of the Ag/MgO interface for Ag atoms atop O atoms in the cross-section perpendicular to the MgO surface and going through the (110) and (100) planes (plots (*a*), (*b*) respectively). The difference is taken with respect to a superposition of atomic densities keeping the same geometry. Iso-density curves for total densities are drawn from 0.0 to 0.1 e au^{-3} with the increment of 0.01 e au^{-3}, whereas the difference maps are drawn from -0.013 e au^{-3} to 0.01 e au^{-3} with the increment of 0.0005 e au^{-3}. The full, dashed and chain curves show positive, negative and zero difference density, respectively.

The HF-CC band structure of the Ag/MgO interface with Ag over O is similar to that from the FLAPW calculations [8] except as regards the absolute energies, which in our case lie somewhat lower. A comparison with the band structures for the isolated Ag monolayer and MgO three-layer substrate shows that the Ag 4p and O 2p bands strongly overlap in energy whereas the Ag 5sp band in the one-metal-layer model used here lies higher and does not overlap with these two bands. This coincidence is again in agreement with the FLAPW calculations [8].

Plots of electron density contours in the cross-section perpendicular to the surface along the (110) direction and along the (100) direction are presented in figure 3. From the difference maps (the total self-consistent electronic density minus a superposition of Ag-atom and Mg^{2+} and O^{2-} densities) shown in the right-hand panels the conclusion could be drawn that a considerable part of the electron density is concentrated in the *gap* position between Ag atoms. In contrast, the charge redistribution between the metal layer and the MgO substrate is small.

Table 2. Overlap populations, $P(e)$, condensed to atoms on the Ag/MgO interface. a_0 is the distance between the two atoms A and B (in Å). Cases A to C correspond to the Ag adsorption over the O atom, a gap and the Mg atom, respectively. The atomic numbering is shown in figure 1.

Case	Atom A	Atom B	a_0	P
A	Ag_1	Ag_3	2.977	0.106
		O_1	2.640	−0.034
		Mg_1	3.376	0.001
	O_1	Mg_1	2.105	−0.007
		O_2	2.977	−0.012
B	Ag_1	Ag_3	2.977	0.106
		Ag_2	4.210	0.015
		O_1	3.349	0.007
	O_1	O_2	2.977	−0.012
		Mg_1	2.105	−0.005
C	Ag_1	Ag_3	2.977	0.101
		Mg_1	3.240	0.002
		O_1	3.864	0.003
	O_1	Mg_1	2.105	−0.006
		O_2	2.977	−0.012

This qualitative observation is confirmed in table 2, demonstrating results of the calculations of the *bond populations* among different atoms (in terms of the Mulliken population analysis). The overlap population between two nearest surface Ag atoms is ≈ 0.1 e per atom and does not depend practically on the Ag adsorption position. This is much larger than the population of the Ag–surface-atom bond which is negligibly small, even in the energetically most favourable case (Ag over O atoms). This demonstrates clearly that no chemisorption takes place in this interface.

The quantitative information on the electron density distribution caused by the interface formation could be learnt from a comparison of the effective charges of atoms in the two isolated silver and MgO slabs and for the Ag/MgO interfaces with different Ag positions (table 3). The immediate conclusion could be drawn that practically no charge transfer takes place between the Ag monolayer and MgO substrate: only 0.04 e is transferred typically

Table 3. Effective atomic charges, $e(0\ 0)$, and dipole, $d(1\ 0)$, and quadrupole, $q(2\ 0)$, moments of the interfacial atoms belonging to different planes (layer No 0 is an Ag monolayer, No 1 is the MgO surface plane nearest to it, etc).

Layer No	Atom	No adsorption		Atop O	Atop gap	Atop Mg
0	Ag					
	$e(0\ 0)^a$	0.047(i)	−0.024(s)	0.028	0.025	0.015
	$d(1\ 0)^a$	0.0(i)	−0.1956(s)	0.1303	−0.0378	−0.065 19
	$q(2\ 0)^a$	0.4563(i)	−0.9197(s)	−2.052	−1.408[b]	−1.314
1	Mg					
	$e(0\ 0)$	1.962		1.960	1.960	1.961
	$d(1\ 0)$	0.016 37		0.023 63	0.0211	0.019 61
	$q(2\ 0)$	−0.018 77		−0.0008	−0.0100	−0.012 31
	O					
	$e(0\ 0)$	−1.957		−1.927	−1.928	−1.939
	$d(1\ 0)$	0.076 76		−0.005 80	0.0704	0.087 83
	$q(2\ 0)$	0.012 24		−0.035 14	0.1256	0.1587
2	Mg					
	$e(0\ 0)$	1.972		1.972	1.971	1.971
	$d(1\ 0)$	0.0		−0.0003	0.001 95	0.001 35
	$q(2\ 0)$	0.020 38		0.020 82	0.023 61	0.022 45
	O					
	$e(0\ 0)$	−1.983		−1.982	−1.983	−1.983
	$d(1\ 0)$	0.0		0.0007	0.001 15	0.0008
	$q(2\ 0)$	0.0107		0.01	0.0105	0.0106
3	Mg					
	$e(0\ 0)$	1.962		1.962	1.962	1.962
	$d(1\ 0)$	−0.016 37		−0.016 31	−0.016 30	−0.016 33
	$q(2\ 0)$	−0.018 77		−0.018 65	−0.018 66	−0.018 70
	O					
	$e(0\ 0)$	−1.957		−1.957	−1.957	−1.957
	$d(1\ 0)$	−0.076 76		−0.076 70	−0.076 70	−0.076 71
	$q(2\ 0)$	0.1224		0.1224	0.1224	0.1224

[a] Isolated three-layer Ag slab; i and s denote the internal and surface slab planes.
[b] Note the large quadrupole moment $q(2\ 2) = 0.5293$ in this position; it is zero in the other two cases.

from the substrate to each Ag atom. The effective charges of the MgO substrate atoms are very close in the interface and isolated slab cases.

Additional information on atom deformations is available from the dipole and quadrupole moments of the surface atoms also presented in table 3. The dipole moments d are matrix elements of the atomic orbitals with the operator $X_0^1 = z$ (the direction pointing outwards from the surface), whereas the quadrupole moments $q(2\ 0)$ and $q(2\ 2)$ correspond to the operators $X_0^2 = z^2 - 0.5x^2 - 0.5y^2$ and $X_2^2 = 3x^2 - 3y^2$, respectively (see more in [12]). Indeed, the conclusion could be drawn that $q(2\ 0)$ quadrupole moments of the surface Ag atoms exceed those for the surface O atoms by an order of magnitude which demonstrates a strong deformation of the Ag atoms.

4. Discussion and conclusion

Based on both the small adsorption energy and the negligible population of the bonds between Ag atoms and substrate atoms, the general conclusion could be drawn that the Ag/MgO interface formation is a result of *physisorption* rather than chemisorption. The largest adsorption energy corresponds to the Ag atoms sitting atop O atoms of the substrate at the distance ≈2.6 Å. This is in agreement with earlier LDA-type studies [7, 8] and demonstrates that the Hartree–Fock method is well suited for the study of metal–oxide interfaces. (For more detailed comparison of these methods, additional calculations with three Ag and three MgO(100) layers should be performed via the HF-CC approach and FPLAPW methods.) Moreover, the HF-CC approach has the advantage of the quantitative analysis of the electron density distribution in terms of the effective charges and quadrupole moments of atoms. From this analysis the conclusion could be drawn that the Ag adsorption energy arises due to the electrostatic interaction of the surface MgO substrate ions with a complicated electronic density redistribution in the vicinity of Ag surface atoms. This is characterized by both large quadrupole moments of Ag atoms and concentration of negative charge ≈0.4 e in the middle of the bond between two nearest Ag atoms, in the region of the so-called *gap position*. Our conclusion about such an electron density localization is confirmed by recent inelastic He scattering studies of the phonon dispersion curves for metals [18]: only introduction of negative pseudo-charges in the gap positions allowed us to get good agreement between theory and experiment.

The idea of pseudo-charges could also explain the disagreement between three SCF calculations (HF-CC, FP LMTO and FPLAPW) and the *image interaction model* [9, 10] giving preference to the adsorption over Mg atoms. Incorporation of this effect into the image interaction model probably could improve its agreement with self-consistent theories. This would be important for further studies of complicated interfaces in terms of such a phenomenological approach.

In conclusion we would like also to stress that in order to simulate theoretically the *real* Ag/MgO interfacial structure, it is necessary to incorporate misfit dislocations into the consideration and then to estimate their effect in the preferable adsorption site and energetics [5, 6].

Acknowledgments

References

[1] Rühle M R, Evans A G, Ashby M F and Hirth J P (ed) 1990 *Metal–Ceramic Interfaces* (Oxford: Pergamon)
    Ernst F 1995 *Mater. Sci. Eng.* R **14** 97 (a review article)
[2] 1994 *Proc. Int. Workshop on Science of Alumina*; *J. Am. Ceram. Soc.* **77** (2) (special issue)
[3] Stoneham A M, Ramos M M D and Sutton A P 1993 *Phil. Mag.* A **67** 797
    Stoneham A M, Harding J and Harker T 1996 *MRS Bull.* **21** 29
[4] Rühle M, Heuer A H, Evans A G and Ashby M F (ed) 1992 *Proc. Int. Conf. on Metal–Oxide Interfaces*;
    Acta Metall. Mater., Suppl. **40** (special issue)
[5] Trampert A, Ernst F, Flynn C P, Fishmeister H F and Rühle M 1992 *Proc. Int. Conf. on Metal–Oxide Interfaces*; *Acta Metall. Mater., Suppl.* **40** S227

[6] Guenard P, Renaud G, Villette B, Yang M-H and Flynn C P 1994 *Scr. Metall. Mater.* **31** 1221

[7] Schönberger U, Andersen O K and Methfessel M 1992 *Proc. Int. Conf. on Metal–Oxide Interfaces*; *Acta Metall. Mater., Suppl.* **40** S1

[8] Li C, Wu R, Freeman A J and Fu C L 1993 *Phys. Rev.* B **48** 8317

[9] Finnis M W 1992 *Proc. Int. Conf. on Metal–Oxide Interfaces*; *Acta Metall. Mater., Suppl.* **40** S25

[10] Duffy D M, Harding J H and Stoneham A M 1992 1992 *Proc. Int. Conf. on Metal–Oxide Interfaces*; *Acta Metall. Mater., Suppl.* **40** S1; 1993 *Phil. Mag.* A **67** 865; 1994 *J. Appl. Phys.* **76** 2791

[11] Dovesi R, Pisani C, Roetti C, Causá M and Saunders V 1989 *CRYSTAL-88, Program No 577, QCPE* Indiana University, Bloomington
Pisani C, Dovesi R and Roetti C 1988 *Hartree–Fock ab initio Treatment of Crystalline Systems (Springer Lecture Notes in Chemistry 48)* (Berlin: Springer)

[12] Causá M, Dovesi R, Pisani C and Roetti C 1986 *Surf. Sci.* **175** 551
Causá M, Kotomin E A, Pisani C and Roetti C 1987 *J. Phys. C: Solid State Phys.* **20** 4391

[13] Dovesi R, Pisani C, Ricca F and Roetti C 1982 *Phys. Rev.* B **25** 3731; 1982 *Z. Phys.* B **47** 19
Causá M, Dovesi R, Pisani C and Roetti C 1981 *Phil. Mag.* **44** 419
Dovesi R, Fererro E, Pisani C and Roetti C 1983 *Z. Phys.* B **51** 195

[14] Causá M and Zupan A 1994 *Chem. Phys. Lett.* **220** 145

[15] Perdew J P and Wang Y 1991 *Phys. Rev.* B **45** 13 244

[16] Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 284, 299

[17] Aprá E, Stefanovich E, Dovesi R and Roetti C 1991 *Chem. Phys. Lett.* **186** 329

[18] Kaden C, Ruggerone P, Toennies J P, Zhang G and Benedek G 1992 *Phys. Rev.* B **46** 13 509
Luo N S, Ruggerone P, Toennies J P and Benedek G 1993 *Phys. Scr.* T **49** 584