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Molecular-orbital study of aluminum clusters containing up to 43 atoms

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The self-consistent-field $X\alpha$ scattered-wave molecular-orbital method has been used to perform electronic-structure calculations for two series of aluminum clusters containing up to 43 atoms, the largest metal cluster so far treated by this method. The first series consisted of clusters of 13, 19, and 43 atoms having the O_h symmetry characteristic of bulk fcc aluminum while the second consisted of 5, 9, and 25 atom clusters having the C_{4v} symmetry appropriate to the (100) surface. The convergence of the calculated results as a function of cluster size has been examined. The largest cluster of each series yields an occupied bandwidth of over 90% [92% (C_{4v}), 99% (O_h)] of the bulk band width derived from x-ray emission spectra. These larger clusters also show reasonable agreement with the main features of density-of-states curves derived from band-structure calculations and those inferred from recent photoemission measurements. The differences and similarities between various cluster- and band-theory results are discussed. Examination of projected densities of states for the various atoms provides a possible explanation of the smaller occupied bandwidth observed in the photoemission spectrum, compared with the x-ray or band-structure results. It is also suggested that similar projected density-of-states plots for the case of transition-metal clusters might prove useful for the study of structure sensitivity in heterogeneous catalysis.

I. INTRODUCTION

The recent reawakening of interest in the field of surface science is at least partly due to the growing awareness that the readily exploitable energy resources of the world are not inexhaustible and the conviction that knowledge gained from the study of surfaces and of chemisorption on them could lead to advances in the field of catalysis which in turn could lead to more efficient energy use. This growing interest from the practical point of view has coincided with, and indeed contributed to, significant advances in both the experimental and theoretical study of surface phenomena. On the experimental side,[1] the advances have stemmed from the development of ultrahigh-vacuum systems in conjunction with a seemingly endless variety of optical, electron, and other spectroscopic techniques known to the surface scientist by acronyms such as LEED (low-energy-electron diffraction), UPS (ultraviolet photoemission spectroscopy), XPS (x-ray photoemission spectroscopy), SIMS (secondary-ion mass spectroscopy), EXAFS (extended x-ray absorption fine structure), etc. Theorists have also made significant progress in understanding the nature of surfaces and the electronic structures of surface-adsorbate complexes.

If one wishes to develop a theory of chemisorption, then a number of different approaches might be taken. Perhaps the most straightforward is to consider a semi-infinite solid, or a slab with the desired surface exposed in interaction with an overlayer of adsorbate molecules.[2,3] The entire system is periodic in two dimensions and extensions of three-dimensional band theory can be used to perform the required calculations. Of course the computational requirements are much greater for the surface case due to the loss of periodicity perpendicular to the surface. A second possibility is to assume that the adsorbate-surface bonding for the case of chemisorption on a metal surface is similar to the bonding in appropriate metal-ligand complexes which are known in inorganic chemistry. Great progress has been made recently[4] in the synthesis of molecules containing several transition-metal atoms interacting with a variety of ligands and it is reasonable to search for analogies between these cluster compounds and surface-adsorbate complexes. In this case the theoretical methods and concepts are drawn from quantum chemistry.

A useful link between these two approaches is provided by the recently developed cluster approach to the theory of solids.[5-8] It has been demonstrated that for certain (not all) properties of bulk solids or surfaces an adequate physical model consists of a finite number of atoms artifically removed from the infinite solid. This cluster of atoms is then treated with a quantum-chemical method. If one accepts for the moment that cluster studies can provide useful information about certain properties of solids, then the following highly desirable situation with respect to the two models mentioned above may result. One can perform calculations on inorganic molecules, with the usual cross-checks with experiments, and from these studies draw conclusions about the nature of metal-ligand bonding. The same theoretical method can then be applied to clusters of various sizes interacting with the same ligands. In this way one can examine the way that the properties change as one goes from the case of a molecule to that of a finite cluster and, finally, in the limit of a sufficiently large cluster, to the case of the infinite solid or surface. In this way one can hopefully obtain information to answer the crucial question which is implicit when one compares the two types of models, namely, in what ways are clusters (of a given size) similar to, and in what ways are they different from the infinite solid as far as a given property is concerned.

In order to carry out a meaningful cluster calculation, the constraints on the theoretical method chosen are quite severe. A minimum requirement if one wishes to compare results for the series which starts with an inorganic molecule and ends with a chemisorbed layer on an infinite surface is that these two endpoints be adequately treated within essentially the same method. If the same mathematical approximations are used throughout the study, and if the method is trustworthy for the two extreme cases, then one can be confident that the similarities and differences found between the clusters and either the solid surface or the isolated molecule are meaningful and not simply a result of differing computational approaches. Further, more practical, constraints also exist. If one wishes to study the convergence of a cluster model as a function of the size of the cluster, then clearly the method chosen must be capable of treating sufficiently large clusters with a reasonable computational effort.

Fortunately the self-consistent-field $X\alpha$ scattered wave (SCF $X\alpha$ SW) method[9,10] satisfies at least these minimum criteria. It has been successfully used to study a number of inorganic complexes[7] and has furnished valuable information on their electronic structure and spectra so that one is confident that an isolated molecule may be adequately treated. Moreover the SCF $X\alpha$ SW method is the discrete analog of the Korringa-Kohn-Rostoker[11-13] method of band theory so that in the limit of the infinite solid SCF $X\alpha$ SW results go over into the results of a well-studied solid-state physics approach.

The $X\alpha$ SW method is also sufficiently rapid that quite large clusters can be treated (see below) in modest amounts of computational time. The number of atoms required in a cluster model will of course depend on which properties of the solid are of interest. Clearly if one is interested, for instance, in properties associated with the Fermi surface of a metal, then very large (computationally intractable) aggregates would have to be considered. On the other hand, if more local aspects of the solid are involved then one may hope that reasonably small clusters could be useful.

With all of the above considerations in mind we wish to present in this paper results of extensive SCF $X\alpha$ SW calculations on clusters of aluminum atoms. Future papers will deal with the interaction of these clusters with atomic and molecular adsorbates. Our choice to study aluminum was motivated by a number of factors. First, as aluminum is traditionally thought of as a prime example of a free-electron metal, it provides a stringent test of the cluster approach. Second, we can make comparisons with previous theoretical work which has used the solid-state viewpoint, e.g., work employing the "jellium" model.[14] Third, unlike the transition metals, only *s* and *p* electrons need to be considered for aluminum, hence larger clusters can be conveniently treated and the convergence of the results as a function of cluster size can be studied. Fourth, recent and ongoing photoemission work[15-17] for aluminum and for oxygen chemisorption on aluminum allows a comparison with experiment and the possibility of a fruitful interplay between theory and experiment. We believe that information obtained on this simpler material will be useful for future studies of transition-metal systems.

We have studied clusters of 5, 9, and 25 Al atoms in the C_{4v} symmetry which represents the Al (100) face and also clusters of 13, 19, and 43 atoms in O_h symmetry, which is more characteristic of bulk aluminum. The C_{4v} clusters have been used to study the chemisorption of hydrogen and oxygen atoms at various positions above and below the surface and details of these latter calculations will be treated in forthcoming publications. Preliminary results of this work have been reported elsewhere.[18-20]

In Sec. II we give the computational parameters and also describe a way of generating various density-of-states curves for finite clusters which may then be compared with corresponding quantities from band-structure calculations. In Sec. III we give a brief review of pertinent results from band-structure calculations and various relevant experimental results. Our new results are presented in Sec. IV and compared with the band-theory results and with experimental quantities. Special attention is paid to the behavior of the cluster results as a function of cluster size.

II. METHOD AND PARAMETERS

The self-consistent-field $X\alpha$ scattered-wave method of Slater and Johnson was used. This meth-

TABLE I. Atomic coordinates (bohrs) of one atom of a symmetrically related group, number of equivalent atoms in group (N), and coordination numbers (nn) for the aluminum clusters. The remaining coordinates can be generated by symmetry operations.

	Atom	x	y	z	N	nn
		I. O_h clusters				
Al_{13}	Al 1	0.0	0.0	0.0	1	12
	Al 2	3.821765	3.821765	0.0	12	5
Al_{19}	Al 1	0.0	0.0	0.0	1	12
	Al 2	3.821765	3.821765	0.0	12	7
	Al 3	7.643530	0.0	0.0	6	4
Al_{43}	Al 1	0.0	0.0	0.0	1	12
	Al 2	3.821765	3.821765	0.0	12	11
	Al 3	7.643530	0.0	0.0	6	8
	Al 4	7.643530	3.821765	3.821765	24	5
		II. C_{4v} clusters				
Al_5	Al 1	2.702396	2.702396	0.0	4	3
	Al 2	0.0	0.0	−3.821765	1	4
Al_9	Al 1	2.702396	2.702396	0.0	4	4
	Al 2	0.0	0.0	−3.821765	1	8
	Al 3	0.0	5.404792	−3.821765	4	3
Al_{25}	Al 1	2.702396	2.702396	0.0	4	8
	Al 2	0.0	0.0	−3.821765	1	12
	Al 3	0.0	5.404792	−3.821765	4	9
	Al 4	8.107188	2.702396	0.0	8	4
	Al 5	5.404792	5.404792	−3.821765	4	6
	Al 6	2.702396	2.702396	−7.643530	4	6

od has been described in detail elsewhere.[9,10] The muffin-tin approximation (nonoverlapping spheres) has been used for the potential. This approximation has been successfully used in Korringa- Kohn-Rostoker (KKR) calculations on bulk aluminum.[21,22] The nearest-neighbor Al-Al distance was taken as that in bulk aluminum, namely 5.405 bohrs (2.86 Å). The exchange parameter α was taken from the compilation of Schwarz[23] and has the value $\alpha = 0.72853$ for all regions of space. The secular determinant was formed using s and p waves in the aluminum spheres and s, p and d waves in the extramolecular region. Two series of clusters were considered. The first series consisted of clusters of 13, 19, and 43 atoms in O_h symmetry. These include, respectively, first, second, and third neighbors of a central atom. The second series was intended to model the (100) face and consisted of clusters of 5, 9, and 25 atoms in C_{4v} symmetry. The 25-atom cluster contains 12 atoms in the uppermost layer, 9 in the second layer, and 4 in the third layer. Up to third nearest neighbors of the central octahedral hole on the uppermost layer are included. The atomic coordinates for all of the unique atoms are shown in Table I along with their coordination number (number of nearest neighbors). It should be noticed that even for the largest clusters there is at most one atom which has its full complement of 12 nearest neighbors. This point will be discussed further below. In order to compare the results of our cluster calculations with those from band theory or with experimental data, we have found it useful to construct various "density-of-states" curves from our calculated molecular-orbital energies and charge distributions.

The total density of states for a bulk solid is given by

$$\rho(E) = \sum_k \delta(E - \epsilon_k), \tag{1}$$

where the sum is over all one-electron states. This expression will also be a very good approximation for a solid with a surface as the relative number of surface states is very small. For the cluster where there is a finite number of discrete states, the δ functions can be replaced by Gaussians and the density-of-states (DOS) written as

$$\rho^c(E) = (2\pi\sigma^2)^{-1/2} \sum_l \exp[-(E - \epsilon_l)^2/2\sigma^2], \tag{2}$$

where the sum is over all discrete states, and σ is the Gaussian width parameter which is related to the full width at half-maximum (FWHM), the FWHM being equal to 2.355σ. In order to gain information about the surface electronic structure or about the electronic structure in a local region of the solid, it is customary to define a local density of states (LDOS) or projected density of states (PDOS) in which local information is projected out of the total DOS. If, for example, one assumes a one-band solid in a linear combination of atomic orbitals (LCAO) framework, then the total DOS can be written as

$$\rho(E) = \sum_m \sum_k c^*_{km} c_{km} \delta(E - \epsilon_k), \tag{3}$$

where the c_{km} are the atomic orbital coefficients, the sum on k is over all states, and the sum on m is over all sites. Note that for a bulk solid with Bloch functions as eigenfunctions, Eq. (3) reduces to Eq. (1). The LDOS or PDOS on atom m is given by

$$\rho_m(E) = \sum_k c^*_{km} c_{km} \delta(E - \epsilon_k), \tag{4}$$

and the corresponding expression for the cluster is

$$\rho^c_m(E) = (2\pi\sigma^2)^{-1/2} \sum_l |c_{lm}|^2 \times \exp[-(E - \epsilon_l)^2/2\sigma^2]. \tag{5}$$

The DOS curves discussed below were generated using Eq. (2), while the PDOS curves were generated by weighting each Gaussian with the calculated charge within the sphere of interest (essentially the $|c_{lm}|^2$ of Eq. (5). This approximation assumes that the charge in the intersphere region is divided among the spheres in the same ratio as the calculated charges within the spheres. It is also possible to decompose the PDOS information into contributions from the various partial waves (s and p for Al), and this has been done.

III. PREVIOUS RESULTS ON ALUMINUM

Aluminum has long been considered to be a metal for which the free-electron theory provides a reasonably accurate description. It has been the subject of a large number of both theoretical and experimental studies. We do not intend to give an extensive review here, and, in particular, will completely ignore the large number of studies aimed at the precise determination of the structure of the Fermi surface since this type of information is beyond the scope of our cluster calculations. We will concentrate instead on those works which give more general information about the electronic structure of bulk aluminum or of the various aluminum surfaces, i.e., those works which try to answer the question: Where are the electrons in aluminum, both in space and in energy? We will emphasize various density-of-states information, total and local. The experiments most relevant to our work are of a spectroscopic nature and in particular photoemission results will be stressed as these provide the most direct link between experimental data and calculated energy levels.

On the theoretical side there have been a number of band-structure calculations for bulk aluminum, including studies by the orthogonalized plane wave[24] method and pseudopotential interpolation of these results[25]; by the KKR method,[21,22] by the augmented plane wave (APW) method,[26-28] and, most recently, by the self-consistent linear-combination-of-atomic-orbitals $X\alpha$ (SCF LCAO $X\alpha$) method.[29] Of these studies only the APW calculations of Snow[26] and the LCAO $X\alpha$ calculations of Tawil and Singhal (TS) were done self-consistently. The former calculations contain a systematic error[27] and so if one is to investigate the effects of self-consistency the results of Tawil and Singhal appear to be the best available. These effects are rather important if one wishes to discuss the density of states. A useful starting point for this discussion is a free-electron DOS which is proportional to $\epsilon^{1/2}$ where ϵ is the energy above the bottom of the band. All of the band-structure calculations find this behavior near the bottom of the valence band, but different results are obtained for the higher-energy part of the band depending on which method is used. The APW DOS is rather close to the free-electron curve throughout the occupied band with the exception of some minor structure due to Van Hove singularities. The results of TS, on the other hand, follow the $\epsilon^{1/2}$ curve only for about 0.2 Ry above the bottom of the band. From here to the Fermi level and above, there are a number of peaks and structure in the DOS. This structure can be related to various splittings of the "free-electron" bands at the zone boundaries, and, in particular, the splittings found at X and at L are significantly larger in the results of TS than in the APW results.

Hence there is still some disagreement about the details of the DOS of bulk aluminum, and while the results of TS are probably not the last word, they do raise the possibility of significant departures from free-electron-like behavior. These departures become even more pronounced at higher energy according to the work of Connolly[28] who has calculated the DOS up to 50 eV above the Fermi level using the Snow potential. As we shall see below there are also indications from ultraviolet photoelectron spectroscopy (UPS) that there is structure in the DOS, although the possibility that the structure is due to intensity matrix element effects cannot be ruled out at this stage. A detailed calculation would be necessary to clarify the situation.

The surfaces of aluminum have received somewhat less attention than the bulk. Non-self-consistent studies were performed by Boudreaux[30] and by Caruthers *et al.*[31] in order to investigate the existence of surface states (states within gaps) for the (100), (110), and (111) surfaces. The only self-consistent studies to date specifically on an aluminum surface are the pseudopotential calculations for Al (111) by Chelikowsky *et al.*[32] in which a repeated slab geometry was used, and a cluster calculation[33] in which only five aluminum atoms were considered (see also below). The density functional work of Lang and Kohn[34] on the jellium model represents a large effort in the study of the surfaces of simple metals. In particular, the charge density, surface energy, and work function have been calculated within this model for a number of values of the background density, including that appropriate to aluminum. Of course as there is no lattice in the model, the departures from free-electron behavior mentioned above cannot be obtained, and, in particular, the study of surface states is prohibited. Nevertheless, the model is instructive and provides a certain conceptual reference point. A future paper[35] will deal with the adequacy of the jellium model for certain chemisorption studies, namely, the adsorption of oxygen and hydrogen atoms.

On the experimental side we will also give only a rather restricted review of those experiments with which our cluster results are compared, and once more ignore the large body of work on the aluminum Fermi surface. The x-ray band emission spectrum of aluminum has been studied by Rooke.[36] He arrived at a value of 11.3 eV (0.83 Ry) for the occupied bandwidth and was also able to correlate the positions of various spectral discontinuities with those of the Van Hove singularities, although the correlation is relatively insensitive to small changes in the energy positions of the bands at points of high symmetry. These results therefore indicate the presence of structure in the DOS, but do not give detailed information as to its exact position in energy nor as to its magnitude. The optical properties of aluminum have been well studied[37,38] and in general are consistent with an approximately free-electron behavior up to the Fermi level. There is a peak in the optical conductivity at about 1.5 eV indicating significant departures from free-electron behavior in this energy range. Weaker features at 0.5 and 2.5 eV have also been reported.

Perhaps the most direct method of obtaining information on the occupied DOS is by photoemission spectroscopy. Comparison between theory and experiment is, however, complicated by a number of factors so that a direct comparison between a calculated (bulk) DOS and an experimental ultraviolet photoemission (UPS) spectrum or x-ray photoemission (XPS) spectrum must be made cautiously. The factors which must be considered in such a comparison are the following: (i) the intensity of photoemission is not directly proportional to the DOS, but also depends on matrix elements linking initial and final states. These matrix elements depend on the energy of the incident photon so that the relative weighting of different parts of the DOS will, in general, change if one changes the frequency of the light source. The matrix elements are also angle-dependent, and so the experimental angles (light incidence and electron detection) must be taken into account. (ii) Depending on the degree of localization of the hole left behind on photoemission of an electron, the remaining electrons will relax to varying degrees and this can cause energy shifts which are not constant over the spectrum. (iii) The photoelectrons have a finite mean-free path which depends on their kinetic energy and therefore on the frequency of the exciting radiation. It is just this finite escape depth which makes UPS quite surface sensitive and has led to its utility in surface studies. Thus, effectively, an experimental UPS spectrum is a weighted average over DOS information [taking into account effects (i) and (ii)] relevant to various surface layers, the weights depending on the photon energy used. It is instructive therefore to compare measured spectra with various projected DOS curves (see below).

The photoemission spectrum for aluminum for various uv photon energies has been studied by Yu *et al.*[17] by Flodström *et al.*,[15,16] and Martinsson *et al.*[39] Studies using x-ray sources have been carried out by Barrie,[40] Flodström *et al.*,[41,42] and by Baird and Fadley.[43] As far as the occupied DOS is concerned, the following observations which are based on the 40.8-eV spectrum of polycrystalline Al (Ref. 16) are relevant. Again the reader is cautioned that a systematic UPS study of single-crystal aluminum has not yet been carried out. In particular, only a small number of photon energies have been used. Nevertheless, comparisons can be made between the available experimental data and the results of band-structure and cluster calculations in the hope that such comparisons will help the experimentalist in the choice and design of further experiments. Within the limits of the caveats given above the UPS spectrum (see Fig. 2, below) indicates a DOS, which is roughly free-electron-like with the following important departures (i) definite structure is observed in the region between the Fermi level ($E_F = 0$ eV) and −5 eV. This structure consists of a valley centered at about −2 eV and a peak at about −4 eV. Possible sources of this structure are discussed in detail in Sec. IV. (ii) The lower energy part of the DOS is severely attenuated. The experimental "band" is only about 7.5 eV wide, whereas the previously mentioned bandwidth from x-ray spectra is 11.3 eV in good agreement with band theory and also with our cluster results (see below). A similar narrowing has previously been observed for other systems such as Ni,[44,45] although it now appears that at least part of the narrowing for Ni is due to angle-averaging effects, Smith *et al.*[46] having found a new low-energy peak for Ni (100) in an angle-resolved study. As we shall see below one of the reasons for band narrowing may be the surface sensitivity of UPS. This feature is discussed in detail in Sec. IV where we present our new cluster results.

IV. RESULTS AND DISCUSSION

The calculated orbital eigenvalues for the various clusters are shown in Fig. 1 and are also gathered in Table II. Also shown are the values calculated for the Fermi level (the energy of the highest occupied molecular orbital) and for the occupied bandwidth. The five-atom cluster has already been studied by Harris and Painter[33] in a study of oxygen-atom chemisorption (see also Refs. 18–20). The remaining clusters have not previously been studied.

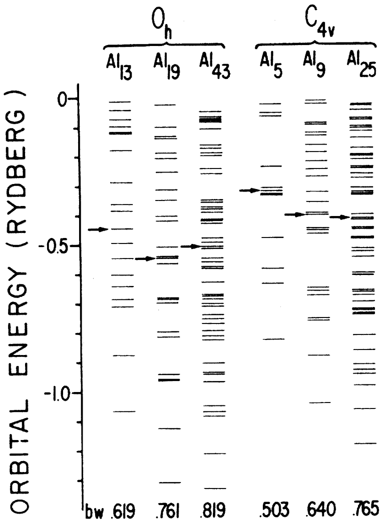

FIG. 1. Calculated orbital eigenvalues (rydbergs) for the aluminum clusters. The arrows indicate the highest occupied molecular orbital (the Fermi level), bw indicates the occupied bandwidth.

If one is interested in the convergence of clusters in order to study bulk or surface properties, then one useful parameter to monitor is the occupied bandwidth, i.e., the energy difference between the lowest valence molecular orbital and the highest occupied molecular orbital. The values in Table II range from 0.503 Ry (6.84 eV) for Al_5 to 0.819 Ry (11.14 eV) for Al_{43}. If we take the value 11.3 eV from x-ray studies[36] as the best experimental estimate, then an Al_{43} cluster treated by the SCF $X\alpha$ SW method accounts for about 99% of the bandwidth. The Al_{25} cluster yields 92% of the occupied bandwidth, and so one may expect that at least for certain properties the larger cluster of each series will yield useful results. Each of these larger clusters contains at least some third neighbors of a central atom (the 43-atom cluster has all third neighbors), and our results indicate that the overall splittings produced by metal-metal bonding are reasonably converged at this stage.

It is apparent from Fig. 1 that the five-atom cluster produces an energy-level spectrum which is much sparser and, at the same time, a bandwidth which is much narrower (only 61% of experiment) than the 25-atom case. If one wishes to model chemisorption on metal surfaces by clusters, then a reasonable representation of the electronic structure over the whole occupied energy range should be sought. Hence in the present case the Al_5 cluster would not be expected to yield reliable results except in special circumstances. In particular, if interaction with an adsorbate which has energy levels near the bottom of the aluminum band is involved, then for Al_5 there are simply no substrate states in this energy range with which the adsorbate states can interact. Indeed, our studies for oxygen adsorbtion[18-20,35] show the five-atom cluster to give qualitatively wrong results. The 43-atom aluminum cluster is the largest metal cluster which has so far been treated with the SCF $X\alpha$ SW method and the relatively good convergence of the bandwidth is further justification for the cluster approach to solids. It should be emphasized that the rate of convergence of cluster calculations can depend rather markedly on the method (the Hamiltonian) used. For instance in recent studies by one of us[47] of the simple Hückel (*s*-band cubium) cluster model it was found that 27 atoms gave only 71% of the infinite bandwidth, and even 1000 atoms gave just 96%. Thus if one were to assume that the simple tight-binding approach was good for metals, the conclusion would clearly be that clusters (even quite large ones) are quite different from the infinite solid, whereas our present results, using a more accurate and self-consistent approach, indicate that the similarities between clusters and the solid are important. It should also be emphasized again that the rate of convergence depends on the property of interest. This feature is also demonstrated in the Hückel cluster results of Messmer.[47] While the bandwidth and the work function are very slowly convergent with the simple Hückel Hamiltonian, being sensitive to interactions over the order of tens of lattice spacings, the local densities of states, which are important for chemisorption studies, for the various surface layers converge quite rapidly and, for example, a $9\times9\times9$ cube of atoms gives results which are very similar to the results for the infinite solid.[2,48]

In order to facilitate further comparisons, we show in Fig. 2 DOS curves generated for each of the clusters by replacing each discrete level with a Gaussian of width parameter $\sigma = 0.05$ Ry. This value of σ was chosen since it gives a "resolution" in the curves which is roughly equivalent to that found in photoemission experiments (see below). Several features of these curves are noteworthy in as far as the convergence properties of clusters are concerned. First, the increase of the bandwidth in each homologous series is graphically illustrated. Comparing the curves for Al_5 and Al_{25}, one sees that a number of gaps in the former are filled in the latter, and that therefore Al_{25} is likely to be a considerably better model. Second, one can compare the results with those of free-electron theory [DOS proportional to $\epsilon^{1/2}$, dashed line of Fig. 2(c) or 2(f)] and with those of band-structure calculations. For the larger clus-

TABLE II. Orbital eigenvalues ϵ (rydbergs) for clusters of aluminum atoms. The levels are labeled according to the irreducible representations of the O_h or C_{4v} point groups. The sequence numbers include only the valence electrons. Also shown are the fermi levels (E_F) and the occupied bandwidths (occ. bw).

I. O_h clusters

Al_{13}		Al_{19}		Al_{43}			
Level	$-\epsilon$	Level	$-\epsilon$	Level	$-\epsilon$	Level	$-\epsilon$
$1a_{1g}$	1.064	$1a_{1g}$	1.305	$1a_{1g}$	1.326	$7t_{1u}$	0.515
$1t_{1u}$	0.874	$1t_{1u}$	1.125	$1t_{1u}$	1.209	$8t_{1u}$	0.509
$1t_{2g}$	0.707	$1e_g$	0.958	$1t_{2g}$	1.082	$5t_{2g}$	0.507
$2a_{1g}$	0.683	$2a_{1g}$	0.955	$1e_g$	1.067	$4t_{2u}$	0.492
$1e_g$	0.639	$1t_{2g}$	0.939	$2a_{1g}$	1.046	$2a_{2u}$	0.478
$1t_{2u}$	0.601	$2t_{1u}$	0.812	$1a_{2u}$	0.964	$3a_{2u}$	0.427
$1a_{2u}$	0.545	$1t_{2u}$	0.794	$2t_{1u}$	0.940	$2e_u$	0.418
$2t_{1u}$	0.493	$3t_{1u}$	0.695	$1t_{2u}$	0.933	$5a_{1g}$	0.414
$3t_{1u}$	0.445	$1a_{2u}$	0.686	$3t_{1u}$	0.901	$9t_{1u}$	0.390
$2e_g$	0.383	$3a_{1g}$	0.682	$2t_{2g}$	0.821	$6a_{1g}$	0.380
$2t_{2g}$	0.362	$2e_g$	0.678	$1t_{1g}$	0.809	$6t_{2g}$	0.372
$1t_{1g}$	0.289	$1t_{1g}$	0.564	$3a_{1g}$	0.790	$5t_{2u}$	0.357
$3a_{1g}$	0.180	$4t_{1u}$	0.544	$2e_g$	0.767	$1a_{2g}$	0.348
$3t_{2g}$	0.121	$2t_{2g}$	0.540	$3t_{2g}$	0.750	$5e_g$	0.260
$2a_{2u}$	0.120	$3e_g$	0.509	$4a_{1g}$	0.736	$6t_{2u}$	0.243
$4t_{1u}$	0.100	$4a_{1g}$	0.419	$1e_u$	0.709	$10t_{1u}$	0.199
$5t_{1u}$	0.075	$2t_{2u}$	0.402	$3e_g$	0.699	$3t_{1g}$	0.192
$3e_g$	0.043	$3t_{2g}$	0.346	$4t_{1u}$	0.684	$7t_{2g}$	0.174
$4e_g$	0.017	$5t_{1u}$	0.313	$2t_{2u}$	0.674	$4t_{1g}$	0.163
E_F	0.445	$4t_{2g}$	0.255	$5t_{1u}$	0.669	$1a_{1u}$	0.111
occ. bw	0.619	$6t_{1u}$	0.208	$6t_{1u}$	0.626	$6e_g$	0.086
		$1e_u$	0.190	$4t_{2g}$	0.581	$8t_{2g}$	0.080
		$2t_{1g}$	0.141	$2t_{1g}$	0.573	$11t_{1u}$	0.076
		$5a_{1g}$	0.135	$3t_{2u}$	0.559	$7a_{1g}$	0.069
		$1a_{2g}$	0.102	$4e_g$	0.547	$3e_u$	0.051
		$4e_g$	0.027		E_F	0.507	
		E_F	0.544		occ. bw	0.819	
		occ. bw	0.761				

II. C_{4v} clusters

Al_5		Al_9		Al_{25}			
Level	$-\epsilon$	Level	$-\epsilon$	Level	$-\epsilon$	Level	$-\epsilon$
$1a_1$	0.823	$1a_1$	1.040	$1a_1$	1.180	$5b_2$	0.415
$1e$	0.632	$1e$	0.878	$1e$	1.061	$10e$	0.400
$2a_1$	0.581	$2a_1$	0.759	$2a_1$	0.980	$10a_1$	0.337
$1b_2$	0.479	$1b_1$	0.751	$1b_2$	0.942	$5b_1$	0.333
$3a_1$	0.334	$3a_1$	0.673	$1b_1$	0.928	$11e$	0.325
$1b_1$	0.331	$2e$	0.658	$3a_1$	0.908	$6b_2$	0.310
$2e$	0.320	$1b_2$	0.648	$2e$	0.861	$12e$	0.280
$4a_1$	0.310	$3e$	0.466	$3e$	0.810	$11a_1$	0.265
$3e$	0.238	$2b_1$	0.455	$4a_1$	0.737	$6b_1$	0.247
$2b_2$	0.067	$4a_1$	0.448	$4e$	0.734	$13e$	0.239
$5a_1$	0.057	$5a_1$	0.400	$2b_2$	0.725	$3a_2$	0.217
$4e$	0.027	$4e$	0.395	$2b_1$	0.720	$12a_1$	0.215
E_F	0.320	$2b_2$	0.359	$5a_1$	0.696	$14e$	0.205
occ. bw	0.503	$5e$	0.325	$1a_2$	0.674	$7b_1$	0.200
		$1a_2$	0.273	$5e$	0.664	$15e$	0.177
		$3b_1$	0.248	$6a_1$	0.657	$7b_2$	0.176
		$6a_1$	0.221	$3b_2$	0.607	$13a_1$	0.143
		$6e$	0.190	$6e$	0.598	$14a_1$	0.121
		$7a_1$	0.167	$4b_2$	0.547	$8b_2$	0.120
		$7e$	0.135	$3b_1$	0.529	$4a_2$	0.111
		$8a_1$	0.125	$7a_1$	0.527	$16e$	0.104
		$4b_1$	0.099	$7e$	0.517	$15a_1$	0.086
		$3b_2$	0.094	$8e$	0.481	$9b_2$	0.083
		$8e$	0.027	$8a_1$	0.478	$8b_1$	0.078
		$9a_1$	0.016	$2a_2$	0.451	$16a_1$	0.052
		E_F	0.400	$4b_1$	0.447	$9b_1$	0.049
		occ. bw	0.640	$9a_1$	0.421	$17e$	0.034
				$9e$	0.419	$5a_2$	0.030
					E_F	0.415	
					occ. bw	0.765	

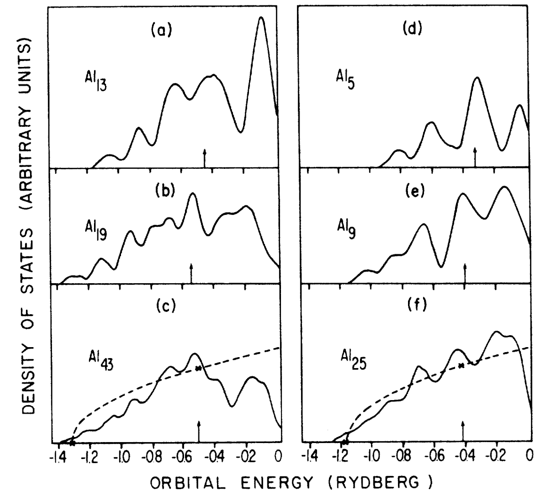

FIG. 2. Density-of-states curves for the clusters generated by replacing each orbital eigenvalue by a Gaussian of width parameter $\sigma = 0.05$ Ry. The curves have been normalized to the same value at the Fermi level (indicated by the arrows). The dashed curves represent a free-electron-like DOS, $\epsilon^{1/2}$ arbitrarily fitted at the positions of the **X**'s.

ters, there is at least a rough correspondence to the $\epsilon^{1/2}$ curve, with, however, some significant differences. The cluster DOS is smaller at low energy than the free-electron DOS and also smaller than the DOS found in band-structure calculations. This can be understood if one remembers that most of the atoms in the cluster have less than their full complement of 12 nearest neighbors. Therefore the full orbital splittings characteristic of bulk aluminum are not present, or, put another way, there are states associated with coordinative unsaturation which in the cluster contribute to the DOS at higher energies (i.e., closer to E_F). Adding more neighbors would tie up these states and increase the DOS near the bottom of the band. A second important difference between our DOS curves and the results of free-electron theory is the presence of structure in our DOS results. The most prominent feature for the occupied band of both Al_{25} and Al_{43} is a valley just below the Fermi level followed by a large peak at about -3.5 eV for Al_{25} and -2.5 eV for Al_{43}. This peak is followed on the low-energy side by a number of much smaller features. In this respect we are in qualitative agreement with the band-theory results of Tawil and Singhal. Indeed there is even a fairly good correspondence between the position of the most prominent features in our results and in the results of TS.

A third interesting feature of the DOS curves is apparent on comparing the results for the two homologous series of O_h and C_{4v} symmetry, respectively. One notices that the O_h curves are significantly less smooth than the C_{4v} curves. This is a result of the higher symmetry of the O_h clusters and the consequent higher degeneracy of their eigenvalues. If one regards the cluster eigenvalues as approximations to band eigenvalues at certain points (or regions) in reciprocal space, then the use of a higher-symmetry cluster puts more severe restrictions on the parts of reciprocal space which are sampled in a cluster calculation than does a cluster of lower symmetry.

A fourth feature which we wish to mention at this stage is the structure just above the Fermi level. For the largest clusters, this corresponds to a valley between two peaks, the peak-to-peak distance being about 2.8 eV for Al_{25} and 1.8 eV for Al_{43}. It is interesting that the DOS results of TS show a large sharp peak at very nearly the same energy as in our Al_{25} calculation. The reflectivity of aluminum departs from the free-electron model due to transitions in the energy range of 1.5 eV. Of course this energy cannot be compared precisely with DOS information because of the necessity to consider intensity matrix elements; however, a maximum in the "joint" DOS near this energy could help to explain this feature.

On the basis of the above discussion we therefore conclude that the largest cluster of each series yields sufficient parrallelisms with infinite or semi-infinite crystalline aluminum to be considered reasonably converged models for our purposes. We wish now to compare our results with experimental UPS results.

The UPS spectrum of a polycrystalline aluminum film taken with He II radiation is shown in Fig. 3 along with the part of the DOS for Al_{25} be-

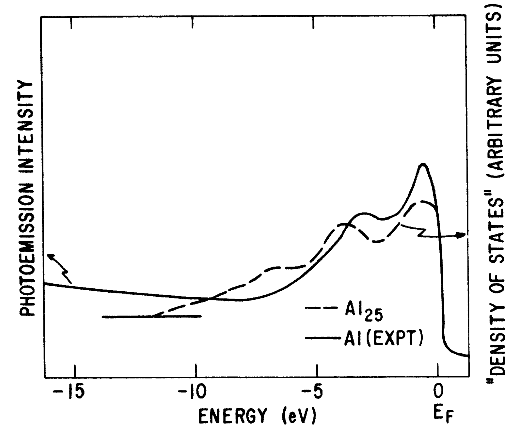

FIG. 3. Comparison of DOS curve from $X\alpha$-SW calculation on Al_{25} with the photoemission spectrum of clean polycrystalline Al as given in Ref. 16.

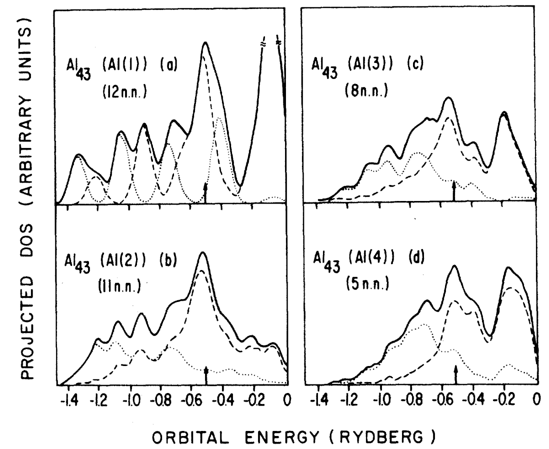

FIG. 4. Projected DOS curves for the atoms in Al_{43} cluster. The numbering of the atoms is the same as in Table I. The number of nearest neighbors (nn) is indicated for each curve. The dotted line represents the contribution from s waves; the dashed line, contribution from p waves.

low the Fermi level. Considering all the caveats mentioned in Sec. III about comparing DOS curves with UPS spectra, the agreement between the two curves is quite remarkable and must be considered strong evidence for the adequacy of the Al_{25} cluster as far as interpreting the general features of the UPS spectrum is concerned. In particular the structure between -5 eV and the Fermi level is satisfactorily reproduced. This lends support to our results and to those of TS concerning departures from free-electron behavior. The region below -5 eV has to be examined carefully. Here the UPS intensity falls off rapidly and, as mentioned above, the bottom portion of the occupied band does not appear in the spectrum. Several possible reasons for this behavior can be considered: (i) the intensity matrix elements for the states near the bottom of the band may be very small; (ii) electron escape depths may be such that the spectrum corresponds predominantly to surface or near-surface atoms and hence the comparison should more properly be with surface DOS and not total DOS information; (iii) the experimental set-up may be such that peaks in this energy region are not observed. A striking example of the occurence of the last situation for Ni may be found in the recent work of Smith *et al.*[46] All of these possible reasons should be considered. Point (iii) would require a detailed angle-resolved and photon-energy dependent study of single-crystal surfaces, and we hope that such studies will soon be forthcoming. In what follows we intend to provide at least partial responses to points (i) and (ii). In order to do this we have generated local DOS curves for all of the unique atoms of the Al_{43} and Al_{25} clusters which are shown in Figs. 4 and 5, respectively. These curves help to respond to point (ii). In addition some information relevant to point (i) can be obtained by decomposing the LDOS curves into contributions from s and p partial waves. If one assumes that the largest overall matrix element differences are likely to be caused by differences in partial wave character, then a predominance of say s character near the bottom of the band coupled with small matrix elements for s states could possibly lead to a rationalization of the low intensity.

The most striking general feature of this set of curves is the correlation between the occupied LDOS bandwidth and the number of nearest neighbors present for the atom in question. Those atoms with fewer neighbors have much narrower LDOS curves and in particular the intensity at the bottom of the band is greatly diminished with respect to that for a "bulk" atom. Thus our results indicate that point (ii) should be retained as a possible explanation of the narrow UPS band. Similar effects have been previously discussed for solid-state models,[45,49,50] but the present results represent the first time that this type of information has been extracted from LDOS results of a cluster calculation.

If one examines the s,p decomposition for the "bulk" atom in both Al_{43} and Al_{25}, it is seen that no clean separation is possible so that in the absence of detailed intensity calculations there is no reason to expect a diminished intensity of bulk photoemission at lower energies. Interestingly,

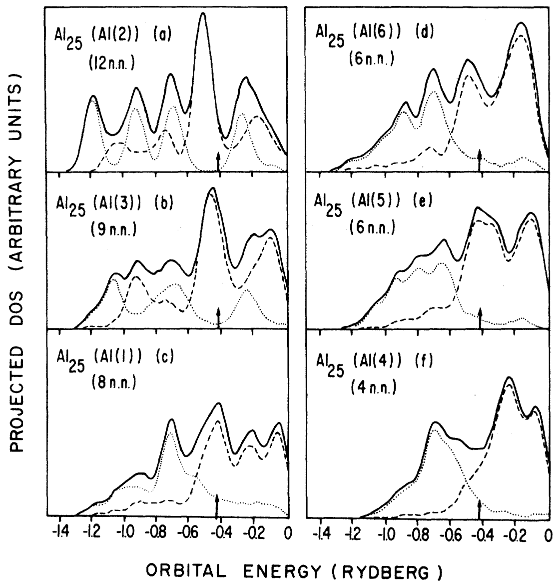

FIG. 5. As in Fig. 4, but for Al_{25}.

for the "surface atoms", i.e., those with fewer neighbors, the separation of *s*-like and *p*-like states is much more apparent. The states at lower energy are predominantly *s*-like, while those nearer the Fermi level are *p*-like. Smaller values of matrix elements for *s* states would then accentuate the band narrowing already present in the overall LDOS.

If one examines all of the curves in Figs. 4 and 5 and attempts to choose those which most nearly correspond to the observed UPS spectrum, namely those with a large LDOS at the Fermi level, followed by a valley, then a peak, and then a rapidly dying tail, then for Al_{25} Fig. 5(c) fits most nearly, while for Al_{43} Fig. 4(d) is the closest. In the case of Al_{25}, this atom corresponds to an atom on a (100) surface while for Al_{43} this atom corresponds to a member of a small (three-atom) segment of a (111) surface. In the formation of a polycrystalline film, it is normal for the surface to be composed mainly of low-index planes so one would expect the contribution from Fig. 5(c) or Fig. 4(d) to the observed UPS intensity to be large. We therefore suggest that point (ii) perhaps accentuated by point (i) may be the principal reason for the observed narrowing of the UPS band. Detailed angular-dependent matrix-element calculations including the effects of the finite mean-free path for electrons will be necessary in order to give a quantitative account of the spectrum. It is now possible, within the framework of SCF $X\alpha$ SW theory, following the work of Davenport,[51] to perform such calculations and they are planned for the near future for the aluminum and aluminum plus oxygen systems.

While we have been concerned above with the photoemission properties of pure aluminum, it is also clear that such information as contained in Figs. 4 and 5, if obtained for transition metals, is potentially useful for studies of chemisorption and catalysis. It is well known in catalysis[52] that the properties of various stepped surfaces and surfaces with kinks or other deformities may be quite different from those of flat low-index surfaces. The various atoms in say Al_{25} can be regarded as models for these nonuniform surfaces and the LDOS curves provide information about the local electronic structure and it is clear from the figures that this can be quite different for atoms in different local environments. If one wishes to consider the chemisorption of an adatom on a given metal atom, then the relative positions of the energy levels [orbital electronegativities (see Johnson[53])] of adsorbate and substrate are important. For instance, consider the adsorption of a hypothetical adatom which has a single energy level at −1.0 Ry on Al_{25}. For this situation, resonant covalent interactions will be largest for those metal atoms which have a large LDOS at this energy.

One is even tempted to speculate about a simple explanation of the existence of so-called structure-sensitive and conversely structure-insensitive catalytic reactions. The former are highly dependent on the physical form of the catalyst used, while the latter are not. If we allow ourselves to greatly oversimplify the situation to the case of a reaction rate being essentially dependent on the resonant interactions mentioned above, then the case already cited of an adsorbate level at −1.0 Ry would be clearly structure sensitive since the LDOS varies greatly from atom to atom at this energy. If, however, the adsorbate level were at, say, −0.6 Ry, then for all of the atoms examined one has to a first approximation the same LDOS and hence one might expect relatively little structure sensitivity. Similar LDOS plots for the case of transition-metal clusters should prove useful in the future in attempting to understand some of the basic concepts of heterogeneous catalysis.

V. CONCLUSION

The present work on clusters of aluminum atoms is the first part of a study on the chemisorption of atoms and molecules on various aluminum surfaces. Before treating the more complicated case of chemisorption,[18-20,35] a careful study of the dependence of the results (primarily with respect to photoemission experiments) on the number of atoms in the model was carried out. It was found that clusters containing at least some third neighbor interactions (Al_{25} and Al_{43}) are able to provide useful information. Smaller clusters are not likely to be adequate, at least for the case of approximately free-electron-like metals, and their use is discouraged. Similar studies for the case of transition-metal clusters, in which the electrons are thought to be more localized, are clearly important and work aimed at determining the cluster size dependence for these metals is currently in progress (see, e.g., Refs. 8 and 53).

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