Study of sorption of oxygen on Al[†]

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uv photoemission study of oxygen sorbed on clean polycrystalline Al is reported. For small exposures of oxygen (0.5–3 L), a resonance level approximately 3 eV wide (FWHM) at 7.2 eV below E_F was observed, and negligible work-function change was detected. These results disagree with recently reported calculation based on the atom-jellium model. We show that the origin of the disagreement is the fact that the model cannot accomodate the tendency of small, very electronegative adatoms such as oxygen to penetrate the metal surface. A generalized model allowing adatom penetration is seen to be consistent with the measurements. An independent model calculation of oxygen chemisorption on a small aluminum cluster based on the Hartree-Fock-Slater self-consistent-field method also confirms the penetration of the oxygen atom into the hole sites in between the aluminum surface atoms. Exposures beyond 3 L do not produce any shift in the resonance position and only a slight lowering of the work function.

In recent years there has been increasing theoretical and experimental attention given to the adsorption of gases on metals. Recently, two of us published the results of self-consistent calculations describing the chemisorption of several atoms, including oxygen, on jellium.[1] The attractive simplicity of the atom-jellium model and its apparently wide range of applicability led us to explore its quantitative accuracy experimentally. We measure two quantities predicted by the theory, the energy of the oxygen $2p$ resonance and the dipole moment on the adatom (as reflected by the change in the work function). The resonance position was predicted to be 2.2 eV below E_F and observed at 7.2 eV; a substantial dipole moment was predicted, but no change in work function was measured. The absence of work-function changes indicates that the oxygen has penetrated the metal surface. Previous experimental studies of Sr and Cs [2,3] have established that oxygen adsorption on these materials occurred beneath rather than on the surface. Such behavior was easy to rationalize for Cs and Sr because of the extremely open nature of the metallic lattices. However, it was surprising to find this type of behavior in Al because this metal is more closely packed, because oxygen does not have a high solubility in Al (as it does in Cs and Sr),[2,3] and because the atom-jellium calculations predict that the oxygen will remain outside the metal. We show the experimental-theoretical difference in both resonance position and dipole moment to be due to an artificial aspect of the model which becomes important when small strongly electronegative adatoms penetrate the metal surface; approximate removal

of this aspect permits self-consistent atom-jellium calculations to be used to interpret the present measurements. The resulting improved understanding of both the oxidation process and the range of validity of the atom-jellium model demonstrates the value of a strong interaction between theory and experiment.

First, let us describe the experiment. The photoemission study of oxygen sorption on Al was performed at $h\nu = 21.2$ eV and $h\nu < 11.8$ eV in a UHV ion-pumped chamber with a base pressure of 4×10^{-11} Torr. A two-staged differentially pumped He resonance lamp equipped with an Al filter provides a monochromatic light source for $h\nu = 21.2$ eV. For $h\nu \leq 11.8$ eV, the vacuum chamber was sealed off with a LiF window and a McPherson 225 monochromator with a hydrogen discharge lamp was used as a light source. In both cases, the light beam was perpendicular to the sample. The energy analyzer was a retarding-field hemispherical can with an extra grid for improved resolution. Data were taken by using ac-modulation technique. The sample was prepared by evaporating a 99.999%-pure Al boule from an electron gun onto a niobium single crystal about 30 cm away. Because of the high chemical reactivity of Al it was difficult to prepare, and prolonged outgassing was necessary to obtain a clean film.

Figure 1 shows the result of oxygen adsorption on clean Al at $h\nu = 21.2$ eV. Since the surface and bulk plasma energies for Al are 10.3 and 14.5 eV, respectively, Al is almost transparent at 21.2 eV with the result that the quantum yield is extremely low. The clean EDC (energy distribution curve)
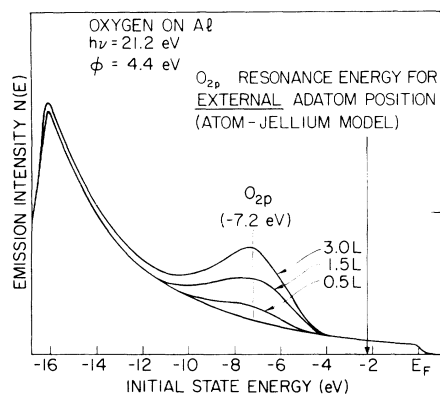
FIG. 1. EDC's at $h\nu = 21.2$ eV showing the formation of the oxygen resonance level 7.2 eV below E_F following oxygen sorption at room temperature.

is characterized by a high scattering peak which decreases monotonically to the Fermi edge. It is important to note that the clean curve gives no evidence of the oxygen peak and that small to intermediate exposures of oxygen cause a single broad resonance band to form at 7.2 eV below E_F (~3 eV FWHM). At higher exposures (not illustrated in Fig. 1) the oxygen peak continues to grow until the reaction saturates. The single resonance suggests noninteracting oxygen ions.[4] At higher exposures (>50 L, 1 L = 10^{-6} Torr sec) a second peak appears at 13.5 eV below E_F.[5] (Similar results were obtained in Ref. 6.) Figure 2 shows the result of oxygen exposure investigated at lower photon energies. At $h\nu = 10.2$ eV the only effect of oxygen adsorption is a uniform drop in emission, and no new structure appears. At $h\nu = 11.1$ eV, the onset of the oxygen peak on the left side of the EDC can barely be seen, in agreement with the 21.2-eV results.

The low-energy data also show that there is no change in the work function ϕ. The work function is given by the photon energy minus the width of the EDC. Any change in work function can be sensitively detected by a change in the low-energy cutoff of the EDC's when they are plotted as in Figs. 1 and 2. Because of the higher resolutions obtainable at low $h\nu$, the EDC's of Fig. 2 give the most-sensitive indications of changes in ϕ. For exposures up to 10 L, no change was detected. Based on knowledge of the instrumentation, the resolution of changes in ϕ was better than ±50 meV. For exposures above 10 L, ϕ decreased by 0.2 eV. This is tentatively associated with the appearance of oxygen close enough to the surface to affect the work function. The decrease in work function suggests that the negative oxygen ions must reside below positive Al surface ions. The overall behavior is qualitatively
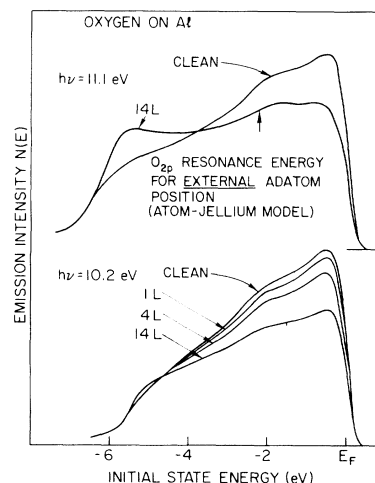

FIG. 2. EDC's at $h\nu = 10.2$ and 11.1 eV showing the effect of oxygen sorption on Al at low photon energies.

similar to the oxidation of Sr and Cs where movement of oxygen into the bulk dominates the oxidation process.[3,4]

We discuss in detail now the relationship of the theory to the measurements described above.[7] In discussing the likelihood of adatom penetration, three facts seem particularly important. First, since the calculated binding energy of an oxygen atom outside the metal surface (5.4 eV in Ref. 1) is of the order of an Al–O bond strength (5 eV),[8] the total energies associated with various arrangements of Al and O atoms on oxidation should differ by only ~$\frac{1}{2}$ eV. Second, there exists positions inside the Al fcc lattice which are more distant from all Al atoms than the Al–O bond lengths in Al_2O_3[9]; oxygen can therefore "fit" inside the Al lattice.[10] Third, access to these positions from outside the metal appears difficult only through the most densely packed face (111) of the crystal, where an oxygen atom must pass closer to an Al atom than the Al–O bond lengths in Al_2O_3. These facts suggest that total energy minima differing by ~$\frac{1}{2}$ eV probably exist both inside the metal and outside close-packed surfaces. It is of interest to note that recent work-function measurements for oxygen atom adsorbed on three low-index faces of Al show almost zero derivative at zero coverage.[11] In view of the present theoretical analysis, this strongly suggests that oxygen-atom penetration exists on different surfaces of single-crystal Al; and is not limited to polycrystalline films. In order to optimize the possibility of observing the external minimum, if it exists at all, one should study very smooth (111) Al single-crystal face at low temperature using oxygen atoms rather than molecules.
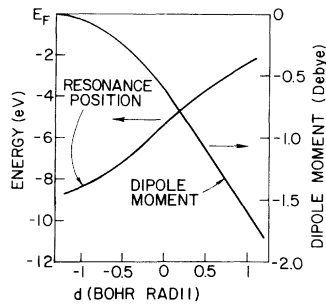
FIG. 3. Dependence of oxygen $2p$ resonance energy and dipole moment on metal-oxygen separation. The sign of the dipole moment is defined so that a negative moment corresponds to an increase in substrate work function. The positive ions of the metal are modeled by a semi-infinite uniform distribution of positive charge extending from $d=0$ to $d=-\infty$. It is to be recalled that in this model each plane of substrate ions has been smeared symmetrically into a homogeneous slab of positive charge, implying that the true position of the plane through the centers of the ions in the outermost layer is half an interplanar spacing behind the background boundary. The physical scale is set by the position of the outermost plane of nuclei at $d=-2.2$ a.u. [Al (111)] and the equilibrium position of a single oxygen atom, calculated to be at $d=+1.1$ a.u. for the atom-jellium model (Ref. 1) and at $d=+0.3$ a.u. when Al pseudopotentials are included to first order (Ref. 12).

The likelihood of adatom penetration is inconsistent with the sharp increase in total energy which is found to accompany oxygen penetration in the atom-jellium model (see Fig. 1 of Ref. 1) and thus illustrates a limitation of that model. This sharp increase stems primarily from the electrostatic energy associated with moving the adatom nucleus directly into the positive background of the jellium. We have quantitatively confirmed this statement by perturbatively replacing the positive background by a semi-infinite fcc lattice of Al pseudopotentials, much as was done in Ref. 12. The perturbation (to first order) reduces the total energy price for the adatom to penetrate the metal from its external equilibrium position[13] to ~3 eV[14] (from ~16 eV). Obviously the first-order pseudopotential model represents a very strong improvement but still is imperfect. Stable adatom positions inside the metal presumably result from higher-order terms (whose importance is sug-

gested by the magnitude of the first-order term) and possible lattice rearrangements.

Although the energy associated with the eight protons of the oxygen nucleus sitting at one point in the perturbing potential can be large, the average of the potential over individual electron states can be quite small. In particular, its effect (again to first order) on the $2p$ resonance position is found to be negligible. Because of this and because the aspect of the model which prohibits adatom penetration is not related to the model's electronic structure, we feel that the shift in the $2p$ resonance energy with penetration can be qualitatively understood using self-consistent atom-jellium calculations for adatom positions other than that dictated by the model's total energy. The results of these calculations are shown in Fig. 3.

As the adatom is moved into the metal, both the $2p$ resonance and the dipole moment move dramatically in the direction of the experimental data. The dipole moment rapidly disappears[15] and the resonance drops quickly from 2 eV (below E_F) through the experimental value of 7 eV (to an interior limit of ~10 eV). Further support of our interpretation is provided by a cluster calculation of an oxygen atom chemisorbed on the (100) surface of Al, based on the Hartree-Fock-Slater consistent-field method. Good agreement is obtained with the oxygen resonance position of the jellium model when the adatom is placed at the outside minimum indicated by the jellium model. However, no total energy minimum was found in the cluster calculation, and when the oxygen atom is moved into the hole site in between the surface Al atoms, the resonance goes deeper in binding energy and broadens.[16]

We are led by these considerations to conclude that, although the degree of adatom penetration reflected in the present data is clearly beyond the scope of the atom-jellium model of Ref. 1, there is an understandable connection between the model and the experiment whose elucidation leads to an improved understanding of the initial stage of the oxidation of an aluminum surface. This work thus indicates the necessity for taking into account the possibility that absorption (i.e., incorporation) rather than adsorption can occur even as the first step in sorption of simple gases.

[1]N. D. Lang and A. R. Williams, Phys. Rev. Lett. 34,
531 (1975). The jellium density used ($r_s=2$) is appropriate to Al ($r_s=2.07$).
[2]C. R. Helms and W. E. Spicer, Phys. Rev. Lett. 28, 565 (1972); 32, 228 (1974).

[3] P. E. Gregory, P. Chye, H. Sunami, and W. E. Spicer, J. Appl. Phys. **46**, 3525 (1975).

[4] For nondissociative-oxygen-molecule adsorption, one would expect two to three molecular-orbital-like resonance levels instead of a single resonance.

[5] The second peak at 13.5 eV below E_F can be resolved only at rather high exposure (>50 L) and is very much lower in intensity than the main peak at 7.2 eV below E_F. Tentatively, we associate this peak with the beginning of the nucleation of aluminum oxide (Al_2O_3).

[6] S. A. Flodstrom, L. Petersson, and S. B. M. Hagstrom, J. Vac. Sci. Tech. (to be published).

[7] Note that the calculated resonance position referred to is that of the peak in the computed density of eigenstates of the local-density approximation to the Kohn-Sham equations [these equations, given in W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965), are used to determine the electron density distribution of the chemisorbed system]. The formal relationship between this state density and the experimentally measurable quasiparticle density of states is discussed in L. J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966). With the exception of extremely narrow resonances (and discrete levels), the positions of the peaks in these two state densities are found to be reasonably close empirically. For example, even in the case of the Zn d band (which has a computed full width at half-maximum of just 1.5 eV) the calculation using the Kohn-Sham equations [V. L. Moruzzi, A. R. Williams and J. F. Janak (private communication)] puts the center of the d band 8 eV below E_F, while the uv photoemission experiment of P. O. Nilsson and I. Lindau [J. Phys. F **1**, 854 (1971)] puts it 9.5 eV below and the x-ray photoemission experiment of L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley [Phys. Rev. B **8**, 2392 (1973)] puts it 10 eV below. See also, for example, the good agreement found between the experimental results of T. Sakurai and H. D. Hagstrum [Phys. Rev. B (to be published)] for atomic hydrogen chemisorbed on Si (111) and the calculations of J. A. Appelbaum and D. R. Hamann [Phys. Rev. Lett. **34**, 806 (1975)].

[8] *Handbook of Chemistry and Physics*, 56th ed., edited by R. C. Weast (Chemical Rubber, Cleveland, 1975), p. F-216.

[9] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1964), Vol. 2, p. 7.

[10] The "room" inside the Al lattice might seem inconsistent with Al's identity as a prototype close-packed metal. It is close-packed, however, with respect to electrons; there is room in between the atomic cores for an electronegative atom such as oxygen which is capable of accepting the Al electrons.

[11] P. O. Gartland (unpublished). See also Ref. 16.

[12] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970); **3**, 1215 (1971). The significance of this perturbation in the present context was recognized by O. Gunnarsson, H. Hjelmberg and B. I. Lundqvist (unpublished).

[13] For adsorption on the (111) face in a threefold (centered) site over a hole in the second layer of substrate atoms, the minimum in the curve of total energy vs distance d (see caption of Fig. 3) corresponds to a binding energy of 5.8 eV (with $d = 0.3$ a.u.) when pseudopotential corrections are included. [The calculated binding energy for the other threefold site and the twofold (bridge) site differ from this by $\lesssim 0.3$ eV.] These computations used the ionic pseudopotential employed by N. W. Ashcroft and D. C. Langreth [Phys. Rev. **155**, 682 (1967)]. The atom-jellium model (Ref. 1) gave a binding energy of 5.4 eV (with an equilibrium d of 1.1 a.u.).

[14] Calculated assuming the atom has penetrated to a tetrahedral hole in the undistorted fcc Al lattice.

[15] The rapidity with which the dipole moment disappears with penetration raises the possibility that the moment observed in the present measurements is consistent with having oxygen atoms outside but very close to the outermost lattice plane (the plane passing through the outermost metal nuclei). However, additional evidence that the oxygen lies inside the surface is provided by the absence of any observed splitting of the oxygen $2p$ resonance and by recent secondary-ion mass-spectrometry measurements [P. H. Dawson, Int. J. Mass. **16**, 269 (1975); Surf. Sci. (to be published); and private communication]. Our calculations indicate that for adatom positions outside the metal corresponding to a small dipole moment, the p_σ states lie $\sim 1\frac{1}{2}$ eV above the p_π states. We believe we would observe such a splitting if it were present.

[16] J. Harris and G. S. Painter, Phys. Rev. Lett. **36**, 151 (1976).