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Abstract. We use a simple semiempirical quantum chemical model at a Hartree level of approximation, supplemented with a pair potential, to study defects (vacancies, self-adatoms and self-adatom clusters) on the Al(001) surface. We calculate their energies and equilibrium configurations and analyse the influence of the full relaxation of all degrees of freedom by comparing our prediction with the available *ab initio* calculations reported in the literature.

1. Introduction

Within the last two decades, much work, both theoretical and experimental, has been done on the study of solid surfaces, their physical properties and the interaction with foreign atoms. It is now well known that surface defects may alter the physical properties of crystal planes such as their structure and dynamics, and also their chemical behaviour.

The kinetics of adsorption and reaction processes deserve considerable attention in technological problems such as epitaxial growth, corrosion and catalysis [1]. Surface-sensitive experimental methods such as low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and field ion microscopy (FIM), provide large amounts of information about the surface structure and its chemical composition. Great advances have also been made theoretically; the techniques of quantum chemistry and first-principle calculations based on local-density formalism have been applied to study adsorption and chemisorption in low-index planes of simple metals, in order to understand specific surface properties and the rather complex processes which often occur in solid surfaces.

Both experimental and theoretical studies predict significant changes in the structure of the substratum when adsorption takes place on a surface, in the total coverage range from a single adatom [2] to complete monolayer coverage [3]. Also induced reconstruction is observed, as is the case for hydrogen on tungsten (001) [4].

It is unfortunate that most of the exciting experimental facts are observed for transition metals while the sophisticated calculations are preferentially done on simple metals. However, there are examples of complex behaviour that can be understood in terms of pictures delivered by simple semiempirical models, such as in Pt(100). In fact, FIM studies revealed that some Pt group metals show unusual behaviour in the structure of self-adatom clusters. In Pt(100) [5] the cluster structure is observed

to oscillate between a chain and an island as the number of adatoms increases from three to six. Embedded-atom method (EAM) calculations successfully predict these structural transformations as due to lattice relaxation contributions [5]. In Ir(001) [6], two-dimensional islands are stable for six or more adatoms. For five or fewer adatoms, linear chains are the most stable.

In general, lattice relaxations are computational intensive and many workers either estimate them through the magnitude of the forces in the ideal configuration or simply neglect their influence. Both are dangerous short-cuts imposed by the cost of the calculation. This limitation is the main motivation in our work on semiempirical quantum description of systems requiring more complexity than that included in the EAM. The semiempirical approach retains only the simplest terms in the many-body electron–electron interaction, namely the Hartree or direct Coulomb term, and includes a pair contribution to give the correct total energy. What is incorporated in this way, in contrast with the empirical EAM, are one-electron properties of the bonding, such as directionality, covalency and ionicity. This approximation has proved to give good results when tested on the predicted structures of small s–p metal clusters and on bulk Al [7]. Also recent results for carbon [8] and silicon [9] clusters using similar approximations give additional support for this type of approach.

In this work we present results on the surface properties, vacancies, adatoms and surface defects of Al(001), and their energetics and equilibrium configurations. Although direct comparison with experiments can be done for few of these properties, our interest in this metal stems from the relative simplicity of its band structure, thus providing a model system to be compared with other predictions based on more elaborate *ab initio* calculations.

2. The model

We use a self-consistent tight-binding or linear-combination-of-atomic-orbitals (LCAO) model for the description of the chemical bonding. Although a localized basis seems inadequate for a free-electron-like metal, it is a good choice for situations without any symmetry.

For our study of Al we adopt a parametrization according to the so-called extended Hückel model [10]. The Hamiltonian is a single-particle spinless LCAO, which retains only one- and two-centre integrals, namely

$$H = \sum_{i,\alpha} \epsilon_{i,\alpha} |i,\alpha\rangle\langle i,\alpha| + t_{i\alpha,j\beta}(|i,\alpha\rangle\langle j,\beta|) \tag{1}$$

where $\epsilon_{i,\alpha}$ is the on-site energy element, associated with the atom located at position r_i and orbital α, and $t_{i\alpha,j\beta}$ is the hopping integral from site j, orbital β, to site i, orbital α; $|i,\alpha\rangle$ represents the orbital α located at site i. Only valence 3s, 3p and 3d electrons are taken into account in the sum over orbitals, giving a basis of nine orbitals per atom. The many-body intra-site interactions are considered in a renormalized diagonal element $\epsilon_{i,\alpha}$ in such a way that, if no charge transfer occurs, it measures the energy level of the valence electron in the atomic limit. Close to defects and surfaces a small transfer of charge is expected. Self-consistent values of the diagonal elements are obtained from Gray's equation [11] (empirical on-site repulsion):

$$\epsilon_{i,\alpha} = \epsilon_{i,\alpha}^0 + U(q_i - z_i). \tag{2}$$

Here $\epsilon_{i,\alpha}^0$ is the αth energy level of the free atom i. The second term expresses the change in the intra-atomic Coulomb potential, q_i is the self-consistent total charge of atom i calculated by integrating the local density of states, z_i is the charge of the free atom i and U is an averge over orbitals of the intra-atomic two-electron Coulomb integral of the valence electrons of atoms i. In our case, U is an adjustable parameter which is chosen to reproduce charge transfer effects in a 55 octahedral Al cluster obtained performing an *ab initio* calculation [12].

The hopping elements $t_{i\alpha,j\beta}$ are given by

$$t_{i\alpha,j\beta} = K S_{i\alpha,j\beta} \tag{3}$$

where K is an adjustable constant chosen to reproduce the band width, and $S_{i\alpha,j\beta}$ are the overlap integrals between atomic s, p and d Slater orbitals [13] with the same exponent $\zeta = 1.167$. The resulting overlap integrals are ten radial functions $(ss_\sigma, \ldots, dd_\delta)$ times an angular part depending on the orientation of the vector $r_j - r_i$. For practical reasons a smooth spatial radial cut-off is imposed:

$$v_{\text{cut}}(r) = [\exp(r - r_{\text{cut}})/\Delta + 1]^{-1} \tag{4}$$

where r_{cut} is a cut-off distance equal to 5.35 Å, between third and fourth neighbours, and Δ is a parameter adequately chosen to avoid spurious forces.

The orthogonal LCAO formulation requires one to solve

$$(\mathsf{H} - \lambda \mathsf{I})\phi = 0. \tag{5}$$

The total energy is calculated as

$$E = E_{\text{coh}} + E_{\text{rep}} \tag{6}$$

$$E_{\text{coh}} = 2 \sum_n \lambda_n f(\lambda_n) \tag{7}$$

$$E_{\text{rep}} = \tfrac{1}{2} \sum_{i,j} V_{i,j}. \tag{8}$$

E_{coh} is given in terms of the doubly occupied molecular levels λ_n, $f(\lambda_n)$ is the Fermi function at zero temperature, λ_n are the solutions of equation (5) and E_{rep} is an adequate repulsive pair potential chosen to reproduce some set of properties, namely the equation of state of Rose *et al* [14] for Al (lattice parameter, cohesive energy and bulk modulus), the interstitial formation enthalpy and the relative stability of the FCC versus the BCC phase.

For the relaxation procedure we need the forces. The electronic contribution is evaluated using the Hellman–Feynman theorem [15]:

$$F_i = \sum_i \langle \phi | \nabla_i(\mathsf{H}) | \phi \rangle + \nabla_i (E_{\text{rep}}). \tag{9}$$

To summarize, in this model the electronic contribution to the total energy contains few parameters: K in equation (3), U in equation (2), and the diagonal energies in equation (1). The repulsive pair potential has the necessary freedom to fit experimental data.

Solving these equations for the largest problem reported in this work (133 atoms) implies finding 200 eigenvalues and eigenvectors out of a 1197×1197 matrix, which is done by either direct diagonalization or using the Car–Parrinello [16] algorithm as implemented in [9]. According to our experience, for this size and fraction of eigenvectors, both procedures require similar computing times.

3. Results

3.1. Bulk properties

The determination of the different parameters involved in the model is done by fitting to bulk properties of the metal. The electronic parameters are K in equation (3), U in equation (2), and the diagonal energies in equation (1). As a consequence of the very large band mixing in Al, not only s and p electrons are included, as we did in previous work [7], but also d electrons. As reported in [17], their influence certainly affects the occupied states of the valence band, mainly for energies close to the Fermi level.

The parameter K and the split between the diagonal energies $\epsilon_{i,\alpha}^{0}$, for $\alpha \equiv s$, p and d, are chosen in order to reproduce some characteristics of the density of states (DOS), such as the band width and the integrated partial DOS as reported in [18]. The resulting values are $K = -1.75$, $\epsilon_{s} = -1.6$ eV, $\epsilon_{p} = 3.2$ eV and $\epsilon_{d} = 11.2$ eV.

The parameter U in equation (2) is set to 5.1 V, the value at which we find the closest agreement with charge transfer effects occurring in an Al octahedral cluster of 55 particles, as predicted by first-principle calculations [12].

The pair potential is adjusted to reproduce the equation of state of Al [14] so that the energy of cohesion, the lattice parameter and the bulk modulus are exactly reproduced. Also used in the fitting procedure are the energy of formation of the dumbbell interstitial, which gives the potential more information about the core behaviour, and the relative stability of the FCC versus the BCC phase. The resulting repulsive pair potential, which is a tabulated numeric function, is shown in figure 1.
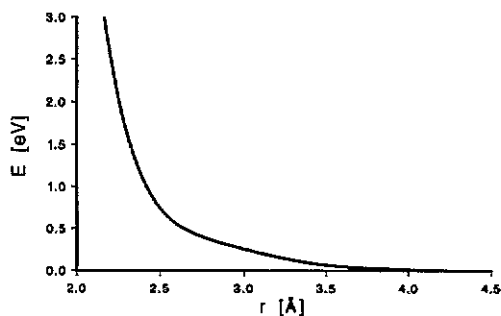

Figure 1. Pair potential designed to fit bulk Al properties. The cut-off is at 4.5 Å, between second and third neighbours.

Table 1 summarizes the experimental data used in the fitting, together with the predicted values for other bulk properties, such as the elastic constants c_{12} and c_{44}, and the vacancy and interstitial formation enthalpies. These predictions show very good agreement with the corresponding experimental values.

3.2. Surface properties

The reliability of the results on surface defects depends on the quality of the free-surface representation. Experimentally, some agreement is found on the behaviour of the Al(001) surface, i.e. no relaxation to within the experimental precision [19–21], but the Al(111) surface is reported to contract by 8.1% [19], to expand by 2.2% [20]

Table 1. Experimental values used to determine the repulsive potential, and predicted properties of the bulk: *, used in the fitting.

	This model	Experimental	
E_{coh} (eV/atom)	*	3.2	[37]
a_0 (Å)	*	4.05	[37]
c_{11} (10^{10} dyn cm^{-2})	*	10.82	[38]
c_{12} (10^{10} dyn cm^{-2})	5.91 [39]	6.13	[38]
c_{44} (10^{10} dyn cm^{-2})	2.83 [39]	2.85	[38]
ΔH_v^f (eV)	0.68 [39]	0.62–0.77	[39]
ΔH_i^f (eV)	2.9	3.0	[39]

or to expand by 0.9% [22], while the Al(110) surface is found to contract by 10–15% [21, 23, 24] and also to oscillate as deeper layers are analysed [25, 26].

On the other hand, recent theoretical calculations for a five-layer film of Al(111) predict a negligible contraction of 0.25% [27]; for nine layers an expansion of 1% [28], and an oscillatory behaviour for three, five and seven layers, due to quantum size effects [29]. The results for Al(001) show no displacement [30].

Surface relaxations and charge densities are related. Departures of the charge neutrality can be induced by surface states. Detailed calculations of band structure for Al(111) and Al(001) [31–33] show no net charge on the outermost layer, a result which is interpreted in terms of the absence of Friedel oscillations due to the large electronic density of Al.

To study the free Al(001) surface we use a six-layer supercell containing 108 atoms, repeated periodically in the x and y directions; the eigenvalues of equation (5) are calculated at the Γ point of the two-dimensional Brillouin zone. In the relaxation procedure, minimization is performed with a steepest-descent algorithm and convergency is achieved when all forces are less than 0.05 eV Å^{-1}. Table 2 shows the predicted values for the surface energy, 0.08 eV Å^{-2}, first-interlayer expansion, 0.7%, and second-interlayer contraction, 1.3%, together with the experimental results. The charge transfer that we obtain is 0.02e leaving the surface layer and spreading in the second and third layers. Considering the limits of precision of both the experiments and the calculations, we consider these results to be in very good agreement.

Table 2. Predicted values for surface energies and layer relaxations.

	This model	Experimental	
γ_{100} (eV Å^{-2})	0.08	0.08–0.09[a]	[28]
Δz_{12} (%)	+0.7	0.0	[19]
Δz_{23} (%)	−1.3	0.0	[19]

[a] These are theoretical values for γ_{110}.

For defects on the surface we use a periodic sample of four layers and 4×4 unit cells in the plane, making a 128-atom supercell. Relaxations are done in such a way that the two bottom layers of the slab are kept fixed at their bulk positions.

3.2.1. Vacancies and divacancies. These were calculated by removing one and two neighbouring atoms respectively from the surface of the supercell to infinity, and relaxing the supercell. The resulting enthalpy of formation for vacancies is 3.32 eV,

lower than the corresponding calculation performed in the bulk, which is 3.88 eV (note that this is not the usual value of vacancy formation enthalpy because the removed atom is located at infinity instead of relocated in a perfect lattice site; the difference is the cohesive energy, 3.2 eV). This result is consistent with the higher coordination associated with one atom in the bulk (12) when compared with this surface (8). It is found that the vacancy nearest neighbours relax outwards by 0.04 Å in the surface plane and 0.08 Å downwards. These relaxations are compatible with the surface under tensile stress as predicted for other Al surfaces by first-principle calculations [28]. In fact Needs evaluated the surface stress tensor for Al(111) and Al(110) surfaces, obtaining a stress that would give a reduction in lattice constant of approximately 4%. He analysed the energetics, arriving at the conclusion that the kinetic and electrostatic terms are the most relevant, while exchange–correlation gives the minor contributions to the stress tensor. We also found a downward relaxation of the nearest neighbours of the vacancy by 4% of the interlayer spacing which is compatible with bond-order bond-length arguments.

The energy of the saddle point for vacancy migration is 0.15 eV, with the atom performing the jump located 0.12 Å above the surface. The relaxation of the two nearest neighbours to this atom, which are located in the second layer, is 0.06 Å parallel to the surface. The second neighbours, contained in the surface plane, relax 0.07 Å away, with a small component in the direction perpendicular to the surface.

For the divacancy the enthalpy of formation is 6.81 eV. The binding energy is then $\Delta E_b = 0.17$ eV, indicating that vacancies strongly repel each other.

3.2.2. Adatoms. The adsorption energies and final configurations of adatoms on the Al surface are obtained by minimization of the total energy starting from a system in which the adatom is placed in a fourfold hollow position over the 128-atom Al supercell, as shown in figure 2.
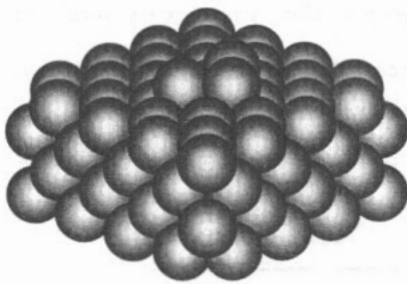
Figure 2. Example of the actual size of the simulations: Al $4 \times 4 \times 2$ cubic cells containing one adatom in a fourfold hollow position.

We perform two types of calculation. First we calculate the energy of the system when only the adatom z coordinate relaxes towards its equilibrium position; all other nuclear positions are frozen. The resulting adsorption energy is 2.53 eV, with the extra atom placed 1.86 Å above the surface. If a full relaxation is performed, the binding energy increases to 2.66 eV, with the adatom closer to the surface as a consequence

of a radial expansion of 0.04 Å of first-nearest neighbours on the surface. The final position of the adatom is 1.77 Å above the surface. Therefore relaxations account for 5% of the adsorption energy and distance to the surface.

The final results for the adsorption energy and position compare well with those in [11], namely 2.93 eV and 1.72 Å respectively. It is important to point out that this comparison is made for perfect crystals having a different cohesive energy: our cohesive energy for bulk Al is 3.2 eV/atom, while Feibelman's [34] result is 3.34 eV/atom. Therefore the cohesive energy of adatoms, when normalized to equal bulk values, are 83% and 88% of the cohesive energy, for our results and the *ab initio* results, respectively.

Next we consider two Al adatoms placed on adjacent fourfold hollow positions. We find that the energy required to separate the adatom pair while they both remain adsorbed is 0.08 eV, only 3% of their adsorption energy. The adatom pair distance is reduced from its unrelaxed value of 2.86 Å by 0.02 Å, and their final z coordinate is increased from 1.77 to 1.91 Å above the surface. This indicates the weakening of the adatom–substrate bonds and the strengthening Al–Al adatom interaction, in excellent agreement with Feibelman's calculations. He predicts a dissociation energy of 0.07 eV [35].

3.2.3. Adatom aggregates. The geometry adopted by small aggregates of adatoms may not be simple because of the competition between several factors. First, the forces between atoms in a small cluster show a complex angular behaviour, giving rise to intricate geometries. Second, the interaction with the substratum imposes restrictions on the cluster geometries. Third, surface relaxations play a non-negligible role, since they can induce structural transformations related to geometrical frustrations. The model we apply in this work, although simple compared with full *ab initio* results, contains the main components of these three factors.

We study clusters of three, four and five Al adatoms on the Al(001) surface relaxing all the degrees of freedom.

Three adatoms may adopt a linear or a triangular configuration. Our result favours the triangular configuration by 41 meV. The average cohesive energy per atom in this configuration is 2.79 eV; when compared with 2.66 eV for a single adatom, it appears that there is a cohesive energy 0.13 eV/atom in the cluster. The average height above the surface is 1.89 Å, with the atom at the rectangular vertex located 0.05 Å lower than its partners (figure 3).
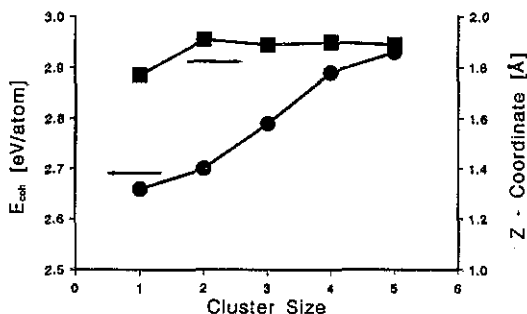

Figure 3. Cohesive energy per adatom in adatom clusters over the Al(001) surface. Also shown are the average distances to the surface.

Four adatoms may adopt linear, T, parallelogram or square shapes. The square shape is favourable by 110 meV with respect to the T shape, by 243 meV with respect to the parallelogram shape, and by 359 meV with respect to the linear shape. The cohesive energy in the square cluster is 0.23 eV/atom; the height above the surface is 1.9 Å.

Five adatoms may adopt

(a) a square shape of second-nearest neighbours with an atom at the centre,
(b) a square of nearest neighbours with an atom on top,
(c) a square of nearest neighbours with an atom on a side or
(d) a linear chain.

The configuration (c) is preferred by 162 meV with respect to (a), by 546 meV with respect to (b), and by 653 meV with respect to (d). The cohesive energy in the cluster is 0.27 eV/atom and the average height above the surface is 1.89 Å.

These reults show that the configuration with the largest number of nearest neighbours is always preferred, regardless of substratum relaxations and angular forces. Al is then apparently much simpler than the cases of Pt and Ir mentioned in the introduction. Figure 3 shows the evolution of the adsorption energy and distance to the surface as a function of the size of the cluster.

4. Conclusions

We presented a self-consistent LCAO model to study some Al surface properties. We have adjusted the model parameters to reflect the bulk behaviour of the material, and we have extrapolated the semiempirical description to different environments, calculating properties of vacancies and adatoms on the Al(001) surface.

Our results are supported by the agreement with several of Feibelman's predictions of adatom properties based on a first-principle calculation, namely the single adatom energy and position, and the binding of two adatoms.

Clusters of adatoms show no structural transitions as a function of their size, as was recently measured in other materials, such as Pt and Ir.

We also study single-adatom diffusion energies. Two possible mechanisms for the self-diffusion on Al(001) surface are possible. In the bridge configuration the adatom is placed above the surface at the same distance from two adjacent binding sites. In the exchange mechanism, two Al atoms are symmetrically adsorbed above a surface vacancy. The adatom originally placed at a fourfold hollow position moves towards the vacancy left by its partner, which emerges towards the nearest equilibrium adatom position. In this way the original adatom is exchanged with a substratum surface atom. We obtained that the usual bridge mechanism is preferred, in contrast with Feibelman's [36] results. Arguments favouring the exchange process are based on the fact that in the saddle point configuration both moving atoms satisfy a local coordination 3, which would be energetically favourable because of the valence 3 of Al.

There are two possible explanations for this discrepancy: one highlights the importance of full relaxation, decreasing the energy of the bridge configuration, and the other recognizes the limitations of the empirical approach for cases of strong covalency, thus increasing the energy of the bridge geometry.

The first possible reason is the influence of the full relaxation in the bridge configuration. The unrelaxed result reported in [36] gives a barrier of 0.65 eV. When

the two nearest neighbours are allowed to relax, the barrier decreases to only 0.63 eV. Our result gives 0.33 eV and 0.11 eV for the unrelaxed and relaxed configurations, respectively. This significant change is due to important displacement of several atoms in the neighbourhood, and not only the nearest neighbours; for instance, the nearest neighbours to the adatom move 0.12 Å away along the $\langle 1, -1, 0 \rangle$, which is three times greater than the result obtained by Feibelman [36]. This explanation gives a plausible reason for our low value of the activation energy in the relaxed bridge configuration. The second possible reason for the discrepancy concerns the quite high value that we obtain for the exchange mechanism, namely 0.63 eV, compared with Feibelman's result of 0.20 eV. This last value is interpreted in terms of the strong covalent bonding between the three nearest neighbours of each partner. It is conceivable that our Slater–Hubbard Hamiltonian is too simple to account correctly for the role of electron correlation in bonding, when the coordination number equals the number of valence electrons. We do not have elements to decide which of these effects is more important. However, even discarding our exchange calculation because of inaccuracy, it is still intriguing that our bridge result, 0.11 eV, is less than the exchange barrier, 0.20 eV, reported in [36]. It is pertinent to point out that the interest in these types of semiempirical approach is to emphasize what is neglected in more powerful calculations, as in this case the full relaxation. Our result on the diffusion of adatoms just sets a warning on the magnitude of relaxations, which are usually discarded using qualitative arguments, and suggests that it would be welcome to perform *ab initio* calculations considering further relaxations.

Acknowledgments

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