spection, $\omega = 0$, $q \to 0$ is a solution of Eq. (2)];
(b) the normal-flapping mode; and (c) the super-
flapping mode. Again, in principle d_{0z}^{-} couples
to density fluctuations, $d_{0x,y}^{+}$ to spin fluctuations,
but only d_{0z}^{-} is easily excited by sound waves.

The coupling of the various modes of $\delta\Delta$ among
themselves at finite q can be neglected for not-
too-large q values.

In conclusion, I suggest sound propagation ex-
periments in the A phase at lower temperatures
(possibly in a magnetic field to suppress the B
phase) and higher frequencies as in Refs. 3–5,
to verify the considerable structure predicted for
the sound absorption by this theory. In particu-
lar, it would be interesting to observe the re-
entrance of the normal-flapping mode at lower
temperatures (around $0.5T_c$) in the absorption of,
for example, 50-MHz sound. The observation of
these phenomena would furnish strong proof for
the realization of the axial state in ^{3}He-A.

I am grateful to D. Einzel, M. Liu, and D. Rain-
er for interesting discussions and to R. Combes-
cot, A. J. Leggett, S. Takagi, and G. E. Volovik
for informing me of their work.

[1]J. C. Wheatley, Rev. Mod. Phys. 47, 415 (1975).
[2]A. J. Leggett, Rev. Mod. Phys. 47, 331 (1975).
[3]D. T. Lawson, W. J. Gully, S. Goldstein, R. C. Rich-
ardson, and D. M. Lee, Phys. Rev. Lett. 30, 541 (1973).
[4]D. N. Paulson, R. T. Johnson, and J. C. Wheatley,
Phys. Rev. Lett. 30, 829 (1973).
[5]J. B. Ketterson, P. R. Roach, B. M. Abraham, and
P. D. Roach, in Quantum Statistics and the Many-Body
Problem, edited by S. B. Trickey, W. P. Kirk, and
H. W. Dufty (Plenum, New York, 1975).
[6]P. Wölfle, Phys. Rev. Lett. 30, 1169 (1973).
[6b]P. Wölfle, Phys. Rev. B 14, 89 (1976).
[7]J. W. Serene, thesis, Cornell University, 1974 (un-
published).
[8]H. Ebisawa and K. Maki, Prog. Theor. Phys. 51, 337
(1974).
[9]R. Combescot, Phys. Rev. A 10, 1700 (1974).
[10]R. Combescot, Phys. Rev. Lett. 35, 1646 (1975).
[11]G. E. Volovik, Pis'ma Zh. Eksp. Teor. Fiz. 22, 234,
412 (1975) [JETP Lett. 22, 108, 198 (1975)].
[12]M. C. Cross and P. W. Anderson, in Proceedings of
the Fourteenth International Conference on Low Tem-
perature Physics, Ontaniemi, Finland, 1975, edited
by M. Krusius and M. Vuorio (North-Holland, Amster-
dam, 1975), Vol. I, p. 29.
[13]A. J. Leggett and S. Takagi, to be published.
[14]B. R. Patton, in Proceedings of the Fourteenth Inter-
national Conference on Low Temperature Physics, Ot-
aniemi, Finland, 1975, edited by M. Krusius and
M. Vuorio (North-Holland, Amsterdam, 1975), Vol. I,
p. 17.
[15]P. Wölfle, in Quantum Statistics and the Many-Body
Problem, edited by S. B. Trickey, W. P. Kirk, and
J. W. Dufty (Plenum, New York, 1975).
[16]P. Wölfle, in Proceedings of the Fourteenth Interna-
tional Conference on Low Temperature Physics, Otanie-
mi, Finland, 1975, edited by M. Krusius and M. Vuorio
(North-Holland, Amsterdam, 1975), Vol. I, p. 25.
[17]L. Tewordt and D. Einzel, to be published.
[18]K. Maki, J. Low Temp. Phys. 16, 465 (1974).
[19]P. Wölfle, Phys. Rev. Lett. 34, 1377 (1975).

Multiple Oxidation States of Al Observed by Photoelectron Spectroscopy of Substrate Core Level Shifts*

S. A. Flodstrom, R. Z. Bachrach, R. S. Bauer, and S. B. M. Hagström
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 7 September 1976)

Substrate core chemical shifts upon chemisorption of oxygen on aluminum are observed
using variable-excitation-energy photoelectron spectroscopy. At low exposures a unique
intermediate oxidation state evolves where the Al $2p$ level is shifted by only 1.3 eV to-
ward higher binding energy as compared to the 2.6-eV shift observed for heavily oxidized
aluminum (Al_2O_3). Simultaneous observation of the O $2p$ resonance shows evidence for a
sharp phase change at exposures close to monolayer formation.

In a photoelectron spectroscopy study of the ini-
tial oxidation of aluminum, we have discovered
a core-level shift of the Al $2p$ atomic energy lev-
el which is considerably smaller than the shift
for fully oxidized aluminum (Al_2O_3).[1] This pre-
viously unobserved but widely sought phenomenon
is observed for oxygen exposures in the range
50–400 langmuir (L) (1 L = 10^{-6} Torr sec). The

onset of a shifted substrate core peak is followed
by an abrupt change in the shape of the O $2p$ res-
onance between 100 and 200 L oxygen exposure.
These observations show the existence of an inter-
mediate oxide phase or a chemisorbed state. The
observation is important not only in understand-
ing the present system but also in the general use
of core-level shifts to study the interaction of

solid surfaces with foreign atoms.

Extensive studies of chemisorption on metal substrates have been performed with x-ray photoemission, which has the attractive feature that both valence bands and core levels can be studied. In these studies, adsorbate core-level shifts induced by a charge transfer between the adsorbate and the substrate have been observed. Most attempts to observe corresponding shifts of the substrate core levels have typically not succeeded.[2,3] The typical behavior observed in metal-oxygen interactions, for example, has been a slight broadening of the metal core level; and, after heavy oxidation, a shifted peak corresponding to the bulk oxide of the metal has appeared.[4,5] In fact, suggestions have been made of an insensitivity of metal core levels to chemisorption.[4]

Aluminum provides a model system to study adsorption phenomena for a free-electronlike substrate. In previous studies of the aluminum-oxygen system,[6] only the valence bands were accessible for study with the 21.2- and 40.8-eV photon energies of He resonance radiation. Sharp resonance states in the valence-band spectral region derived from O $2p$ states for low oxygen coverages were observed on clean aluminum substrates. The measurements presented here correlate these adsorbate states with the interface behavior of the metal substrate. The variable-excitation-energy photoemission experiments use the 4° beam line at the Stanford University Synchrotron Radiation Project.[7] Measurements can be made in the 30–500-eV photon energy range. In this study, photon energies in the range of 100 to 250 eV were used to excite Al $2p$ electrons which have a binding energy of 73 eV; 50-eV photons were used to observe the O $2p$ states which have a binding energy of $\simeq 7.1$ eV. The kinetic energy range of 30 to 170 eV of the core photoelectrons provides measurements with maximum surface sensitivity; escape depths of only approximately 5 Å occur within this range.[8,9]

The angle of incidence of the linearly polarized ($\approx 85\%$) light with respect to the normal of the sample was 70°. The kinetic energies of the electrons were analyzed in a double-pass cylindrical mirror analyzer[10] with its optical axis located 20° off the normal of the sample; the relative energy resolution of the analyzer is $\Delta E/E = 1.6\%$.[10] The photon energy resolution is approximately 0.1 eV at 100 eV and varies as $(\hbar \omega)^2$.

The aluminum samples were prepared by evaporation *in situ* onto *in situ* cleaved germanium crystals. The pressure of the sample chamber
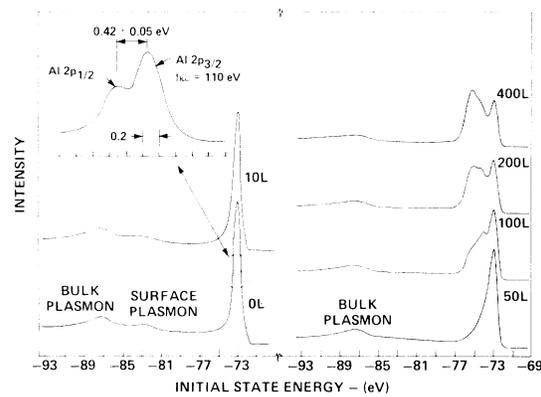

FIG. 1. Photoelectron spectra of the Al $2p$ region for clean and oxygen-exposed aluminum films at a photon energy of 170 eV. The oxygen exposures are given in langmuirs (1 L = 10^{-6} Torr sec). The expansion shows the resolved Al $2p$ doublet obtained at a photon energy of 110 eV.

was 1×10^{-10} Torr and rose to 1×10^{-8} Torr during the evaporation. However, the base pressure was reached within 60 s after the evaporation.

A sensitive test of surface cleanliness is to study the region of O-$2p$-derived levels in the valence-band region at low photon energies.[6] In recording spectra of freshly evaporated aluminum films using 50-eV photons, we saw no evidence of any structure due to oxygen adsorption; the detection limit is of the order of 0.01 monolayer coverage.

Figure 1 shows an extended spectrum of the Al $2p$ core-level region obtained from a clean aluminum film for a photon excitation energy of 170 eV. The absolute binding energy of this level with respect to the Fermi level was determined at 90 eV photon energy to be 73.0 ± 0.1 eV by recording the Al $2p$ peak and the valence band with a well-defined Fermi level in the same spectrum. By reducing the pass energy of electrons in the analyzer from 25 to 10 eV (i.e., to $\Delta E = 0.16$ eV), the Al $2p$ doublet was resolved, as seen by the inset in Fig. 1. The energy separation between the two peaks is 0.42 ± 0.05 eV.

Apart from this primary Al $2p$ structure, there is a tailing effect seen in Fig. 1 (0 L) on the high-binding-energy side; we attribute this to a many-body effect corresponding to the excitation of electron-hole pairs near the Fermi level simultaneously with the creation of the $2p$ hole.[11,12] More important for this study, the spectrum clearly displays the loss structure caused by plasmon creation. The behavior with oxygen exposure of the pronounced surface plasmon at

around an initial energy of -83 eV compared to
the bulk plasmon loss at -88 eV yields the damp-
ing of Al surface excitations due to the creation
of strong Al-O bonds. The details of the plasmon
loss as a function of excitation energy will be pre-
sented elswehere.[13] Examination of Fig. 1 during
the initial chemisorption (10 L) of oxygen on alu-
minum shows that the $2p$ peak changes very lit-
tle. In fact, the most pronounced feature change
in the spectrum is a decrease in the surface-
plasmon loss peak, proving that the aluminum
atoms in the surface layer are becoming involved
in bonding oxygen atoms. By contrast, the O $2p$
resonance seen in Fig. 2 is already a strong fea-
ture at this oxygen exposure. As the adsorption
proceeds, the changes in the Al $2p$ level become
more pronounced. In the exposure range 50–100
L, the evolution of a second peak corresponding
to a binding energy higher by 1.3 eV becomes
visible. At 50 L oxygen exposure the surface-
plasmon loss peak has completely disappeared.
The spectrum for 100 L exposure shows the be-
ginning of a third peak, which has grown to an
intensity equal to that of the -1.3-eV peak at an
exposure of 200 L. The third peak corresponds
to an increase in binding energy of 2.4 eV, which
corresponds closely to the chemical shift of 2.7
eV reported[1] for bulk aluminum oxide (Al_2O_3).
We, therefore, assign this peak to an alumina-
type coordination of the Al with the oxygen. By
400 L, this chemically shifted peak is 2.6 eV be-
low the clean-metal substrate peak and dominates
the spectrum. We assign this to the formation of
an oxide layer of nearly stoichiometric Al_2O_3.

Figure 2 shows the valence-band region as a
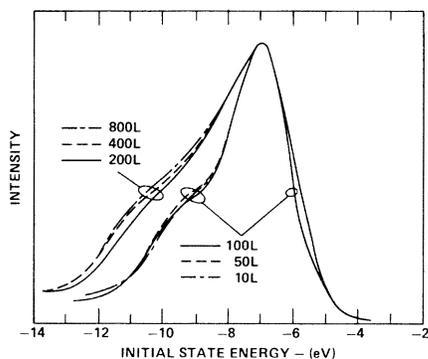function of oxygen exposure. An abrupt change

in the shape of the O $2p$ resonance occurs be-
tween 100 and 200 L. Above 200 L, the shape re-
mains nearly constant.

In Fig. 3 the integrated intensity of the O-$2p$-
derived peak in the Al valence band is plotted as
a function of oxygen exposure. This curve satu-
rates above 400 L, showing that the sticking prob-
ability for oxygen on the surface has dropped to
a very low value. For exposures greater than
400 L, we are primarily studying oxygen adsorp-
tion on alumina; that some oxygen uptake is still
possible can be judged by the intensity increase
observed in the 2.6-eV shifted alumina $2p$ peak
as compared to the metal Al $2p$ peak. The mech-
anism for this uptake is still not understood.
However, from knowledge of the escape depths
of the photoelectrons, the alumina layer can be
estimated as $\simeq 5$ Å for an oxygen exposure of 5
$\times 10^4$ L. At this exposure the maximum oxide-lay-
er thickness had not been reached. In x-ray pho-
toelectron spectroscopy measurements, the ratio
between the oxide-peak and the metal-peak inten-
sities has been observed to reach an equilibrium
value after heavy oxygen exposures.[1]

A further remark concerning the high-exposure
spectra should be made. The shoulder on the low-
er binding energy side of the -2.6-eV peak clear-
ly seen in the 400-L oxygen-exposed spectrum in
Fig. 1 seems to remain even at higher exposures
(>800 L), although its intensity is hard to judge
because of the simultaneous intensity increase of
the -2.6-eV peak. The shoulder at 400 L clearly
derives from the first oxidation state giving rise
to the shifted -1.3-eV peak.

After the formation of a monolayer of alumina
has taken place, it is obvious that further Al-O
interactions take place either on the vacuum inter-
face or on the metal interface of the alumina lay-
er. Our data do not allow a distinction to be made

FIG. 2. The O $2p$ peak at $\hbar\omega = 50$ eV for 10- to 800-L
oxygen exposures shown on a direct intensity scale ver-
sus energy. Peak heights are normalized to the same
value for different exposures to demonstrate changes
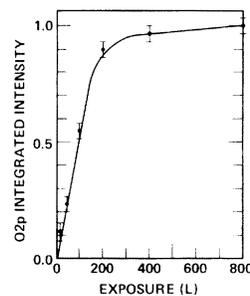in line shape.

FIG. 3. Intensity of the O $2p$ derived peak in the Al
valence band as a function of oxygen exposure. Maxi-
mum intensity is normalized to 1.

between these two alternatives. Tentatively we interpret our observation as reflecting in either case that the interaction yields an initial oxidation state at the interface, which corresponds to our observed peak at − 1.3 eV.

The initial adsorption of oxygen on aluminum is characterized by an almost constant rate of oxygen uptake up to an exposure of 150 L (Fig. 3).[14] During this phase of the oxygen-aluminum interaction, the narrow shape and binding energy of the O-$2p$-derived peak remain constant, as shown in Fig. 2, indicating that one type of Al-O bond dominates. A simultaneous observation of the Al $2p$ region shows that the main change in the spectra is the appearance of the unique − 1.3-eV peak, demonstrating that the formation of alumina is preceded by a bound precursor state. The observation of the − 1.3-eV peak is consistent with the assumption by Lang and Williams[15] of a charge transfer between the oxygen atoms and the aluminum substrate during the initial oxygen-aluminum interaction. However, at 50 L exposure a spectral feature at − 2.4 eV shows that some aluminum atoms have a chemical environment similar to the one in Al_2O_3. At 100 L oxygen exposure the − 2.4-eV feature is clearly visible as a shoulder on the − 1.3-eV peak. Thus during the initial-phase oxygen adsorption, the O $2p$ spectra show evidence for one type of Al-O bonds, but the Al $2p$ spectra show aluminum atoms in different chemical surroundings with respect to oxygen.

For higher oxygen exposures the − 2.4-eV peak shifts to − 2.6 eV. Its intensity increases gradually, and at 400 L exposure it dominates the chemically shifted structure in the Al $2p$ spectra. We interpret this as being due to the formation of a monolayer of nearly stoichiometric Al_2O_3 on the aluminum, causing both the increase in the − 2.6-eV peak and the drop in oxygen uptake. At 100–200 L oxygen exposure the O $2p$ resonance broadens dramatically on the high-binding-energy side (Fig. 3). This change in shape, having a phase transformation character, is interpreted as a change from the resonance-type Al-O bond to the type of Al-O bonds found in Al_2O_3. This change reflects the formation of an O $2p$ band as the oxygen density gets high enough for oxygen-oxygen interaction. The contrasting monotonic intensity increase of the − 2.6-eV peak and the sharp change in the O $2p$ resonance level due to Al_2O_3 formation is attributed to the difference in probing core versus valence-band levels; i.e., the

core levels are sensitive to the local chemical surroundings of the atom, but the valence-band levels directly show the bonding mechanism.

In summary, we have observed a previously undetected intermediate oxidation state of aluminum preceding the formation of alumina. The features in the shifts of the substrate core levels, correlated with changes in the oxygen valence levels, provide detailed information about the Al-O interaction. Work is now in progress to study these and related phenomena on single-crystal faces.[15]

The support of J. C. McMenamin and H. A. Six is gratefully acknowledged.

[1]A. Barrie, Chem. Phys. Lett. 19, 109 (1973).
[2]J. C. Fuggle and D. Menzel, Surface Sci. 53, 21 (1975).
[3]A. Barrie and A. M. Bradshaw, Phys. Lett. 55A, 306 (1975).
[4]C. R. Brundle, Surface Sci. 48, 99 (1975).
[5]C. R. Brundle and A. F. Carley, Chem. Phys. Lett. 33, 41 (1975).
[6]S. A. Flodstrom, L. G. Petterson, and S. B. M. Hagström, J. Vac. Sci. Technol. 13, 280 (1975); K. Y. Yu, J. N. Miller, P. Chye, W. E. Spicer, W. D. Lang, and A. R. Williams, Phys. Rev. B 14, 1446 (1976).
[7]F. C. Brown, R. Z. Bachrach, S. B. M. Hagström, N. Lien, and C. Pruett, in Vacuum Ultraviolet Radiation Physics, edited by E. Koch, R. Haensel, and C. Kunz (Pergamon, Elmsford, N.Y., 1975), p. 785.
[8]C. R. Brundle, J. Vac. Sci. Technol. 11, 212 (1974).
[9]J. C. Tracy, J. Vac. Sci. Technol. 11, 280 (1974).
[10]Physical Electronics Industries, High Precision Energy Analyzer No. 15-255G; spectra were recorded with a constant pass energy of 25 eV, yielding a ΔE = 0.4 eV.
[11]G. D. Mahan, Phys. Rev. 163, 612 (1967).
[12]S. Doniach and M. Šunjić, J. Phys. C 3, 285 (1970).
[13]S. A. Flodstrom, R. Z. Bachrach, R. S. Bauer, J. C. McMenamin, and S. B. M. Hagström, J. Vac. Sci. Technol. (to be published).
[14]C. Martinsson, L. G. Petterson, S. A. Flodstrom, and S. B. M. Hagström, in Proceedings of the Conference on Photoemission from Surfaces, Noordwijk, Holland, September 1976, European Space Agency Report No. ESA SP-118 (to be published).
[15]N. D. Lang and A. R. Williams, Phys. Rev. Lett. 34, 531 (1975).