Bonding of oxygen on aluminum: Relation between energy-band and cluster models*

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(Received 6 July 1977)

A study of some factors which influence the position and shape of the resonance bands of adsorbates on surfaces is presented with emphasis upon the case of oxygen chemisorbed on aluminum. A twofold approach has been taken to determine the relative roles of local and delocalized electron effects: the energy-band structure for a thin film geometry is correlated with the eigenvalue spectrum from a "surface-molecule" cluster model. Oxygen resonance features are found to depend mainly upon a bond mechanism involving orbitals directed parallel to the surface such that the local bonding in the cluster model provides a reasonable description of the resonance position. Delocalization of the substrate electrons in the plane is found to provide a bulklike background against which the localized resonance is observed.

I. INTRODUCTION

The dissociative chemisorption of oxygen on aluminum has been the subject of a variety of experimental[1-4] and theoretical[4-7] studies. While there is agreement between the atom-jellium model[5] and the structural cluster approach[6] on the position of the oxygen resonance for large separations, at closer adatom distances the structural details of the surface become important, leading to some differences. But within structural models which treat the substrate quite differently, it has been found that features of the adsorbate electronic structure are very similar. For example, results of an energy-band treatment[8] using potential and geometrical parameters consistent with those of a cluster model can be directly related to the adsorbate features of the cluster.

The evolution of the resonance in the band model from the localized-cluster spectrum is discussed in this paper. The origin of the observed insensitivity of some of the O resonance features to substrate details is related to the mode of chemisorptive bonding. The relative effects of substrate thickness, adsorbate configuration (site and coverage dependencies), interadsorbate interactions, and the effects of wave-vector modulations on the resonance features are discussed. It is found that for this system, characterized by rather strong adsorbate resonance structure, the major features of the resonance are determined by bonding with the near-neighbor substrate atoms. The main effect of increasing substrate thickness is to produce a more bulklike substrate density of states, against which the adsorbate structure is observed. It is in this sense that the surface molecule and thin-film models are both valid for describing the adsorbate structure of this type system.

II. METHOD

The electronic structure of surface systems is generally treated in one of two ways: the "surface-molecule" cluster approach in which an atom or molecule at the surface and a limited number of near-neighbor substrate atoms forms a molecular cluster, and the boundary condition is taken to approximate the environment in which it is embedded. This permits the use of molecular-orbital theories[9] at various levels of sophistication. The second approach is based on an energy-band model in which two-dimensional periodicity in the surface plane is assumed,[10] and the unit cell extends into the surface with boundary conditions defining either a film structure[11,12] (matching into vacuum) or a semi-infinite solid[13] (matching into bulk). Three-dimensional repeated-slab models[14] are also being explored. The delineation of the ranges of applicability of these two general approaches is usually clear. Low surface order, the low coverage limit in chemisorption or localization in the property of interest appear better suited for a localized surface-molecule model.

There are obvious shortcomings with the surface-molecule model for chemisorption related to broken bonds and finite cluster size. Care must be exercised in its use to assure that the number of atoms included converges the calculated quantity of interest. An attractive alternate way to account for the lateral extent of the surface is afforded by the thin-film energy-band model. In this approach, the basis set is Bloch-like with regard to translations in the surface, but atomiclike in the normal direction, so that the electrons are delocalized in two dimensions only. This approach offers the distinct advantage of allowing the spatial extent of the surface to be included in a simple way.

The linear-combination-of-atomic-orbitals (LCAO) band method used in this work is based on the discrete variational method[15] (DVM) as previously adapted to a thin-film geometry.[11] Briefly, the basis set is written in the form

$$\chi_j(\vec{k}, \vec{r}) = C_j \sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu} \phi_j(\vec{r} - \vec{R}_\nu - \vec{\mu}_j) \, ,$$

where C_j is a normalization constant, and ϕ_j is an atomiclike function located at the site defined by the vector $\vec{\mu}_j$ within the surface cell at lattice position $\vec{R}_\nu$. The wave vectors $\vec{k} = (k_x, k_y, 0)$ and the lattice vectors are confined to the xy plane. Normal to the surface the basis functions behave like

$$\chi_j(\vec{k}, z) \propto f(z) e^{-\alpha z} \, ,$$

where $f(z)$ is a polynomial in z. The basis is thus Bloch-like for translations in the surface, allowing itinerant electron behavior in the plane of the

(a)

(b)

FIG. 1. (a) Atom sites on the (001) surface of fcc. Lattice vectors $\vec{a}_1$ and $\vec{a}_2$ define the intersection of surface unit cell with plane; (b) the corresponding two-dimensional Brillouin zone (lower) with minimal region shaded.

surface, while the atomlike character normal to the surface makes the basis suitable for molecularlike bonding in that direction. In computations with this scheme no "tight-binding" approximations or averages of the potential are invoked. While this energy-band formulation is rigorously applicable only in the limit of ordered substrate and overlayer geometry, many cases of surface disorder can be well approximated by an ordered model. The criteria for this to be a valid approximation will be discussed later in the text.

With this basis the usual linear variational problem is solved for the Hartree-Fock-Slater self-consistent-field Hamiltonian using an exchange parameter $\alpha = 0.73$, this choice being consistent with our earlier cluster calculations.[6] Within the DVM model, all matrix elements are evaluated by numerical quadrature within the surface unit cell. The intersection of this surface cell defined by primitive lattice vectors $\vec{a}_1$ and $\vec{a}_2$ is shown in Fig. 1(a) for the (001) surface of a cubic lattice (the unit cell is of infinite extent normal to the surface). The corresponding two-dimensional Brillouin zone appears in Fig. 1(b) and is defined by reciprocal-lattice vectors $\vec{b}_1$ and $\vec{b}_2$. The minimal region of the Brillouin zone $\Gamma X M$ is shown as the shaded part. In these calculations eigenvalue convergence to better than ~0.005 Ry in the energy range of interest is achieved with respect to both integration of matrix elements and basis set size (all core functions are included).

III. RESULTS

A. Energy-band structure

It is instructive to trace the evolution of the oxygen resonance as it is affected by interactions both within the overlayer and between adsorbate and substrate. In Fig. 2 are shown the band structures for an oxygen (1×1) monolayer at a height $z = 2.0$ a.u. above the Al surface, both in the absence of the substrate (broken curves) and in the field of the Al substrate (solid curves) but suppressing hybridization effects. The attractive Al field stabilizes the monolayer bands by ~3.0 eV to center the p bands ~11.2 eV below vacuum while the total bandwidth is increased from ~1.7 to 2.3 eV. In both cases the p_z band is below or within the p_x, p_y bands except in the volume about the M point. The dispersion relations correspond closely to those obtained by Liebsch;[16] however, the model potential used in the latter work results in a much larger width (~4.5 eV).

In our earlier calculation using a surface-molecule model, we took one oxygen atom above the hole site of an (001) Al surface ($z = 2.0$) and the
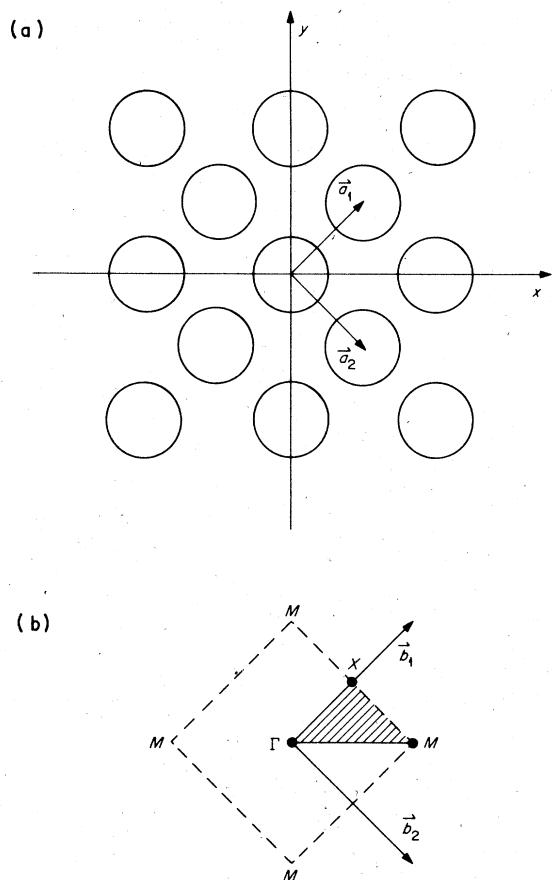
FIG. 2. Band structure of an oxygen monolayer with lattice vectors appropriate to the (001) surface of Al: in absence of substrate (upper dashed curves); in presence of Al substrate but omitting hybridization with Al orbitals (lower solid curves).

five nearest neighbors (four in the top plane and one directly beneath the oxygen). Including more atoms in these planes generates an extended three-layer thin film comprised of an oxygen (1×1) monolayer on a two-layer Al substrate. The calculated band structure appears in Fig. 3; the oxygen "resonance bands" (broken curves) show the integrity of the overlayer bands of Fig. 2 is maintained on the surface. Hybridization among overlayer and substrate orbitals results in an in-

creased oxygen p bandwidth [to ~3.3 eV (Ref. 17)]. The "hybridization shift" (defined as the energy shift in excess of that due to the substrate field alone) varies from nearly zero (at the top of the band) to ~-1.7 eV for states at the bottom of the band. These shifts are obviously large for levels (such as Γ_1) involving the oxygen $2p_z$ state, which probes the surface. Interestingly, the largest shift occurs for a level (X_3) which corresponds to a state formed by oxygen orbitals $\phi = (2p_x + 2p_y)$

FIG. 3. Band structure of a two-layer (001) Al film with a (1×1) oxygen overlayer in hole-centered configuration. Adatom separation $Z = 2.0$ a.u. corresponds to nearly touching atomic radii. The dash-dot curves denote the oxygen resonance bands.
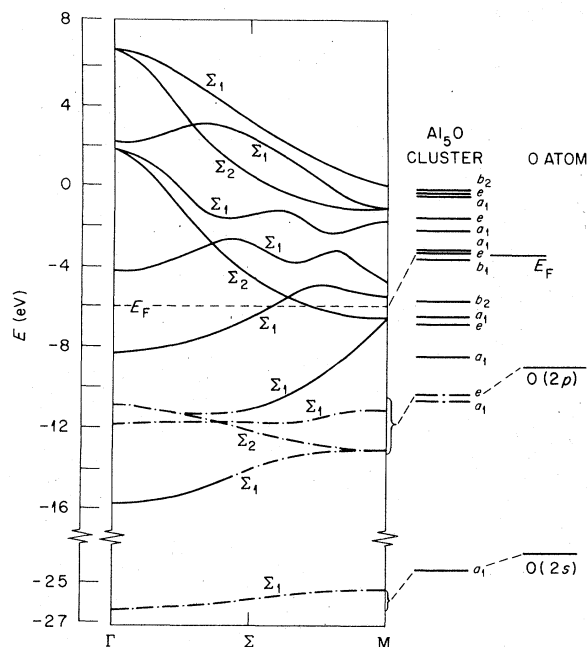
FIG. 4. Evolution of oxygen atomic $2s$ and $2p$ levels (far right) into discrete spectrum of Al_5-O cluster (center), and in Bloch representation, the resonance bands for corresponding extended system (left). Adatom separation $Z = 2.0$ a.u.

directed parallel to the surface towards neighboring Al sites and hybridized with the $3s$ orbitals on those sites.

The qualitative features of the electronic structure in the energy-band model are in accord with the results of our cluster calculation for the Al_5-O surface molecule,[6] e.g., the existence of an oxygen p resonance at the bottom of the Al complex for an adatom separation of 2.0 a.u. This correspondence is apparent in Fig. 4 which shows the energy bands along the Σ direction, the Al_5-O cluster eigenvalues and the free-atom energy levels to indicate the origin and development of the oxygen resonance (dash-dot curves). There is a progressive stabilization of levels as the system size increases. The oxygen $2s$ and $2p$ derived structures and the cluster Fermi level all drop about the same amount in going from the free atom to the band limit.

B. Chemisorptive bonding

An analysis of the Bloch wave functions indicates that the bonds between the oxygen overlayer and the Al substrate are covalentlike in structural character and bear a close resemblance to the local

bonds of the Al_5O cluster[6] (with due regard for the differences in normalization). While the p orbitals are mixed for general $\vec{k}$, there is a major distinction between resonance levels composed primarily of orbitals oriented parallel (p_x, p_y) and normal (p_z) to the substrate.

The covalent nature and differences between these bond types are illustrated by the plots of the p-band wave functions for the M point in Fig. 5. Contours are plotted in the xz plane bisecting the oxygen atom and two near-neighbor Al sites in the top layer and one Al atom in the second. The integrity of the oxygen $2p_x$ and $2p_z$ atomic character is clearly seen. One of the doubly degenerate M_5 states appears in Fig. 5(a) and shows constructive bonding through the p_x orbitals on the oxygen and first-layer Al sites, with a negligible contribution from the second layer.[18] The M_1 state of the p_z band appears in Fig. 5(b), illustrating strong σ-like bonding between the oxygen and second-layer Al sites beneath. The Al $3s$ orbital contribution is about twice as large as the Al $3p$ for this state; the first-layer Al contributions are negligible.

It should be emphasized that reference to the bonding as "covalentlike" is only to describe the spatial character of the solutions. The orbital structure alone does not determine the charge transfers in the system. In the present case, the oxygen p band is fully occupied, which would indicate significant charge transfer to the oxygen sites. However, the nature of the orbitals of the p band is such that an appreciable amount of the resonance charge occupies the interstitial volume, particularly for the (p_x, p_y)-bond-type. As a result the calculated transfer of charge from the Al sites is not as large as in Al_2O_3, for example.

An important aspect in considering bonding in the energy-band model is that bond formation is dependent on the wave-vector modulation. The phase constraints determine the relative importance of the overlayer orbitals in establishing bonds with the substrate. For example, in Fig. 6, the $2p_x$ orbital on the oxygen site at the center of the figure is shown interacting with the $3p_x$ orbitals on four near-neighbor Al sites. This wave-vector phasing corresponds to the point M in the zone. Modulation of this wave along the [100] direction alternates the sign on successive atomic planes such that constructive bonds are formed between each neighboring pair of oxygen-aluminum sites. At the zone center with unit phasing everywhere, the oxygen antibonds with Al sites in alternate rows (1 and 3) such that level Γ_5 lies above M_5. The p_z band dispersion is not so large since the major bond mode does not involve orientation in the plane defined by the wave vectors.
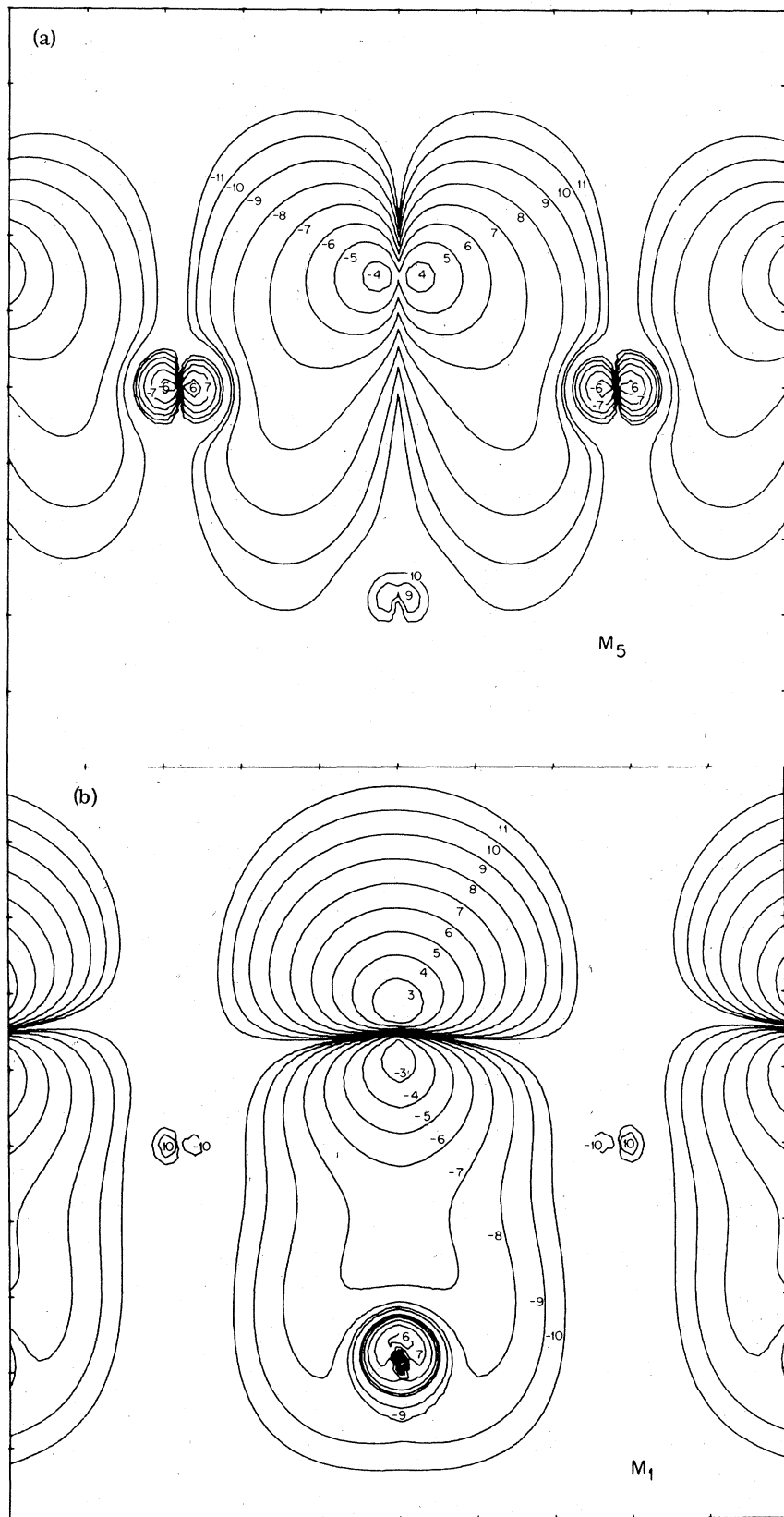
FIG. 5. Bloch wave func-
tions for (1×1) oxygen
overlayer in hole-centered
configuration on Al (001)
two-layer film for (a) level
M_5 and (b) level of M_1 of
the oxygen resonance of
Fig. 3. The XZ plane of the
figure bisects the oxygen,
two of the near-neighbor Al
sites in the top plane and
the Al site beneath. The
maximum value shown is
3.367 for contour label 1;
adjacent contours differ by
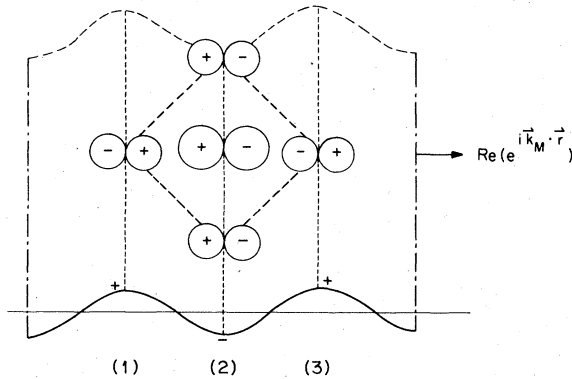a factor of 1.75 and the
sign of contour label de-
notes that of the wave func-
tion.

FIG. 6. Wave-vector modulation effects on Bloch-orbital components for oxygen-Al p bonding of state M_5 (Fig. 3). Al sites are at the corners of the square and the central unit cell oxygen site is at the center. The real part of the phasing of the Al orbitals is shown.

C. Resonance dependence on film thickness

The difference observed in these two bond modes suggests that the p_x, p_y bands are rather insensitive to the presence of atoms below the top layer while the p_z band is more sensitive to the further layers. The evolution of these bands for increasing number of Al layers verifies that this is the case. In Fig. 7 we show the change in the Σ bands as the number of substrate layers is increased. The most striking feature is the invariance of the resonance structure and position as defined by the limits of the oxygen p_x, p_y bands (Γ_5-M_5), and the constancy of the Fermi energy measured with respect to vacuum. Qualitatively, the oxygen resonance features are determined by bonding with the

near-neighbor Al sites, and including more Al layers simply fills in the background structure, against which the resonance is observed, to approach the bulk limit.

There are differences in how the bond types are distributed in energy. The oxygen p_x, p_y orbitals enter the resonance bands in a region of only ~3.0-eV width, but there are significant p_z-bonding contributions in symmetry type-1 bands over a larger energy range. No new states of Σ_2 symmetry are introduced near the resonance when more Al layers are added (accounting for the resonance invariance), however, each Al layer brings in a new Σ_1 band at the bottom of the complex. The new Σ_1 states involve hybridization with previous states, so that the Σ_1 band with the largest oxygen p_z component (the one in the resonance complex) is shifted slightly higher with each new layer. Hybridization among the Σ_1 bands leads to oxygen $2p_z$ charge sharing into these new bands, but the $2p_z$ charge on the O site still originates mainly from the Σ_1 band within the resonance. The differences in sensitivity to the number of substrate layers is suggestive that, in a more general context, features of adsorbate electronic structure dependent on bonds directed parallel to the surface are more surface sensitive than those properties associated with normal bonding which probes the underlying bulk structure.

As the number of Al layers is increased in the absence of the oxygen overlayer, the band structure approaches the (001) projection of the bulk band structure[19] (including surface perturbations). The bulk band structure calculated in the DVM approach[15] using the same potential parameters (α
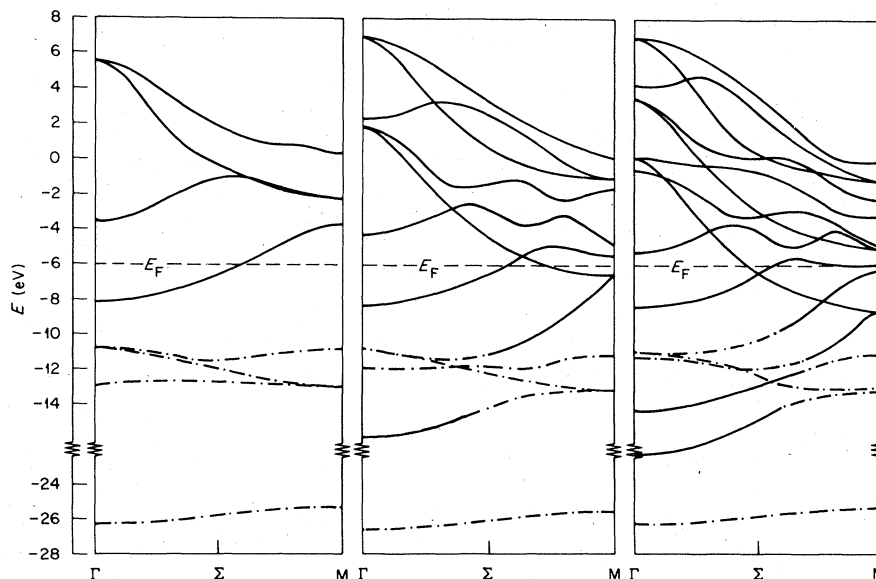

FIG. 7. Development of substrate and resonance bands (broken curves) as the number of substrate layers is increased from one to three (left to right, respectively) with fixed overlayer separation of 2.0 a.u. Resonance position, as defined by the doubly degenerate levels at Γ and M, and Fermi level show insignificant shifts.
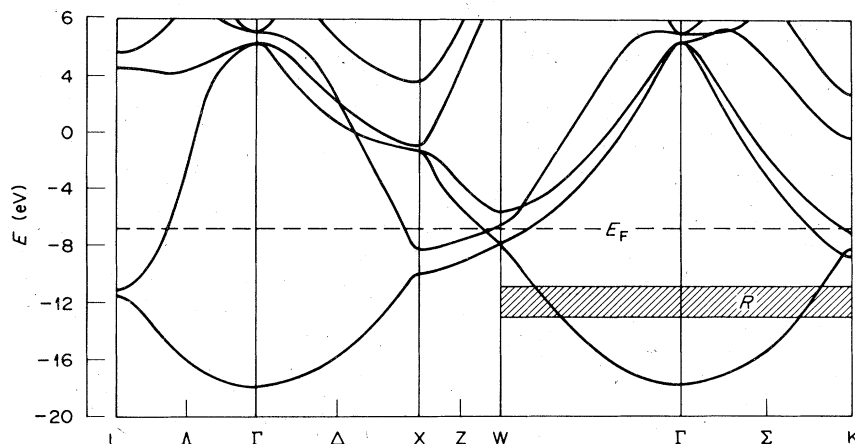
FIG. 8. Band structure of bulk Al for same potential parameters used in layer calculation. Position of oxygen resonance as defined in Fig. 3 is shown as shaded inset. Transition state shifts place the resonance ~2.2 eV lower than ground-state position shown.

= 0.73) as used in the surface calculations is shown in Fig. 8. The band structure agrees well with that obtained in the LCAO self-consistent calculation of Singhal and Callaway[20]; the occupied bandwidth (0.816 Ry)[21] of the present non-self-consistent calculation is also in good agreement with that calculated by Faulkner with the Korringa-Kohn-Rostoker method (~0.818 Ry).[22]

Comparing with the thin-film band structure, the Fermi energy is observed to fall in about the same position (within ~0.8 eV). We have thus sketched in Fig. 8 the oxygen resonance width and position as referenced with respect to vacuum. The resonance falls in the free-electron-like Al sp band about 5.2 eV below E_F, and to a first approximation, from the observed invariance of the oxygen features to the number of layers, represents the structure probed in a photoemission experiment. To go further in interpreting the photoemission data is complicated (even if the bond-site parameters were known) due to the requirements necessary to adequately describe the process.

At a simpler level, transition-state[23] calculations for excitations of the isolated Al_5O cluster yield a uniform shift of the resonance levels to a greater binding energy by ~2.2 eV. It is well known that transition-state shifts from the ground-state eigenvalue spectrum decrease with increasing delocalization of the orbital involved.[23] If we take the extreme limiting case of partitioning the excitations as arising from (a) localized "surface-molecule" states involving the oxygen interacting only with its nearest-neighbor Al sites and (b) delocalized Bloch substrate states, this model would yield a displacement of the resonance excitations by ~2.2 eV with respect to the bulk Al background to give a ~2.3-eV-wide resonance ~7.4 eV below E_F.

There are a number of complicating factors in comparing with experiment for adsorption on the (001) face of Al. The O $2p$ peak has been observed to be strongly defined only on the Al (111) face, and the Al $2p$ core shift corresponding to the oxide is exhibited directly without showing a smaller "chemisorption" shift as observed on the (111) face.[3,24] Work-function data of Gartland[25] further indicate that an island oxide growth mechanism characterizes the (001) surface. The openness of the (001) face as compared with the (111) is certainly consistent with these observations.

D. Coverage dependence

A notable aspect of the photoemission data for O_2 chemisorbed on Al is that the resonance features (such as general line shape and position) do not change greatly for a rather large range of oxygen exposure.[1,2,24] This observation gives support for the surface moelcule model in that the local bonding is indicated to dominate the long-range interactions.

In the thin-film band model it is assumed that the overlayer is ordered—an idealization for most cases. However, the band model is also applicable in many instances in which the overlayer is disordered or the coverage is lower than assumed in the model. This is demonstrated by the results shown in Fig. 9 for the coverage dependence of the resonance for oxygen in $C(2 \times 2)$ and (1×1) structures on an Al (001) monolayer. The $C(2 \times 2)$ unit cell is twice as large as that for (1×1) coverage, and the Brillouin zone is correspondingly smaller by a factor of 2. The resonance width along the Σ_1 direction decreases to less than half that in (1×1) coverage, however, the position with respect to E_F remains about the same. The correlation with the cluster results remains valid—the dominant factor in determining the O resonance *position* is the bonding of each O atom with the near-neighbor
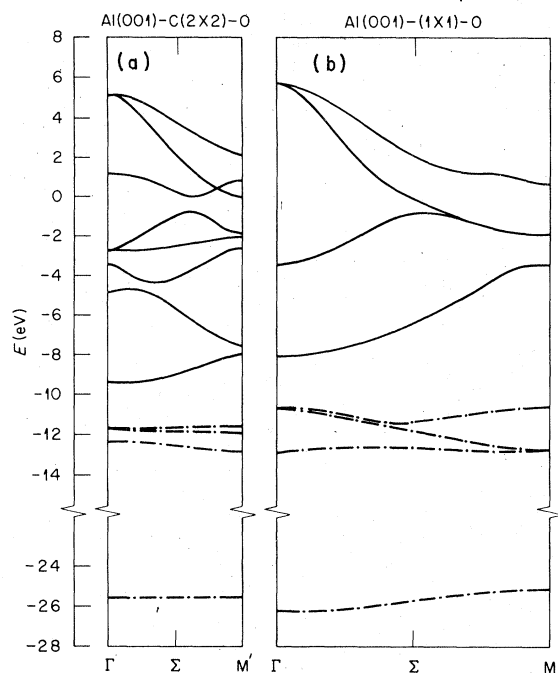
Al(001)-C(2×2)-O   Al(001)-(1×1)-O

FIG. 9. Sensitivity of resonance features to coverage. The resonance bands (broken curves) for (a) $C(2\times2)$ structure and for (b) (1×1) coverage are shown.

Al atoms. Interadsorbate interactions influence the details of the band such as its width to about the same extent as the adsorbate-substrate interaction. Thus while the width and structure of the adsorbate resonance bands depend upon the interadsorbate interactions and are coverage dependent, the position of the resonance is determined by interactions between the adatom and near neighbor substrate atoms and is coverage independent.

It is interesting to note the connection between the band structures for the two coverages of Fig. 9. If we ignore the O bands, the substrate bands along $\Gamma M'$ in (a) can be reproduced to a good approximation from those in (b) by reflection of the bands about the midpoint of the Γ-to-M line. This is a consequence of the double unit-cell character in the substrate for $C(2\times2)$ coverage.

E. Site dependence

An outstanding problem in chemisorption studies is the determination of stable adsorption sites. Although it is not presently practical to address this problem by determining minima in the energy surface, in a simpler nonpredictive capacity, correlations can be sought between the measured spectra and those calculated for various adsorption structures. In this connection, we briefly note in the following the sensitivity of the resonance to several bond structural parameters. In

contrast to the dependence on coverage, the resonance features are sensitive to the details of the bond site since the local bonding is directly a function of the bond geometry.

Previous cluster calculations[6] have shown that the resonance shape and position are sensitive to adatom-substrate separation. This is true in the present study as indicated in Fig. 10 where the band structure along ΓM is shown for oxygen (1×1) overlayer separations of 0.0, 2.0, and 5.0 a.u. from a single-layer Al substrate. The resonance falls deeper in the band and broadens somewhat as the oxygen overlayer is brought into the substrate plane in hole-centered sites.[26]

The resonance features are also quite sensitive to the type of bond site. In Fig. 11 the band structure along Σ corresponding to bonding in an overhead (1×1) configuration (A) is compared with results for hole-centered (1×1) coordination (C). In both cases, the overlayer separation corresponds to nearly touching atom spheres, with a monolayer Al substrate. In the hole-centered site, the resonance is only about 0.6 eV broader, but lies ~2.4 eV lower than for the overhead site. While the one-electron eigenvalues do not suffice to determine the relative energies of different adsorption structures, the greater stability of the bands for the hole-centered configuration is suggestive that this is a preferred adsorption site for the (001) face.

While the local density of states on the oxygen site has been reported[27] to yield a resonance shape comparable to experiment,[1] there is also the possibility of coexistent adsorption sites. In the present case the A and C sites yield resonances ~2.4 eV apart which can be compared with the photoemission data of Flodstrom et al.[1] which shows a shoulder at ~2.6 eV below the main peak. The
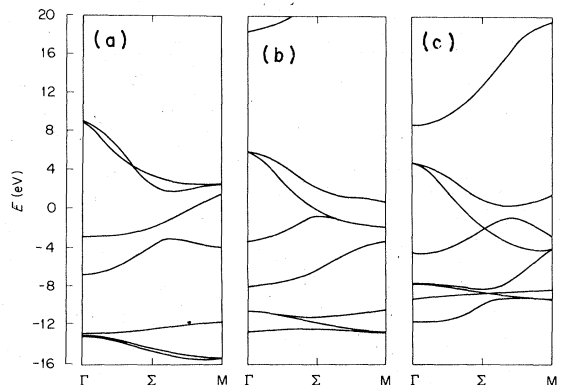
FIG. 10. Sensitivity of layer band structure to (1×1) overlayer separation (hole-centered symmetry) going from adatom height of (a) 0.0 a.u. to (b) 2.0 a.u. to (c) 5.0 a.u.
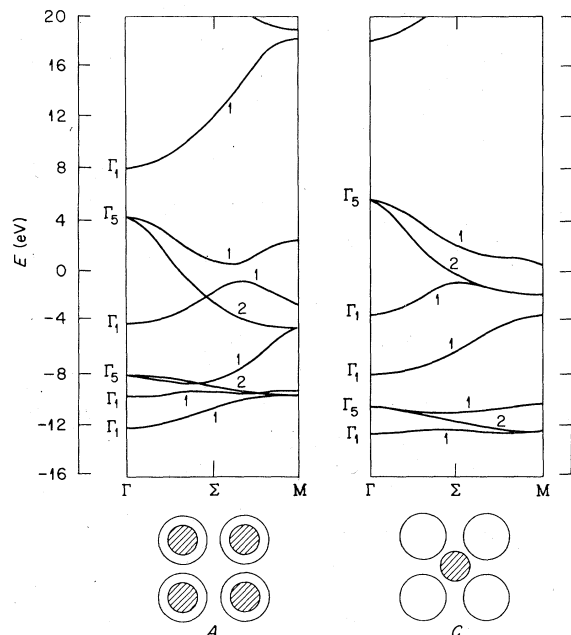
FIG. 11. Comparison of band structures along Σ for oxygen overlayer in hole-centered C configuration (right) and overhead A symmetry (left). Nearly touching atomic radii apply in both cases; overlayer-substrate coordination is indicated in the sketches at bottom (oxygen atoms are shaded).

matrix elements and populations of various adsorption states would determine the relative peak heights in this case.

IV. SUMMARY

The evolution of the electronic structure as one progresses systematically from finite cluster to extended thin films of increasing thickness indicates how the local-bonding features, such as those associated with the oxygen resonance, emerge from the near-neighbor adsorbate-substrate interactions. The chemisorptive bond for oxygen on Al (001) involves mainly the nearest-neighbor substrate atoms, with interadsorbate interactions playing a secondary role. It is in this sense that the various thin-film energy band and surface molecule models agree with regard to the resonance features. The major bond mode is largely insensitive to the far neighbors—the effect of the latter is mainly to contribute to the breadth of the background structure in which the resonance lies. The localization of the adsorbate bonding also relates to the observation that the

calculated spectra from the idealized models compare well qualitatively with data pertaining to systems with considerable disorder.

Although adsorbate clustering, amorphous-overlayer formation, and surface reconstruction are complicating factors in such strongly interacting systems, the idealized band model can be usefully employed to describe certain local-bonding features. If, as in the present case, a close correspondence exists between the surface molecule and band models, then the *local* environment is probably of more importance in determining chemsorption features than long range ordering of the substrate or overlayer. It then becomes crucial to know the local structural parameters for the chemisorbed species.

The resonance structure and position are sensitive to local bond site and adatom separation. Correlations between calculated and experimental spectral features to determine these parameters are difficult because of competing influences of self-consistency, orbital relaxation shifts, and the matrix elements for the photoemission process. Encouraging progress has been made recently in treating these problems however,[28] with experiment and model calculations indicating that it is possible to resolve the chemisorption states for atomic adsorbates of the type considered here.

It is of interest to know under what conditions an energy-band model is appropriate for systems with deviations from perfect order. In the present case the observed correlations with the surface molecule results do support the use of the band model to describe one-electron features in chemisorption systems where local bonding is important. In general, low coverage and/or disordered adsorption can be treated in a high coverage, ordered approximation if interadsorbate interactions are small compared with the adsorbate-substrate bonding. The importance of interadsorbate interactions can be determined from adsorbate electronic structure features in the absence of the substrate. A useful criterion to assess the band model relates to that associated with the surface molecule approach: the adsorbate-substrate interaction should dominate the interadsorbate one, and not be appreciably perturbed by it.

ACKNOWLEDGMENT

*Research sponsored by the Department of Energy under contract with Union Carbide Corp.

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[17] In the hybridized bands, the major part of the charge on the oxygen sites originates in the set of bands in the range defined by Γ_5 to M_5, and in the following this separation will be taken as defining the resonance width.

[18] The nodel plane between the oxygen and aluminum sites is that of the atomic node of the Al $3p$ orbital.

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