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Oxygen Chemisorption of a Small Aluminum Cluster

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The chemisorption of O on the (100) surface of Al is studied within the Hartree-Fock-Slater self-consistent field model using a multiple-scattering method. Good agreement is obtained with the spectral results of the jellium calculation of Lang and Williams when the O-metal distance approaches their equilibrium separation. For adsorption at a hole site, we argue that the O($2p$) resonance should be deeper in the band and broader than suggested by the jellium model.

Most discussions of the chemisorption problem emphasize the extended nature of the substrate[1-3] and as a result are in terms of models where local aspects of the bonding are rather crudely treated. Alternatively a local framework can be adopted, including with the adatom a few substrate atoms in positions fixed by the bulk. This "surface molecule"[4] can then be treated by methods applicable to molecular systems. The advantage of such an approach over the currently popular jellium model, which emphasizes the electron-gas-like behavior of the substrate, is the consistent treatment of the atomic nature of substrate and adsorbate. The disadvantage is that the coupling between surface molecule and bulk is poorly described.

In this Letter we describe a self-consistent solution of the Hartree-Fock-Slater equations[5] for atomic oxygen chemisorbed on a cluster of five aluminum atoms arranged to simulate the hole site on the (100) metal surface (Fig. 1). The calculation was carried out using the multiple-scattering method as adapted to treat the bound states of a finite molecular cluster,[6] using the usual muffin-tin model potential. The states were obtained as symmetrized partial-wave expansions including s and p waves for the atomic sites with d waves added for the boundary. Self-consistent eigenvalues, charge density, and total energy of the cluster were calculated for various positions of the oxygen atom. Similar calculations have recently been reported[7] for a Ni substrate. Our choice of Al was motivated by two criteria: Firstly, for an s-p bonded substrate, the d-wave resonance is high in energy suggesting that, as a first approximation, d waves in the atomic spheres may be omitted. Secondly, the simple-metal character of Al enables us to

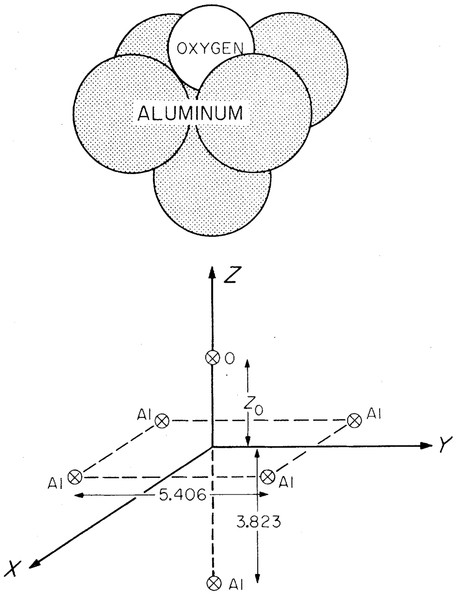

FIG. 1. Cluster geometry. In the lower part of the figure the crosses denote the positions of the nuclei. The outer bounding sphere (see Ref. 6) was chosen so that it just touches the outermost muffin tin. Distances are in a.u. and the atoms in the x-y plane represent four nearest-neighbor atoms of the (100) surface.

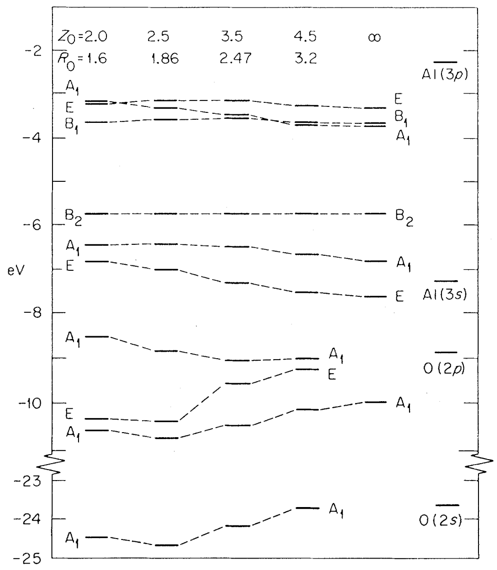

FIG. 2. Eigenvalues of the starting potential (overlapped neutral-atom potentials). The coordinate Z_O refers to the distance shown in Fig. 1. R_O is the radius of the oxygen muffin tin, chosen so that this just touches those of the aluminum atoms in the surface layer.

compare it with the jellium model, for which an essentially exact solution is available.[3]

The calculational procedures for this problem have been described previously.[8] For the exchange-correlation potential, an $X\alpha$ approximation[5] was used with $\alpha = 0.73$. From the lowest-lying occupied states, a new charge density and muffin-tin potential were constructed and iterated until the eigenvalues for successive potentials changed by less than 1%. At each stage the average intersphere potential was determined by numerical integration.[9]

The eigenvalue spectrum of the starting potentials for various separations of the O atom from the Al surface appears in Fig. 2 (distances are in atomic units throughout). At the right of the figure are the levels of the five-atom Al cluster alone ($Z_O = \infty$) and the valence eigenvalues of the isolated neutral Al and O atoms. Including the O atom in the cluster introduces three new levels originating mainly from the O(2s, 2p) states. The O(2s, 2p_z) states form σ-hybridized orbitals (of type A_1) and the O(2p_x, 2p_y) states mix with the Al partial waves to form E-type degenerate π bonds. Each symmetry type forms bonding and antibonding combinations and theses levels shift as expected as the O-atom approaches the surface. Iteration to self-consistency changes this simple picture significantly, however. Self-consistent eigenvalue spectra for three positions of the oxygen nucleus are shown in Fig. 3. By each level the corresponding fraction of the charge located in the O sphere is noted. The re-

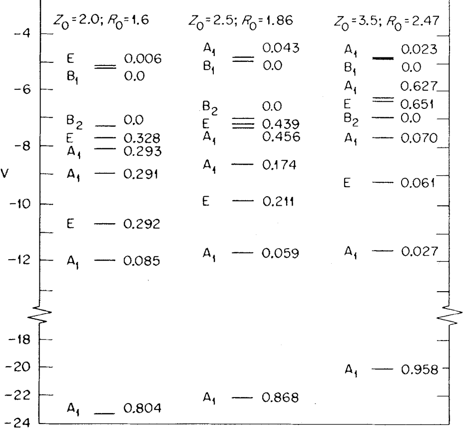

FIG. 3. Eigenvalues of the fully self-consistent potential. The labeling is the same as in Fig. 2. The number next to each level denotes the fraction of its charge which is located in the oxygen muffin tin.

sulting picture of the energy distribution of the electron density in the O sphere (the "local density of states") shows some interesting general features. As the oxygen moves away from the surface, the O(2p) resonance moves to the Fermi level (not the neutral-atom limit) and the system stabilizes when the O charge is shared with degenerate Al cluster states. This is, of course, inevitable since the tunneling of electrons from the metal will continue until a common Fermi level is established. As the O atom approaches the surface, the fraction of charge located in the O sphere decreases and spreads over a larger energy range. At a distance of 3.5, the p-like charge in the O sphere arises mainly from the σ and π levels which lie close together about 1.5 eV below the Fermi level. As Z_O decreases, these levels drop further and lose charge to other states lower in energy. At $Z_O = 2.0$ the O charge is distributed rather equally among four levels.[10] There is also a reduction in the charge transferred to the O sphere, reflected by a corresponding drop in the O(2s) level. The significant π bonding between the O atom and substrate generates considerable interstitial charge density (see Fig. 4); thus the charge transfer in the oxygen sphere is not fully indicative of charge shifts in the system as a whole.

It is interesting to compare our results with those of Lang and Williams[3] (LW) who discuss the chemisorption of O, H, and Li on a jellium substrate. For oxygen they found a minimum in the binding-energy curve with the O nucleus a distance of 1.1 from the edge of the positive background (equivalent to $Z_O = 3.0$[11]). To compare we interpolate our results for $Z_O = 2.5$ and 3.5. Firstly, we agree roughly on the position of the Fermi level [−4.0 eV (LW) and −4.8 eV]. Secondly, our metal band, though substantially narrower than that of LW, is not unphysically narrow. Thirdly, the O(2s) states lie at −20 eV (LW) and 21 eV. The position of this level provides a measure of the charge distribution, being particularly sensitive to the charge density in the O sphere.[12] Finally, our energy distribution of the charge density in the oxygen sphere shows a sharp peak 2 eV below the Fermi level with some tailing on the low-energy side, precisely the same features as found by LW. The extent of agreement between these two quite different calculations is remarkable and we regard it as a sign that the essential element in this system is a proper treatment of the charge transfer, i.e., self-consistency.[13]

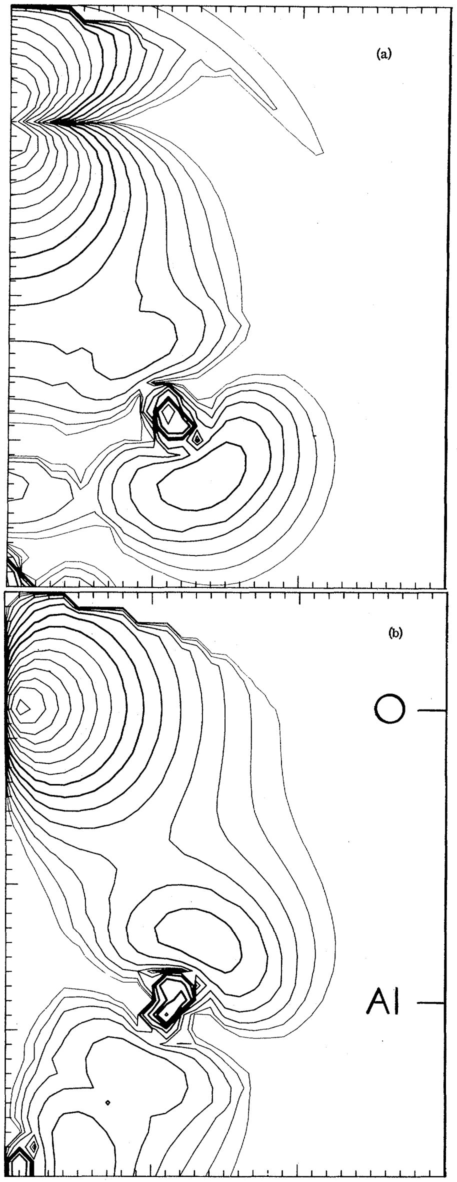

FIG. 4. Charge densities for eigenstates corresponding to the sharp O(2p) resonance for symmetry types (a) A_1 and (b) E showing σ and π bonding, respectively. The plot is for the plane $x = y$ (Fig. 1) with $Z_O = 7.0$. The vertical position of the O and four nearest Al atoms is noted on the right. Adjacent contours differ by a factor of 2.

Although our eigenvalue spectrum shows good agreement with LW at the jellium equilibrium separation, calculation of the total energy of our cluster, while subject to further refinement, shows no minimum there. This is not surprising, however, since the jellium energy curve represents, in a sense, an average between bonding at hole and atom sites.[14] Simple geometric considerations suggest that for a hole site, which one expects to be favored, the O-surface-plane distance is much less than 3.0. (For O on Ni, for instance, this distance is 1.86.[15]) In fact, $Z_O = 3.0$ would correspond, in our configuration, to an Al-O bond length of 5.0, much greater than the larger of the two bond lengths observed in alumina, namely, 3.7.[16] Recent work-function measurements[17] for O adsorbed on all three low-index faces of Al showed almost zero derivative at zero coverage, indicating at most a small charge transfer. While this does not support the dipole moment calculated at equilibrium separation by LW, it is consistent with our results for $Z_O = 2.0$ (more so than for $Z_O = 3.0$). As noted earlier, the energy distribution of the electron density in the O sphere is very sensitive to the O-surface-plane distance. A change of Z_O from 3.0 to 2.0 shifts the O($2p$) resonance deeper in the band and broadens it considerably. We thus suggest that any resonance observed for O adsorbed on Al(100) will be broad (probably more than is the case for Ni where it is a few volts)[18,19] and centered deeper in the band than predicted by the jellium model.

In concluding, we note that the relationship between the eigenvalue spectrum and measured energy distributions is not a simple one and may differ from one spectroscopy to another. It is quite difficult to estimate the effect of relaxation on the observed spectrum and, in connection with our statements concerning the O($2p$) resonance, we expect that the existence of a well-defined resonance in the eigenvalue spectrum is probably a prerequisite for finding one in, say, an ion-neutralization spectroscopy, ultraviolet photoemission spectroscopy, or field-emission experiment.

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[12] We note that the factor $\alpha = 0.73$ differs only slightly from the value employed by LW ($\alpha = 0.67$); use of the same value would improve the agreement for this level.

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