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The Influence of the Cluster Models on the Study of Electronic Structure of MgO/Ag Interface

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Abstract: We performed local density calculations of energy eigenvalue, bond order and the density of states of MgO(100)/Ag(100) interface using discrete variation Xα method for different cluster models. Several cluster models are chosen for exploring the bond orders of the metal–ceramic interface. The bond order analyses suggest that the cluster model is important for the study of the electronic structure of the metal–ceramic interface using quantum chemical calculation methods. The larger cluster model is not definitely better than the smaller one. The results obtained from different cluster models show bonding essentially electrostatic at the (100)Ag/(100)MgO interfaces, and covalent effects are felt to be small.

1 INTRODUCTION

Surfaces and interfaces dominate many of the technologically important processes in solid materials, such as catalysis, sintering, bonding and oxidation. The study of metal–ceramic interfaces poses some formidable challenges both experimentally and theoretically. These range from the complexity of interface formation and structure, the nature and role of interdiffusion at the interface, the nature and strength of bonding, the work of adhesion, etc., to the complexities of understanding interface failure. Much less work has been done on the theoretical side to investigate metal–ceramic interfaces. Now the methods of atomistic simulation are increasingly used to study a wide range of problems in the physics of metals and ceramics.[1-3] The computational methods themselves include static relaxation, molecular dynamics and more recently Monte-Carlo simulation. The aim is to study equilibrium configurations, their energies with respect to the perfect bulk systems, and in the case of MD dynamical processes. The electronic structure of the interfaces, which is the basis for material properties, has not yet been explored extensively. The theoretical treatment of bonding ranges from first principles calculation to the phenomenological modeling of interfaces, yet the applicability of each specific method is entirely dependent on the systems. Two types of approach have been taken so far, one of which is a cluster calculation where the interface is modeled by atomic clusters.[4] The other type of approach is an energy band calculation.[5,6]

The MgO–noble metal interface has been studied experimentally by a few authors.[7] The most preferred orientation relations between the noble metal and MgO surfaces are found to be (100)metal/(100)MgO, and <110>metal/<110>MgO, i.e the orientation with the highest symmetry.[7] We have chosen to study the Ag/MgO system because of the following reasons: (i) This interface type occurs with the highest frequency in epitaxy and in sintering experiments between many rock salt structured oxides and fcc metals, and may thus be assumed to be particularly stable. (ii) The high symmetry of the interface allows calculations to be made with a relatively small cluster. (iii) The lattice misfit between Ag (bulk lattice parameters a_0 = 0·4086 nm) and MgO (a_0 = 0·4212 nm) is only 3%. (iv) The system MgO/Ag which represents one of the most extreme cases in terms of dissimilarity has been studied experimentally and theoretically by a few authors.[8]

In this work we used embedded cluster discrete variation Xα method to study the electronic structure of the MgO/Ag(100) interface with Ag located above O sites according to other theoretical results and Ag–O distance equal to 5·1 Å.[8] Several cluster models are chosen for the study of the influence of the cluster models on the electronic structure of the interface. The electronic properties of bulk

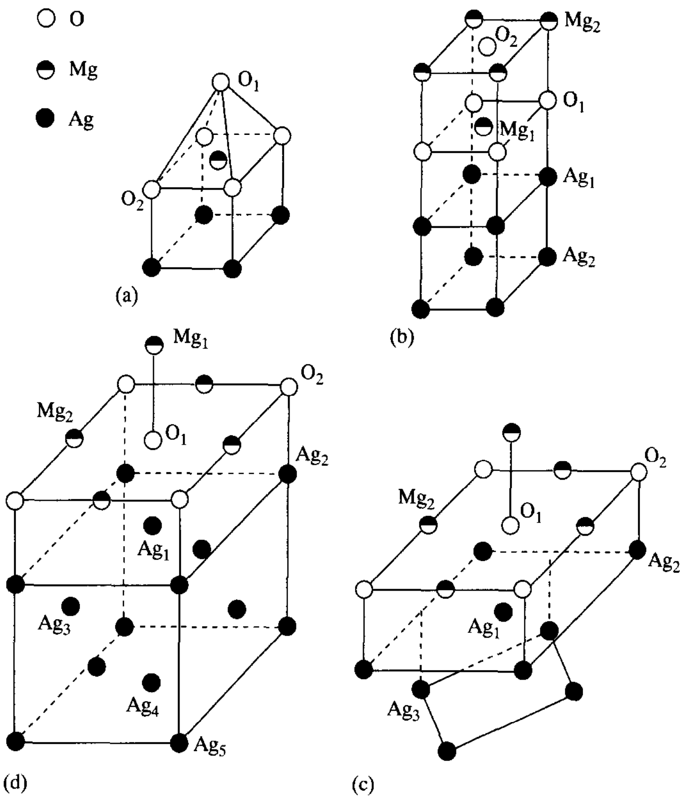

Fig. 1. The cluster models of Ag/MgO(100) interface.

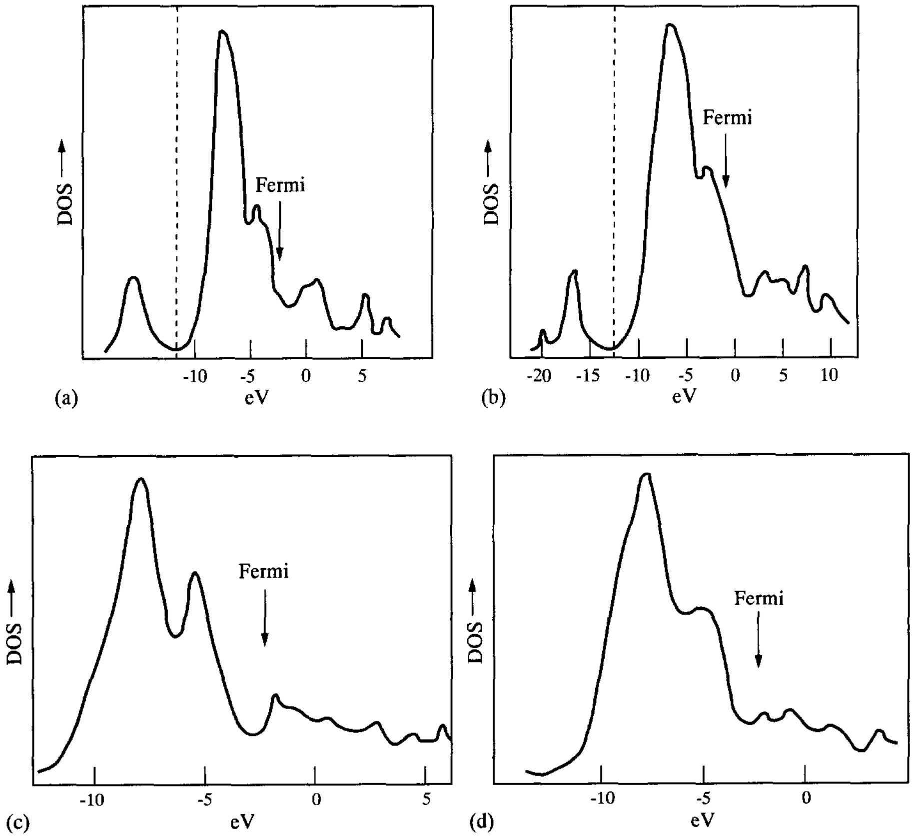

Fig. 2. The density of the states of models (a)–(d)

MgO obtained by applying the MgO_6 cluster model serve as a basis for carrying out comparisons with the results from the interface studies.

2 THE BOND ORDER AND CLUSTER MODELS

In this paper the discrete variation Xα method was employed to calculate the electronic structure of the metal–ceramic interface. The discrete variational Xα method is a first-principle local density technique originally developed by D. E. Ellis. This SCF solution of one-electron secular equations in the local exchange approximation yields the one electron eigenvalues and orbital wave functions. The DV-Xα method has several advantages over other first-principle methods due to its computational efficiency. Much larger molecules can be handled than in HF calculations. In this method, an exchange correlation between electrons is included by means of a local exchange correlation potential Vxc. The matrix elements of the Hamiltonian and the overlap integrals are calculated by a linear combination of numerically generated atomic orbitals for a characterization of the electronic structure and chemical bonding in clusters. It is useful to investigate the level structure, charge distribution in a cluster and the bond order between atoms.[9,10] For these purposes, the Mulliken population is employed. The orbital populations are convenient for defining the number of electrons occupying a given atomic orbital, and by summing them up the effective charge on the atom can be estimated.

The cluster models chosen for the study of the electronic structure of the Ag/MgO(100) interface are given in Fig. 1(a)–(d), where (a) MgO_5–Ag_4; (b) Mg_5O_5–Ag_8; (c)Mg_6O_5–Ag_9; (d) Mg_6O_5–Ag_{14}. In each cluster model the Ag atom is above the O atom according to Freeman's results[11] where the preferred site of the overlayer Ag atom was found to be above the O site of the clean MgO(001) surface. All clusters in Fig. 1 are calculated by the DV-Xα method, and the core orbitals of each atom are frozen.

3 DISCUSSION

In the present paper the electronic structure of the MgO was calculated by DV-Xα method using the model MgO_6. The calculated results of cluster MgO_6 will compare with the results of the interface (Ag/MgO). The direct energy gap is 8·1 eV which is in good agreement with the experimental value of 7·8 eV. The band structure is determined by valence bands of predominantly $O_{2p}(1t_{1g}3t_{1u}, 1t_{2u},2e_g,1t_{2g},2t_{1u},2a_{1g})$ character with a width of 2·74 eV. To investigate the bond order between atoms, the Mulliken population is employed. For MgO_6, bond order between Mg and O is 1·32 which shows the bond order of Mg–O in bulk MgO is 1·32. The configuration of the valence orbital for atom Mg is $3s^{0\cdot42}3p^{0\cdot72}$ and for atom O is $2s^{1\cdot98}2p^{4\cdot17}$.

The cluster models (a)–(d) are oriented in standard C4v symmetry. The numbers of each type of atom in the cluster models are, respectively: in (a) O_1 : 1, O_2 : 4, Mg : 1, Ag : 4; in (b) O_1 : 4, O_2 : 1, Mg_1 : 1, Mg_2 : 4, Ag_1 : 4, Ag_2 : 4; in(c) O_1 : 1, O_2 : 4, Mg_1 : 4, Mg_2 : 1, Ag_1 : 1, Ag_2 : 4, Ag_3 : 4, in (d) O_1 : 1, O_2 : 4, Mg_1 : 4, Mg_2 : 1, Ag_1 : 1,Ag_2 : 4, Ag_3 : 4, Ag_4 : 1, Ag_5 : 4. To investigate the influence of the cluster model on the electronic structure of metal–ceramic interface, we performed DV-Xα calculation on several cluster models shown in Fig. 1 (a)–(d). The bond orders of Mg–O for (a) and (b) are, respectively, 1·28 and 1·19. Although having a little difference between them they are all close to the result of solid MgO. But the bond orders of Mg–O for models (c) and (d) are negative which is different from that of the solid due to the difference of the coordination of atom O in model (c) and (d) compared with (a) and (b). The environment of the atom which locates at the centre of the cluster model, such as Mg in (a), Mg_1 in (b), O_1 and Ag_1 in (c) and (d), is similar to that in the bulk solid. The differences of the bond orders between atoms for each cluster arise from their environments. The bond orders of Ag–O for (a), (b), (c), (d) have little disparity. The bond order of Ag–O in model (a) is 0·09, and the bond orders of Ag_1–O and Ag_2–O in model (b) are, respectively, 0·12 and –0·002, in model (c) O_1–Ag_1:–0·117, O_1–Ag_2: 0·083, O_1–Ag_3: –0·013, in model (d) O_1–Ag_1: –0·016, O_1–Ag_2: –0·07, O_1–Ag_3: 0·01, O_1–Ag_4: 0·00, O_1–Ag_5: 0·00. The results obtained from these models show that the metal–ceramic interface between Ag and Mg can be modeled by one layer of Ag adsorbed on the Mg(100) surface. The very short range of the surface effect found in the Ag(100) surface provides good support for using model (a) to estimate the metal–ceramic interface electronic structure. The configurations of each atom in models (a)–(d) are presented in Table 1. The bond order of Ag–O and the configurations of the atoms in these models show that there is a small charge transfer from O to Ag. Bonding at the (100)Ag/(100)MgO interface is essentially electrostatic; covalent effects are felt to be small. The charge distributions of the molecular orbitals show the HOMO (highest occupied molecular orbital) consists of Ag(5s) and O(2p), and LUMO (lowest unoccupied molecular orbital) consists of Ag(5s), O(2p), and Mg(3s). Figure 3 gives the

Table 1. The configurations of the atoms in models (a)–(d)

	Mg₁		Mg₂		O₁			O₂		
	3s	3p	3s	3p	2s	2p	3s	2s	2p	3s
(a)	0·56	0·90			1·97	4·28	0·04	1·97	4·24	0·00
(b)	0·62	0·89	0·89	0·66	1·92	4·48	0·13	1·77	4·65	0·24
(c)	0·76	0·84	1·54	0·30	1·62	4·82	0·17	1·94	4·51	0·03
(d)	0·65	0·79	1·38	0·33	1·74	4·71	0·62	1·90	4·54	0·03

	Ag₁		Ag₂		Ag₃		Ag₄		Ag₅	
	4d	5s	4d	5s	4d	5s	4d	5s	4d	5s
(a)	9·96	0·83								
(b)	9·96	0·84	9·96	1·09						
(c)	9·92	0·86	9·95	0·85	9·86	1·23				
(d)	9·91	0·92	9·94	1·04	9·85	1·06	9·95	0·99	9·91	1·19

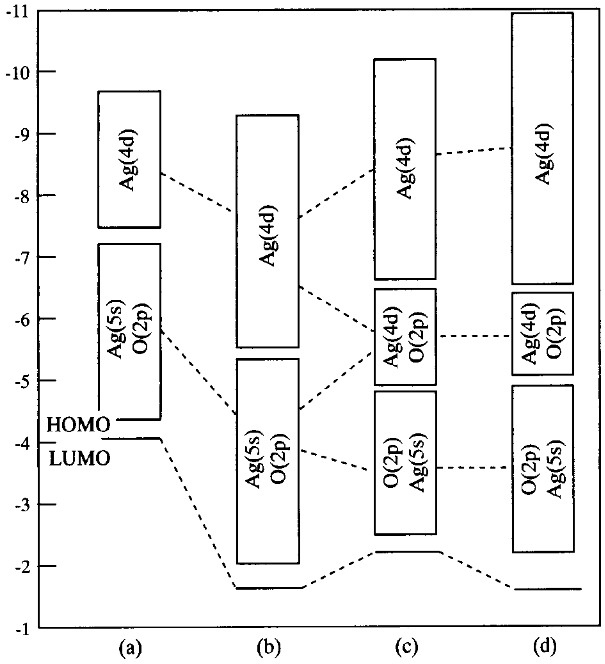

Fig. 3. Correlation diagram of the energy levels for the cluster models (a)–(d).

energy level correlations of different clusters and Fig. 2 is the density of the states of these clusters. The results obtained from different cluster models are almost the same although they have a small difference. The larger cluster model is not definitely better than the smaller one.

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