The MgO(110) surface and CO adsorption thereon: I. Clean (110) surface

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Abstract. The MgO(110) surface has been studied using for the first time the exact-exchange Hartree–Fock approach within a crystalline-orbital LCAO formalism. The results obtained for slabs of different thicknesses (up to four planes) are presented and discussed. Unlike the (100) surface considered earlier, the symmetrical relaxation (compression) of the surface plane is found to be considerable (6.7% of the distance between two bulk planes) but the rumpling remains small (about 1.5% or less). The almost fully ionic character of the chemical bond, which was found earlier for bulk MgO and its (100) surface, is also maintained at the (110) surface in spite of a certain redistribution of the electronic charge at the surface. The surface energy (5.1 J m⁻²) exceeds that obtained for the (100) surface by a factor of 2.5. The nature of the surface states is discussed by analysing the projected density of states.

1. Introduction

The theoretical investigation of the surfaces of ionic crystals is of interest since it can give valuable information about intimate mechanisms of such processes as corrosion, catalysis, crystal growth and dissolution (Batra and Kleinman 1984, Shluger *et al* 1984, Stoneham 1979). At present, computer simulations enable stable structures for the perfect crystal surfaces to be predicted (Tasker and Duffy 1984), differences in the properties of the bulk and surface defects to be found (Evarestov *et al* 1983) and positions favourable for chemisorption to be identified (Colbourn *et al* 1983).

In the last few years the surfaces of magnesium oxide (MgO), which is interesting both as an active photocatalyst and as a simple model of a large class of oxides, have been calculated by means of quite different methods and models and, in particular, using the cluster model (*ab initio* calculations by Colbourn and Mackrodt (1984) and by Colbourn *et al* (1983), CNDO calculations by Smirnov and Tsyganenko (1984), Xα calculations by Satoko *et al* (1978)) and the periodic slab model (model potential calculations by Tasker and Duffy (1984) and Slater–Koster-type calculations by Lee and Wong (1978)). It has been recently shown by Ermoshkin *et al* (1982) that even for alkali halides, which are almost completely ionic crystals, the split-off of surface states is appreciably affected by the redistribution of the electronic charge that takes place at the surface; therefore, simple electrostatic models (Levine and Davison 1970) or even more

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sophisticated but non-self-consistent approaches (Zavt and Saks 1972, 1977, Saks and Zavt 1978) should be used with certain precautions. For these reasons, *ab initio* calculations become of obvious importance. The exact-exchange Hartree–Fock (HF) crystalline-orbital LCAO SCF CRYSTAL computer code (Pisani and Dovesi 1980, Dovesi *et al* 1983) has been recently employed to investigate the properties of bulk MgO and its (100) surface (Causà *et al* 1986a, b, c, d). The bulk calculations (Causà *et al* 1986a, b, c) provided energy data, the band-structure, x-ray structure factors, Compton profiles and accurate wavefunctions, which may serve as a reasonable starting point for surface calculations. These studies have confirmed the almost completely ionic character of the chemical bond in MgO and the existence of the O^{2-} ion in the crystalline field, in line with the results of Abarenkov and Antonova (1979). The study of the MgO(100) surface performed by Causà *et al* (1986d) did not indicate essential changes in the ionic character of the bonding near the surface, contrary to the hypothesis expressed by Rieder (1982). No considerable relaxation and rumpling (i.e. displacements of Mg^{2+} and O^{2-} ions inwards and outwards respectively, from the surface plane) were found to occur.

This paper is the first of two papers dealing with the clean MgO(110) surface and with CO adsorption thereon, respectively. The main interest in the (110) surface is that it serves as an auxiliary model for the realistic solid surface, because it could be considered as a set of (100) surfaces with steps every lattice parameter (see, e.g., Tasker and Duffy 1984). Surface relaxation effects could be more pronounced here because the distance between nearest (110) planes is less than in the (100) case by a factor of $2^{1/2}$. Also, surface ions are now only fourfold coordinated compared with the fivefold coordination at the (100) surface.

The plan of the present paper is as follows. In § 2 the model adopted and the computational aspects are discussed. In § 3 the results obtained for the clean surface are dealt with using a three-layer slab. Surface energy, atomic relaxation and rumpling, electronic charge distribution, atomic multipoles and surface density of states are reported. General conclusions are drawn in § 4.

2. Model and computational aspects

In our previous study of the MgO(100) surface (Causà *et al* 1986d) a detailed discussion was given of the computational conditions to be adopted. Two problems were analysed, in particular: first, how thick the slab parallel to the surface under study had to be for appropriately simulating the surface properties of the crystal and, second, whether the basis set that had proved adequate for bulk MgO was still acceptable for surface atoms or needed some changes.

As regards the first question, the description of the electronic structure at the surface and the evaluated surface energy appeared to converge very rapidly with increasing slab thickness; even a single-layer slab was found to be a realistic model for studying the (100) surface properties of MgO. The basis set question is more delicate; in essence, it concerns the description of the outer 3sp shell of Mg. For the bulk, where the completely ionic configuration Mg^{2+} is a good description of the magnesium ion, an adequate choice for the outer-shell atomic orbitals were single Gaussians with a relatively large exponent α^{Mg} of 0.4 au. At the (100) surface, the ionicity was slightly decreased and a more expanded 3sp shell was found to perform better, especially as far as energy was concerned. The difference was not very important, however, and, in the end, all calculations were performed using the same basis set as in the bulk.

Both problems must be reconsidered in the present case where, because of lowered coordination of (110) surface atoms with respect to those at the (100) face, we can expect more pronounced differences between the surface and bulk properties. To explore the dependence of the electronic properties on the atom coordination, we performed first of all a series of calculations for 1D (linear chain) and 2D (slab) systems, using the basis set of bulk MgO.

The essential results are reported in table 1. Consider first the 1D systems. The

Table 1. Dependence of total energy E and Mg outer 3sp shell population c on the dimensionality of a system. The bulk basis set and Mg–O distance $d = 2.105$ Å are used. The energies refer to the Mg–O pair and are subtracted from the bulk cell energy ($E = -274.6624$ au). The surface energies defined as $S = 0.5\,(nE_b - E^n)$ (where E_b and E^n are the bulk and the n-plane slab total energies, respectively) and upper valence band-widths W are also given for different slabs.

Number of planes or chains	E (au)	c (au) Surface	c (au) Internal	S (au)	W (au)
Bulk MgO	0.0	—	0.035	—	0.19
2D (110) planes					
4	0.0507	0.076	0.045	0.101	0.24
3	0.0690	0.080	0.040	0.103	0.24
2	0.1017	0.089	—	0.102	0.16
1[a]	0.2600	0.124	—	0.130	0.15
1D (110) chains					
3	0.2681	0.140	0.127	—	0.10
2	0.2519	0.122	—	—	0.07
1	0.2176	0.106	—	—	0.04
1D (100) chains					
3	0.1091	0.087	0.081	—	0.11
2	0.1298	0.091	—	—	0.08
1	0.2176	0.106	—	—	0.04

[a] For a single (100) plane, $E = 0.0594$ au and $c = 0.069$ au.

chains of alternating atoms . . . –Mg–O–Mg–O– . . . interact repulsively or attractively according to whether they are disposed to simulate the (110) or the (100) surface structure. Consequently, while the (100) single plane is a highly stable, highly ionic structure, the (110) single plane is quite unstable, and its ionicity decreases appreciably, even if the adopted basis set strongly favours an ionic solution. However, when slabs of different thicknesses are considered, it is seen that even a two-plane slab gives results close to those of the four-plane slab and that the ionic solution at the surface is again favoured, because of stabilisation from underlying planes.

We checked the effect of the expansion of the outer 3sp shell of Mg and 2sp shell of O atoms at the (110) surface, thus allowing for larger delocalisation of the electronic charge. However, no essential changes were found in the relaxation and surface energy even if the total energy change was greater than that for the (100) surface (e.g. for $\alpha^{Mg} = 0.3$ au the surface energy calculated for the relaxed three-plane slab was 0.096 au, i.e. the relative deviation is 3%). This is why in the present study we adopted the same basis set as in the previous study of the (100) surface. For a realistic study of the (110) surface,

slabs containing at least two layers must be considered. In the following, clean-surface results refer to three-plane slabs while, for the study of CO adsorption to be presented in the following paper, two- and three-plane slabs were used to simulate the adsorbing semi-infinite crystal.

3. Results for the clean (110) surface

3.1. Geometry and surface energy

The surface geometry was optimised by looking for the minimal total energy with respect to inter-plane distance and to rumpling of Mg^{2+} and O^{2-} ions at the surface layers. We have obtained 6.7% compression of the surface planes (in units of the interplane distance $d = 1.487$ Å) and rumpling of about 1.5% or less, while no appreciable relaxation and rumpling have been observed by Causà *et al* (1986d) for the (100) surface.

The surface energy for the relaxed structure is $S = 0.093$ au per molecular surface unit, compared with $S = 0.103$ au for the unrelaxed structure (table 1). This is about three times the value ($S = 0.029$ au) obtained for the (100) surface and confirms that the (110) surface is much more unstable with respect to relaxation.

3.2. Electronic charge distribution

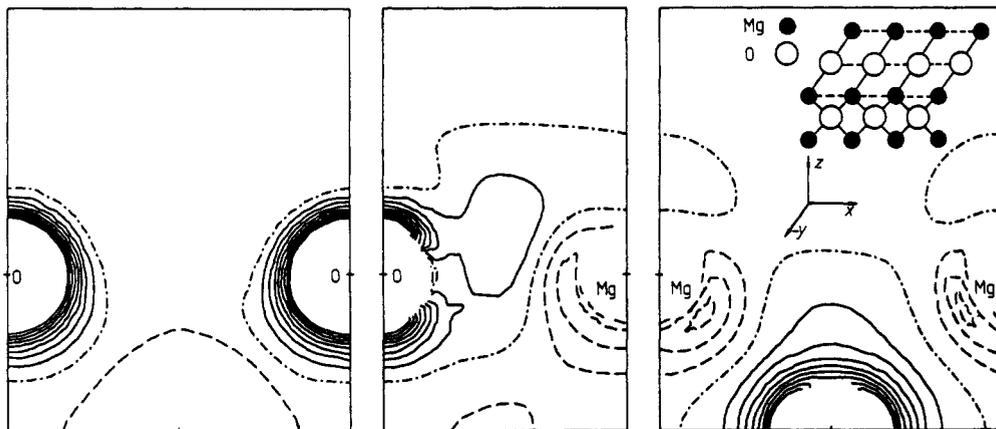The electronic charge distribution at the (110) surface is shown in figure 1. It is seen that

Figure 1. Electronic charge differences $\Delta\rho$ in a vertical section of the MgO relaxed slab consisting of three (110) planes: ——, positive values; – – –, negative values; – · –, zero values. $\Delta\rho$ is the difference between the charge density obtained in the present self-consistent calculation and that obtained as a superposition of ionic distributions. For the isolated Mg^{2+} solution the Mg 1s and 2sp atomic orbitals are used which are the same as in the periodic calculations. In turn, for the O^{2-} ion the Watson (1958) solution was used. The discrepancy in the inner part of O^{2-} is due to the different descriptions in that region of the O^{2-} ion in these two calculations. The difference between contiguous lines is 0.0025e au^{-3}. For comparison, the mean valence electron charge density in the bulk is 0.0794e au^{-3}. The schematic diagram at the top right represents the geometry of the slabs and the directions of the coordinate axes.

Table 2. Electronic charge e, dipole moment d and quadrupole moment q of the surface and internal ions for the unrelaxed and relaxed three-plane slabs. The quantum numbers $(l\,m)$ of cubic harmonics X_l^m are shown in parentheses; they correspond to $X_0^1 = z$ (the direction pointing outwards from the surface), $X_0^2 = z^2 - \frac{1}{2}x^2 - \frac{1}{2}y^2$ and $X_2^2 = 3x^2 - 3y^2$.

Atom	$e(0\,0)$ Surface	Internal	$d(1\,0)$ Surface	Internal	$q(2\,0)$ Surface	Internal	$q(2\,2)$ Surface	Internal
O								
Unrelaxed	9.92	9.99	0.058	0.0	0.025	0.301	−0.637	0.047
Relaxed	9.79	9.97	0.085	0.0	−0.045	0.210	−0.792	−0.031
Bulk	—	9.98	—	0.0	—	0.0	—	0.0
Mg								
Unrelaxed	10.06	10.04	0.010	0.0	−0.046	0.043	−0.225	0.165
Relaxed	10.20	10.04	0.011	0.0	−0.048	0.047	−0.247	0.133
Bulk	—	10.02	—	0.0	—	0.0	—	0.0

the O^{2-} ions at the surface are expanded in the direction of the nearest surface Mg^{2+} ions. Unlike the (100) surface, O^{2-} ions in the second (110) plane below the surface are slightly expanded in the direction perpendicular to the surface. In contrast, Mg^{2+} surface ions are deformed very weakly and are also slightly less ionic than in the (100) case (table 2).

A quantitative measure of the electronic charge redistribution is given in table 2, where the electronic charge e, the non-zero by symmetry dipole moment d and quadrupole moment q components for different electronic shells λ of Mg and O are reported. The general shell multipole moment γ_{em}^λ is defined as follows:

$$\gamma_{lm}^\lambda = \sum_{\mu \in \lambda} \sum_\nu \sum_g P_{\mu\nu}^g \langle \chi_\mu^0 | X_l^m | \chi_\nu^g \rangle$$

where χ_ν^g is the νth atomic orbital centred in cell g, X_l^m is a spherical harmonic with l, m quantum numbers, $P_{\mu\nu}^g$ is the density matrix and the index g runs over all direct lattice vectors.

The data in table 2 confirm the smallness of the surface ion deformation but indicate also the appreciable sensitivity of the electronic charge distribution to surface relaxation, e.g. the $q^0(2\,0)$ values for the relaxed and unrelaxed surfaces have different signs. The multipole moments $q^0(2\,2)$ confirm the above-described electronic charge redistribution along the (110) surface.

Finally, bond populations at the surface (denoted by s) and at the internal (denoted by i) plane are found to be very small, e.g. $0.009e$ for Mg^s–O^s, and $-0.03e$ for Mg^i–O^i, $-0.02e$ for both O^s–O^s and O^i–O^i and almost zero for all Mg–Mg pairs. This confirms once more the above-stated ionic character of the chemical bond at the (110) surface.

3.3. Surface density of states

Additional information about the electronic structure at the (110) surface can be obtained from the density-of-states (DOS) data for the three-layer slab. To discuss these data, it is useful to recall the corresponding HF results for bulk MgO (Causà *et al* 1986a); the topmost group of valence bands, associated with O p orbitals has a band-width of

5.1 eV and is separated by a large gap (15.9 eV) from the underlying O s band, which is much narrower (1.9 eV). In figure 2, we give only total and projected DOSS for the O p bands. It can be seen that essentially the decrease in the electrostatic potential at the surface O ions due to the lack of two out of six nearest-neighbour Mg ions destabilises the corresponding p levels by about 3 eV; p_x and p_z orbitals, which are perpendicular to the surface chain (. . . –Mg–O–Mg– . . .) are particularly affected. A similar 'electro-
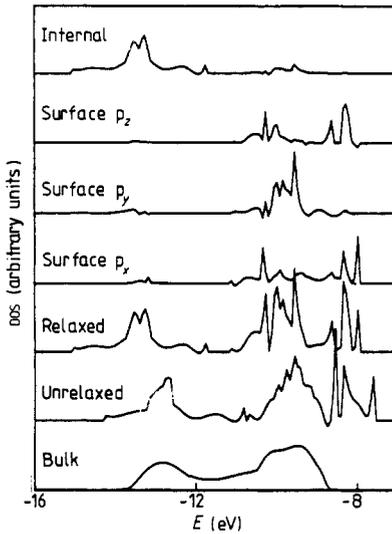

Figure 2. Total DOSS for MgO bulk and three-plane (110) relaxed and unrelaxed slabs and DOSS, projected onto different p atomic orbitals of internal and surface O^{2-} ions.

static' shift of the surface O 2s and 1s levels takes place with respect to those of the internal oxygen levels. Apart from this main effect, the fine structure of the DOS is appreciably different from that of the bulk and is indicative of some electronic redistribution which, if it is to be accurately taken care of, requires an SCF calculation. The effect of relaxation is that the surface chains approach the underlying ones in the central plane (see §3.1), and the electrostatic potential at the surface and subsurface O sites increases. As a consequence, p states associated with surface O ions are stabilised; in a three-layer slab, this stabilisation effect is still larger for ions in the central plane, and there is an overall increase in band-width by about 0.5 eV. These types of effect are absent in the (100) case (Causà *et al* 1986d) because the electrostatic interaction between planes parallel to that surface is negligible. It is worth mentioning that surface states similar to those described here have been found by Lee and Wang (1978) using both a Green function method and an LCAO semi-empirical technique. However, in their case, the split-off from the edge of the valence band was very small and almost identical in the (110) and (100) cases, in sharp contrast with the present results. The disagreement is possibly due to their failure to take into account properly the electrostatic field at the (110) surface.

In view of the large changes in the distribution of one-electron energy levels after the formation of the (110) surface, it may be wondered whether films as thin as those considered here are adequate models for this surface. There are some reasons for a

positive answer to this question. It may first be observed that the composition of the p eigenvectors associated with surface chains is not essentially altered with respect to the corresponding, more stable ones in the interior; since all those p states are occupied, the one-electron density matrix at the surface again describes an essentially ionic structure, and the sizes and shapes of the ions are only marginally altered with respect to the interior, as can be seen in the maps in figure 1. However, the electrostatic field at the surface of a three-layer slab closely reproduces that of a semi-infinite structure. As a consequence, the chemical characterisation of surface ions cannot be changed significantly by increasing the slab thickness. The destabilisation of surface levels has a counterpart in the high formation energy of this surface and can lead to relatively high reactivity of (110) surface O ions with respect to electrophilic reactants.

4. Conclusion

It has been shown that the MgO(110) surface is much more disturbed than the MgO(100) surface. This is seen from the considerable atomic relaxation and the increase in surface energy. The effective charges of the surface ions are somewhat reduced with respect to those in the bulk, the difference being $0.07e$ and $0.03e$ for O and Mg, respectively; however, the electronic structure at the surface remains essentially ionic. There is a certain disagreement between our prediction of rumpling of about 1.5% or less for both the MgO(100) and the MgO(110) surfaces and the value of 5% obtained for the (100) surface by Lewis and Catlow (1985) using atom–atom potentials. In contrast, the atom–atom potential calculations of Mackrodt and Tasker (1985) yield estimates of the surface energies for both MgO(100) and MgO(110) surfaces ($S = 0.0215$ au and 0.0825 au, respectively) in good agreement with our findings. Finally, the topmost valence states, which are associated with surface p orbitals on O ions are appreciably destabilised with respect to those on internal atoms and to those occurring in the (100) case. This could be of some consequence in the reactivity properties of surface O ions.

Acknowledgments

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