

## The electronic structure of oxygen ions in the step on the (001) surface of MgO

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 3471

(<http://iopscience.iop.org/0953-8984/3/20/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 11/05/2010 at 12:06

Please note that [terms and conditions apply](#).

## The electronic structure of oxygen ions in the step on the (001) surface of MgO

I V Abarenkov† and T Yu Frenkel‡

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK

Received 19 June 1990, in final form 25 February 1991

**Abstract.** In the present paper the confining potential and the wave functions of the oxygen anion in the step on the (001) surface of MgO are calculated from first principles. The confining potential is found strong enough for the  $O^{-2}$  anion in the step to be stable. The method is described and the calculated potential and wave functions are given in the paper.

### 1. Introduction

The structure and properties of defects in a crystal surface are of particular interest because defects strongly influence physical processes on the surface. Due to the very nature of the problem it cannot be solved by experimental means only. It is necessary to employ the electronic structure theory, which, together with experiment, could provide an adequate physical model. Also, for surface defects such as steps the electronic structure problem is difficult because the system under consideration has only one-dimensional periodicity with low symmetry and low coordination. To the authors' knowledge there are only a few wave-function calculations with the cluster method and geometry calculations with the atom–atom potential method [1–8].

For ionic and covalent solids it is expedient to describe the surface with defects in terms of interacting atoms or ions. Therefore, one of the appropriate methods for the calculation of the electronic structure of surface defects is the variable potential (vp) method developed for the bulk crystal [9, 10] and applied to the ideal surface [11]. In this method the local orbital description of a crystal is used and the crystal is considered to be constructed from ions. The vp is an *ab-initio* method based on the variational principle for the total electronic energy of the crystal.

### 2. Method

Let us consider a large but finite crystal and assume that at each lattice site  $g$  of this crystal there is an ion with several one-electron functions (orbitals)  $\varphi_{g,n}(\mathbf{r})$  localized around this site. The orbitals  $\varphi_{g,n}$  are supposed to be solutions of the system of equations

$$(F_g + V_g)\varphi_{g,n} = \varepsilon_{g,n}\varphi_{g,n} \quad (1)$$

where  $F_g$  is the Fock operator (non-linear) of a single ion  $g$ , and  $V_g$  describes the field of

† On leave from the Physical Department, Leningrad University, Leningrad, USSR.

‡ Permanent address: Physical Department, Kemerovo University, Kemerovo, USSR.

the rest of the crystal. The orbitals on the different sites are not required to be orthogonal. Equation (1) is similar to the exact Adams–Gilbert equation but, instead of the very involved operator, the potential  $V_g$  in the VP method is assumed to be a local one and to have an analytic expression with parameters. So (1) is the system of Hartree–Fock equations for every ion  $g$  in the external potential  $V_g$ , the equations for different sites not being coupled explicitly. The parameters in  $V_g$  have to be adjusted so as to bring the total energy of the crystal to minimum. The dependence of the energy of the crystal on these parameters is defined by the following process.

- (i) Select the set of parameters for the potential  $V_g$ .
- (ii) Calculate, to self-consistency, the Hartree–Fock problem (1) for every ion in the selected potential  $V_g$  and obtain the local orbitals  $\varphi_{g,n}$ .
- (iii) Calculate the total electronic energy of the crystal with obtained orbitals  $\varphi_{g,n}$  and with the exact Hamiltonian.

With the help of this process one can employ any suitable procedure to minimize the energy with respect to the parameters. The potentials  $V_g$  for different sites  $g$  are not independent because they are being adjusted simultaneously to minimize the same total energy of the crystal. Consequently, the equations (1) for different  $g$  are also not independent, but their coupling is hidden in the minimization procedure. In the VP method the potential  $V_g$  plays an intermediate role to define the subspace of trial functions (through equation (1)) for the energy functional. However, once the potential is found it can easily be used for some qualitative arguments.

In MgO the  $\text{Mg}^{2+}$  ion is rather tightly bound (the ionization potential of  $\text{Mg}^{2+}$  is 80 eV) and there is only a small difference between the free ion and the one in the solid. Therefore for practical reasons we took orbitals of the free  $\text{Mg}^{2+}$  as the cations  $\varphi_{g,n}$  orbitals. Contrary to that, the free  $\text{O}^{2-}$  ion is unstable and it is the crystal environment which stabilizes it. So in this case the potential  $V_g$  is the confining potential. The results of calculations for bulk MgO [10] and CaO [12] show that the confining potential is strong enough to help oxygen to hold two extra electrons and to become the  $\text{O}^{2-}$  ion.

In [11] it was shown that the confining potential for the surface anion in the (001) surface of MgO does not differ substantially from that of the bulk anion. The reason is as follows. The confining potential can be divided into a long-range (electrostatic) part and a short-range part. Both parts of the confining potential change considerably when transferring from the bulk to the surface but change in opposite directions, so for the surface anion the absence of the short-range repulsive potential from the vacuum region essentially compensates for the attractive electrostatic potential from the semi-infinite crystal. Moreover in [13] it was shown that the same compensation should take place in the cases in which the anion is in different positions in the surface step, or even in the kink. The fact that for both (001) and (011) surfaces of MgO the value of the surface  $\text{O}^{2-}$  dipole moments found in [14, 15] are one order of magnitude smaller than those obtained by a simple multiplication of the  $\text{O}^{2-}$  polarizability in MgO [16] by the electrostatic field, confirms the said compensation.

In this paper the electronic structure of  $\text{O}^{2-}$  ions in the step on the (001) surface of MgO is considered. Only the anions at the top of the step (anions T in figure 1) and at the bottom of the step (anions B in figure 1) were calculated here. All the surface ions except T and B were assumed to be ideal surface ions [11] and the rest of the crystal was assumed to be composed of the ideal bulk ions [10].

In analogy with the cases of the bulk or the ideal (001) surface of MgO, the confining potential for step anions was assumed to have the spherically symmetrical form

$$V_g(r) = V_{og}[1 - (1 - e^{-\alpha_g r})^{n_g}] \quad (2)$$

with three parameters  $V_{og}$ ,  $n_g$  and  $\alpha_g$ . In spite of lower coordination in positions T and B, the approximation (2) is a reasonable one because the cancellations of the long-range and the short-range parts of the confining potential due to the particular symmetry of the system [13] results in a smoothing of the potential. The spherical symmetry of the confining potential (2) means that the spherically symmetric part of the  $O^{2-}$  deformation is assumed to be the most important. Indeed in the Hartree-Fock calculations of MgO it was found [17] that the deformation of the bulk  $O^{2-}$  anion due to the tetrahedral distortion of the crystal was essentially spherically symmetric. Moreover, it should be noted that the potential (2) defines the symmetry of non-orthogonal orbitals and the orthogonalization procedure reduces this symmetry to that seen in the actual crystal.

The essential feature of the VP method is the energy expression. In this paper, as in our previous papers [9-11], we adopted the cluster expansion for the energy

$$E = \sum_g E_g + \sum_{g_1 > g_2} E_{g_1, g_2} + \sum_{g_1 > g_2 > g_3} E_{g_1, g_2, g_3} + \dots \quad (3)$$

The one-body term,  $E_g$ , is the self-energy of ion  $g$ , that is the value of the energy functional of the free ion calculated with orbitals  $\varphi_{g_n}$  of the crystal ion. The two-body term,  $E_{g_1, g_2}$ ,

$$E_{g_1 g_2} = e_{g_1} e_{g_2} / |R_{g_1} - R_{g_2}| + \Pi_{g_1 g_2} \quad (4)$$

is the sum of the long-range electrostatic term ( $e_{g_1}$  and  $e_{g_2}$  are the charges of the corresponding ions,  $g_1$  and  $g_2$ ) and the short-range term,  $\Pi_{g_1 g_2}$ , which contains different two-centre molecular integrals (overlap, Coulomb, exchange, Coulomb-exchange, etc) calculated with the orbitals  $\varphi_{g_1 n}$  and  $\varphi_{g_2 n}$ . Two-body terms were calculated in this work without additional approximations. The three-body terms,  $E_{g_1, g_2, g_3}$ , are very complicated. Apart from the different three-centre molecular integrals, they contain the inverse of the total overlap matrix of three ions. That makes the summation in (3) for low-symmetry systems, such as the surface step, unpractical. But three-body terms are comparatively small; they have order of magnitude  $S^2$ ,  $S$  being the maximum of the absolute values of overlap integrals (usually  $S \approx 0.1$  for ionic crystals). Calculating the three-body term within the  $S^2$  approximation and omitting all the multipole terms except those with  $l=0$  (see [9-11] for details) one can find the following expression for  $E_{g_1 g_2 g_3}$ ,

$$E_{g_1 g_2 g_3} = (t_{g_1 g_2 g_3} + t_{g_2 g_3 g_1} + t_{g_3 g_1 g_2})/3 \quad (5)$$

where

$$t_{g_1 g_2 g_3} = -2e_{g_3} \sigma_{g_1 g_2} (1/|R_{g_1} - R_{g_3}| + 1/|R_{g_2} - R_{g_3}| - 2/|R_{g_1 g_2} - R_{g_3}|). \quad (6)$$

Here

$$\sigma_{g_1, g_2} = \sum_{n_1, n_2} \left| \int \varphi_{g_1, n_1}^*(r) \varphi_{g_2, n_2}(r) dr \right|^2 \quad (7)$$

is the sum of the squares of the moduli of the overlap integrals between orbitals of ions  $g_1$  and  $g_2$ .  $R_{g_1 g_2}$  in (6) is equal to the cation radius-vector if ions  $g_1$  and  $g_2$  are cation and

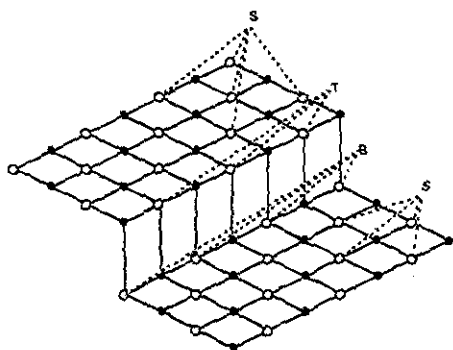


Figure 1. (100) surface of MgO with a step. ○: oxygen anion, ●: magnesium cation.

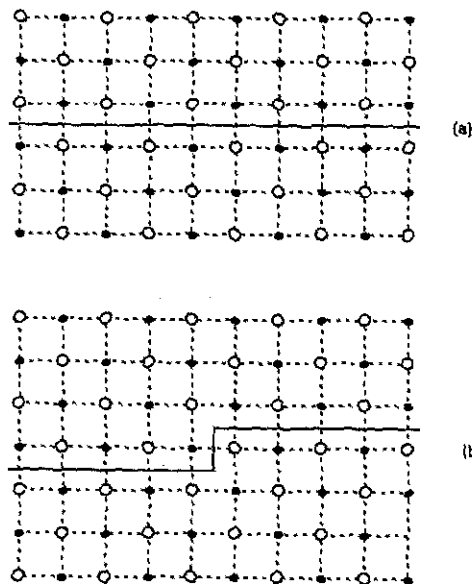


Figure 2. Separation of the crystal into parts (side view): (a) with ideal surfaces; (b) with surfaces with one step.

anion and is equal to  $(R_{g_1} + R_{g_2})/2$  if ions  $g_1$  and  $g_2$  are both cations or both anions. All  $n$ -body contributions with  $n > 3$  were omitted in the present work because they are of order of magnitude  $S^{n-1}$ , and the  $S^2$  approximation was already used in the three-body calculations.

It should be pointed out that although in the VP method the cluster expansion is used, this method is not the usual cluster method, because it does not single out the cluster from the rest of the crystal for a different approach. In the VP method all ions are treated in the same way. The cluster expansion, (3), is the expression which substantially helps the infinite summation over the crystal.

It is evident that in order to calculate wave functions of the step anions, only those terms in the energy expression which explicitly depend on the shape of these orbitals should be considered. It was found most convenient to obtain the expression for such terms by considering the separation of the crystal into two halves. Let  $E_0$  be the energy of the whole crystal,  $E_1$  the energy of one half of the crystal with ideal surface and  $E_2$  the energy of one half of the crystal with a surface with one step on it. Then the energy of the ideal surface is

$$W' = (2E_1 - E_0)/2 \quad (8)$$

and the energy of the surface with one step is

$$W'' = (2E_2 - E_0)/2. \quad (9)$$

Hence the energy of the step is

$$W = E_2 - E_1 = W'' - W'. \quad (10)$$

The separation of the crystal into parts can be considered as proceeding in three stages.

First, all the crystal orbitals are frozen to their nuclei and the relative positions of ions in each part are also frozen; then the parts are separated from each other to infinite distance. Second, the relative positions of ions in each part are kept frozen; but the orbitals are unfrozen so the ions are allowed to electronically relax. Third, the positions of the ions are also unfrozen, so ionic relaxation can take place together with a small additional electronic relaxation. Let  $W_1$ ,  $W_2$  and  $W_3$  be the energies of these three processes, respectively. Then

$$W = W_1 + W_2 + W_3 = (W_1'' - W_1') + (W_2'' - W_2') + (W_3'' - W_3'). \quad (11)$$

In practice, to calculate the value  $W_1$  one has to draw a surface dividing the crystals into parts (figure 2) and sum up the energies of broken bonds (including both the electrostatic and the short-range contributions).

Due to the one-dimensional periodicity of the crystal with the surface step it is not possible to consider the infinite total energies  $W_1$ ,  $W_2$  and  $W_3$  of the whole crystal but rather to consider the energies per unit cell  $w_1$ ,  $w_2$  and  $w_3$ . These are finite in spite of the infinite size of the unit cell because of the cancellation of the infinite sums in  $W'$  and  $W''$ .

We did not take into account the  $w_3$  contribution because estimations show that its influence on the orbitals of the anions is rather small. The displacements of the ions in the ideal (001) surface of MgO and in the step are also small and the experimental data concerning these displacements are uncertain. Therefore all the calculations reported here were carried out for the geometry corresponding to the ideal lattice.

To calculate  $w_1$  and  $w_2$  it is necessary to perform summation (3) over the crystal (infinite, semi-infinite with the ideal surface or with the step on the surface). The structure of (4) and (6) makes it possible to fulfil the summation of the long-range and the short-range terms separately. The long-range terms give rise to the various lattice sums which could be calculated using any conventional method of summation. As to the short-range contributions, we retained only  $\Pi_{g_1g_2}$  and  $\sigma_{g_1g_2}$  corresponding to the nearest neighbours and to the nearest anions because all others were found to be small, as is usually the case for ionic crystals. To distinguish between different ions we shall use the following notations for the subscript  $g$ :  $g = C$  for cations (as mentioned above, we assume the orbitals of cations in any position are the same),  $g = A$  for the bulk anion,  $g = S$  for the surface anion and  $g = T, g = B$  for anions in the step (see figure 1).

Thus, for example,  $\Pi_{TC}$  is the short-range interaction energy between the anion on the top of the step and the nearest to it cation. With these notations and after the summation over the crystal we obtain,

$$w_1 = -2(\Pi_{CA} + \Pi_{AA}) + 5.966\sigma_{CA} + 1.300\sigma_{AA} \quad (12)$$

$$w_2 = W_T - W_S + W_B - W_A + \sum_{i,j,k,l} [C_{ij,kl}(\Pi_{ij} - \Pi_{kl}) + D_{ij,kl}(\sigma_{ij} - \sigma_{kl})]. \quad (13)$$

The sum in (13) is somewhat artificial. It is written to make the expression compact and contains seven terms only, the indices of the summation and the values of coefficients for every term being shown in table 1. The numerical coefficients in (12) and (13) arise from various combinations of bulk and surface lattice sums.

### 3. Results and discussion

According to the  $\nu_P$  method the orbitals of  $O^{2-}$  ions T and B should be found by minimization of  $w_2$  alone because  $w_1$  does not depend on these orbitals. The anion B

Table 1. Coefficients in equation (13).

| <i>i</i> | <i>j</i> | <i>k</i> | <i>l</i> | $C_{j,kl}$ | $D_{j,kl}$ |
|----------|----------|----------|----------|------------|------------|
| C        | T        | C        | S        | 4          | -4.890     |
| A        | T        | A        | S        | 1          | 0.904      |
| B        | T        | A        | S        | 2          | 1.812      |
| S        | T        | S        | S        | 3          | 2.356      |
| B        | C        | A        | C        | 6          | -8.953     |
| A        | B        | A        | A        | 1          | 4.380      |
| B        | S        | A        | S        | 3          | 2.450      |

Table 2. The one-electron wave functions of oxygen in the step (oxygen T) with the Slater-type-orbital basis.

| $n_s$           | $\zeta_s$ | $C_{1s}$ | $C_{2s}$ | $n_p$           | $\zeta_p$ | $C_{2p}$ |
|-----------------|-----------|----------|----------|-----------------|-----------|----------|
| 1               | 7.6169    | 0.8958   | -0.1999  | 2               | 1.5566    | 0.5854   |
| 1               | 12.2200   | 0.0643   | -0.0091  | 2               | 3.4300    | 0.3136   |
| 2               | 2.7615    | 0.0047   | 0.6453   | 2               | 8.1268    | 0.0098   |
| 2               | 7.0898    | 0.0521   | -0.0721  | 3               | 1.2500    | 0.2286   |
| 2               | 1.4861    | -0.0007  | 0.4632   |                 |           |          |
| $\epsilon_{nl}$ |           | -20.375  | -1.0802  | $\epsilon_{nl}$ |           | -0.3643  |

Table 3. Parameters (in au) of anions on different sites.

| Site | $V_{og}$ | $\alpha_g$ | $E_g$   | $W_{int}$ | $\epsilon_{2p} - V_{og}$ | $q_g$ |
|------|----------|------------|---------|-----------|--------------------------|-------|
| A    | -0.90    | 0.74       | -74.312 | -1.41     | 0.50                     | -1.47 |
| S    | -0.90    | 0.65       | -74.343 | -1.52     | 0.44                     | -1.40 |
| T    | -0.79    | 0.65       | -74.357 | -1.32     | 0.43                     | -1.36 |

has six nearest neighbours, the same as the bulk anion, and eleven second-nearest neighbours in comparison with twelve for bulk anion. Therefore, anion B should not differ significantly from the bulk anion and at first one can neglect this difference. In this case  $E_B = E_A$  and also part of the sum in (13) vanishes. The parameters of the potential  $V_T$  for anion T were chosen as described in our previous papers [9-11], namely  $n_T = 10$ ,  $V_{0T} = -0.79$  au (the Madelung potential for the site T),  $\alpha_T$  is a variational parameter. The energy  $w_2$  was found to have a minimum at  $\alpha_T = 0.65$ . The corresponding orbitals of the oxygen T are given in table 2. The potential parameters  $V_{0g}$ ,  $\alpha_g$ , the self-energy  $E_g$ , the non-electrostatic part of the interaction energy  $W_{int}$  of the oxygen anion with the rest of the crystal, the 2p one-electron energy with respect to the bottom of the potential well,  $\epsilon_{2p} - V_{0g}$ , are given in table 3 for different lattice sites.

To consider the stability of the  $O^{2-}$  anion at the site T, equation (1) was solved for an  $O^-$  anion in the confining potential found for the  $O^{2-}$  anion. The results of the calculations are as follows. The self-energy of the  $O^-$  anion at the site T is only 0.7 eV

greater than the energy of the free  $O^-$  anion, and the deformation of the  $O^-$  anion is rather small. The difference between the self-energies of the  $O^{2-}$  and  $O^-$  anions at the site T is 11 eV. This quantity can be considered as the localization energy for the second electron of the  $O^{2-}$  anion at site T. The energy of the short-range (repulsive) interaction with the crystal environment of the  $O^{2-}$  anion is 3 eV greater than that of the  $O^-$  anion, and the long-range (electrostatic) interaction of the  $O^{2-}$  anion is 21 eV smaller than that of the  $O^-$  anion. Hence it takes 7 eV to remove one electron to infinity from the  $O^{2-}$  anion at site T, and therefore the  $O^{2-}$  anion at site T is stable.

The values of  $E_g$ ,  $W_{int}$ , and  $\epsilon_{2p} - V_{0g}$  from table 3 show that the localizing effect of the crystal environment on the step oxygen is similar to that for the bulk or surface anions. At the same time the confining potential for the anion T is weaker than that for the anion S, and consequently the electronic shells of the T anion are more diffuse than those of the S anion. To estimate this effect, the charge inside the ionic sphere

$$q_g = 8 - \int_V \sum_n |\varphi_{g,n}(r)|^2 dr \quad (14)$$

was calculated for  $O^{2-}$  in different positions. In (14) the integration is over the volume of an ionic sphere with radius 1.4 Å which is an appropriate value for the  $O^{2-}$  anion. The results of these calculations (see table 3) show that the charge inside the ionic sphere decreases in succession from the bulk to the ideal surface and to the surface with the step, but not substantially.

Calculations in which both T and B anions were allowed to relax were also carried out. The following potential parameters were chosen:  $n_T = n_B = 10$ ,  $V_{0T} = -0.79$ ,  $V_{0B} = -0.90$ ,  $\alpha_T$  and  $\alpha_B$  were variational parameters. The energy  $w_2$  was found to have a minimum at  $\alpha_T = 0.64$ ,  $\alpha_B = 0.71$ . Hence the confining potential for the B oxygen is in between the confining potentials for the bulk and the ideal surface, being closer to that of the bulk. Consequently the deformation of the anion B is smaller than that of the S oxygen, making it very small as expected. The value of  $\alpha_T$  had changed only a little when the ion B was allowed to relax, so the additional deformation of the anion T is very small indeed. Therefore, the conclusion about the stability of  $O^{2-}$  anions is valid in this case too.

## Acknowledgments

One of us (IVA) has pleasure in thanking Professor V Heine for the invitation to the Cavendish Laboratory and his warm hospitality and members of the TCM group for their friendly cooperation. Authors are also indebted to Dr V R Saunders for interesting and helpful discussions.

## References

- [1] Tsang Y W and Falicov L M 1975 *Phys. Rev. B* **12** 2441
- [2] Kunz A B, Guse M P and Blint R J 1976 *Int. J. Quant. Chem. Symp.* **N 10** 283
- [3] Kunz A B and Guse M P 1977 *Chem. Phys. Lett.* **45** 18
- [4] Colbourn E A, Kendrick J and Mackrodt W C 1983 *Surf. Sci.* **126** 550
- [5] Colbourn E A and Mackrodt W C 1983 *Solid State Ionics* **8** 221
- [6] Tasker P W and Duffy D M 1984 *Surf. Sci.* **137** 91



- [7] Fowler P W and Tole P 1988 *Surf. Sci.* **197** 457
- [8] Yanagihara T and Yomogita K 1989 *Surf. Sci.* **219** 407
- [9] Abarenkov I V and Antonova I M 1979 *Phys. Status Solidi b* **92** 389
- [10] Abarenkov I V and Antonova I M 1979 *Phys. Status Solidi b* **93** 315
- [11] Abarenkov I V and Antonova I M 1986 *Sov. Phys. Solid State* **28** 2020
- [12] Antonova I M 1979 *Phys. Status Solidi b* **94** K165
- [13] Abarenkov I V, Antonova I M and Frenkel T Yu 1990 *Poverchnost N* **1** 272 (Engl. Transl. 1990 *Phys., Chem. Mech. Surf.* **6** 66)
- [14] Causa M, Dovesi R, Pisani C and Roetti C 1986 *Surf. Sci.* **175** 551
- [15] Causa M, Dovesi R, Kotomin E and Pisani C 1987 *J. Phys. C: Solid State Phys.* **20** 4983
- [16] Abarenkov I V, Bratzev V F and Tulub A V 1986 *Sov. Phys. Solid State* **24** 153
- [17] Saunders V R 1990 private communication