

Surface core-level shifts of the Al(100) and Al(111) surfaces

R. Nyholm, J. N. Andersen, J. F. van Acker, and M. Qvarford

*Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Sölvegatan 14, S-223 62 Lund, Sweden
and MAX-LAB, Box 118, Lund University, S-221 00 Lund, Sweden*

(Received 23 August 1991)

The surface core-level shifts of the Al(100) and Al(111) surfaces have been measured by high-resolution photoelectron spectroscopy. For the Al(100) surface we obtain a value of (-96 ± 5) meV. This value is in excellent agreement with a recent *ab initio* calculation by Feibelman. The surface core-level shift of the Al(111) surface is found to be close to zero, and an upper limit of 15 meV is obtained.

Surface core-level shifts play an important role in the understanding of the electronic and geometrical properties of surfaces and much effort has been put into measuring them by high-resolution photoelectron spectroscopy. The shifts are of fundamental importance because they can be related to quantities like segregation and surface energies,¹ thus providing values for these quantities that may, for example, be used to test the accuracy of *ab initio* calculations of total energies in bulk and surface impurity systems. In addition to this, the sensitivity of the core-level binding energies to the chemical environment provides means to investigate the bonding at, e.g., compound surfaces.¹ The systematic collection of data on single-crystal faces of the pure elements is of importance in order to understand such more complicated compound surface systems. A lot of experimental data has been collected during the past years, but still important determinations are lacking or uncertain. One of these cases is the surface core-level shift of different crystal faces of aluminum,²⁻⁴ normally regarded as one of the prototype free-electron metals. The situation seems to be especially unsettled for the (100) surface.

Using tunable synchrotron radiation for the excitation, Eberhardt, Kalkoffen, and Kunz,² for the (100) surface, observed a broadening of the Al $2p$ core levels in surface-sensitive spectra as compared to bulk-sensitive spectra. This effect was suggested to be due to a crystal-field splitting for the surface atoms while a possible surface core-level shift was estimated to be less than -40 meV.² Chiang and Eastman³ used partial yield measurements on the Al $2p$ absorption edge to deduce a surface core-level shift of -57 meV, finding no unusual large extra broadening of the surface core level. Subsequent calculations by Wimmer *et al.*⁵ showed that a surface-induced crystal-field splitting of the $2p_{3/2}$ level of 38 meV could be expected for the (100) surface atoms. These authors⁵ also calculated a surface core-level shift of -120 meV for the $2p$ level, neglecting final-state effects. Later Kammerer *et al.*⁴ performed a series of measurements on the simple metals Na, Mg, and Al. For Na and Mg, surface core-level shifts could be accurately determined.⁴ For Al(100), however, the authors state that no definite conclusions could be drawn from the experimental results. This surface showed an increase in linewidth for surface-sensitive spectra which was interpreted as due to either a surface

core-level shift (-120 meV) or to a broadening from a crystal-field splitting, as proposed earlier by Eberhardt, Kalkoffen, and Kunz² and Wimmer *et al.*⁵ Finally, Feibelman⁶ has recently calculated the surface core-level shift for the Al(100) surface taking full account of final-state relaxation effects to obtain a value of -97 meV. For the Al(111) surface it seems to be accepted that the surface core-level shift is small. In Ref. 4 no shift could be detected for this surface within the quoted experimental accuracy of ± 50 meV.

In an effort to resolve these differences we have studied the Al(100) and Al(111) surfaces with a much better experimental resolution than in previous experiments. We are able to show beyond doubt that the Al(100) surface has a surface core-level shift to lower binding energies. The absolute value is (-96 ± 5) meV in reasonable agreement with the value proposed in the work of Kammerer *et al.*⁴ and in most excellent agreement with the calculations of Feibelman.⁶ For the Al(111) surface we find that a possible surface core-level shift must be smaller than 15 meV.

The experiments were performed at beamline 22 at the MAX-I storage ring in Lund, Sweden. This beamline is equipped with a modified SX-700 plane grating monochromator. The photoelectron spectra were recorded with a hemispherical electron energy analyzer (mean radius 200 mm).⁷ The total experimental resolution in the present measurements was around 50 meV, the contributions from the monochromator and electron energy analyzer being about equal. In order to decrease the core-level linewidths the measurements were made at 100 K. For the Al(111) surface we observed a decrease in total linewidth from 150 meV (full width at half maximum) at room temperature to 110 meV at 100 K. This decrease in linewidth, which is due to a smaller phonon broadening at low temperature, is essential for the accurate determination of the very small surface core-level shifts of Al. All experiments were made under ultrahigh vacuum (7×10^{-11} Torr). The crystals were cleaned by cycles of argon ion sputtering and annealing to about 450 °C. The cleanness was checked by recording valence electron spectra and by observing the C $1s$ and O $1s$ core-level regions. After the cleaning procedure the surface quality was monitored by low-energy electron diffraction (LEED). Clear and distinct (1×1) LEED patterns with small spots and

low background were observed in all cases.

In Fig. 1 are shown high-resolution Al $2p$ photoelectron spectra from the Al(100) surface measured at different photon energies. The photon energies are chosen so that the kinetic energy of the emitted $2p$ core electrons are scanned from below to above the minimum in the escape depth curve.⁸ It is clearly seen that both spin-orbit components have a doublet structure. This is a much improved situation compared with previous measurements,^{2,4} where only a broadening of the $2p$ spin-orbit components could be observed as the spectra became surface sensitive. From the changes in relative intensity as the photon energy, and thereby the escape depth, is varied, the structure at the low binding-energy side is identified as due to emission from surface atoms. This assignment is furthermore consistent with the observed intensity variations in spectra recorded at different electron emission angles.

A quantitative measure of the surface core-level shift was obtained by two different analyzing methods, one based on a decomposition of the spectra and one based on a fitting procedure.

The first method used was to apply a curve fitting procedure using a Doniach-Sunjić⁹ line shape convoluted with a Gaussian function describing the phonon broadening and the experimental broadening.¹⁰ We found that although it was always possible to obtain a good fit assuming equal Gaussian widths of the surface and the bulk such a fit could always be improved by making the surface Gaussian broader than the bulk one (typically 110 meV for the surface as compared to 65–70 meV for the bulk, both including the experimental broadening). This is, as has been discussed for other systems,¹¹ due to the larger vibrational amplitudes of the surface atoms which will give rise to a larger phonon broadening for the surface atoms and possibly also due to a larger degree of disorder at the surface. The described fitting procedure gives a surface core-level shift¹² of -96 meV with an accuracy of ± 5 meV.

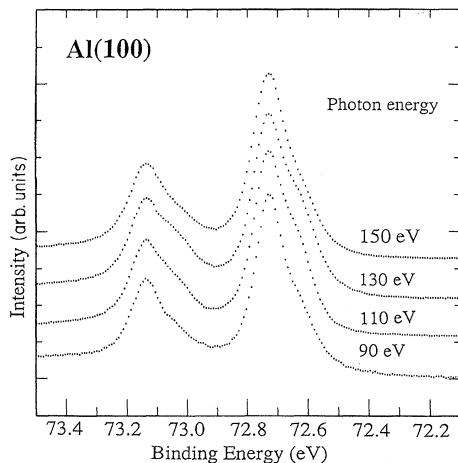


FIG. 1. Al $2p$ photoemission spectra from an Al(100) surface using the indicated photon energies and normal emission of the photoelectrons. Sample temperature is 100 K.

In the decomposition method¹³ one assumes that the spectrum is the sum of two components, surface and bulk, and that the mathematical relation between the line shapes of these two components is known. This method is thus independent of any theoretical model for the fundamental line shape, the only requirement being knowledge of the relation between the line shapes of the components. The simplest version of the method is to assume that the surface and bulk peaks have the same line shape. One enters the intensity ratio between the bulk and the surface emission and the surface core-level shift and tests if this gives a reasonable decomposition. We find this method to be very sensitive to the value chosen for the surface core-level shift; it is only possible to obtain meaningful decompositions for an energy window of typically 5 meV for one particular spectrum, outside of this energy window the decomposed spectra contain oscillations. The decompositions are less sensitive to the chosen intensity ratio. The surface core-level shift¹² resulting from this simple procedure is (-101 ± 5) meV. This value is significantly larger than the one we obtain from the fitting procedure. Furthermore, the decomposed bulk peak is broader than the peak we measure for the Al(111) surface which is clearly an unreasonable result. These problems are related to the assumption of equal line shapes for the components. As the surface peak is generally expected to be broader than the bulk peak, we therefore applied a decomposition procedure where the surface line shape is the bulk line shape convoluted with a Gaussian.¹¹ Using this broadened surface line shape led, as expected, to smaller values for the surface core-level shift. Gaussian broadenings consistent with the results of the fitting procedure gives (-95 ± 5) meV.¹² Also, the width of the decomposed bulk line is now no longer larger than the Al(111) spectrum, see below. We show in Fig. 2 an example of such a decomposition.

Concerning a possible crystal-field splitting,^{2,5} we note that there is no sign that the surface related $2p_{3/2}$ line is broader than the $2p_{1/2}$ line, which it should be if crystal-field splitting was significant (only the $2p_{3/2}$ level is expected to be split⁵). Thus the present results demonstrate that there is no significant crystal-field splitting of the

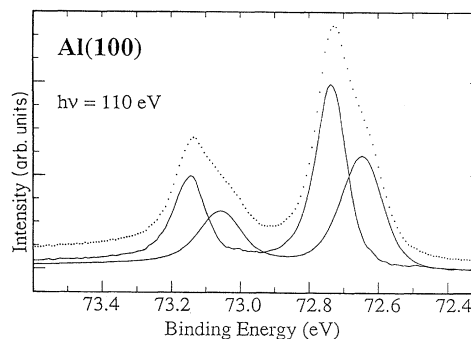


FIG. 2. Decomposition of an Al(100) spectrum (see text) using a surface shift of 93 meV and an extra Gaussian broadening of 85 meV of the surface peak. Dots, experimental spectrum; lines, decomposed peaks.

Al(100) surface atom $2p_{3/2}$ level. Instead a value of (-96 ± 5) meV is established for the surface core-level shift of the $2p$ level for this surface.

Recently, Feibelman⁶ has calculated the surface core-level shift for the Al(100) surface from first principles taking full account of final-state relaxation effects. This is done by calculating the difference in total energies of systems with the core-ionized Al atom at the surface and in the bulk, respectively. The core-ionized Al atom is treated within the $Z+1$ approximation, i.e., as a Si impurity. The resulting value for the surface core-level shift is -97 meV, in excellent agreement with our experimental determination. It should, though, be noted that according to Feibelman⁶ his value should be reduced by 26 meV if the systematic errors for Si impurities are equal to those of Al adatoms. We believe that the present measurements lower the level of error in measurements of the surface core-level shift for Al(100) to a limit where even more accurate calculations and a closer look at this point may be warranted. Of more general interest to the calculation and estimation of core-level shifts is the fact that the calculations of Feibelman make use of the so-called $Z+1$ approximation, that is, when calculating the total energy the final-state core-ionized Al atom is replaced by a Si atom, the next element. The present excellent agreement between experiment and theory demonstrates how well the final-state core-ionized site is approximated by a $Z+1$ impurity. In this connection it should, however, be noted that the quite good agreement with the calculations of Wimmer *et al.*⁵ shows that differences in final-state relaxation effects between surface and bulk Al atoms are small. This point is further discussed in Ref. 6. Finally it is noted that the presently measured shift is in excellent agreement with the value of -106 meV derived in Ref. 4 from surface energies of Al and Si.

Turning now to the results from the Al(111) surface, these are completely different from those of the (100) surface. As seen from Fig. 3, there is no sign of any surface core-level shift in the Al $2p$ spectra. Also, we find no change in the $2p$ line shape when the surface sensitivity of the spectra is changed. This is in agreement with the previous results of Kammerer *et al.*⁴ and indicates that the surface core-level shift of the Al(111) surface is close to zero. This conclusion is further supported by the comparison between the Al(111) spectrum and the bulk peak decomposed from the (100) spectrum shown in Fig. 3. The difference in line shape between these two peaks is hardly noticeable,¹⁴ i.e., there can be no significantly surface shifted component in the (111) spectrum. We can test the hypothesis that there is a nonzero surface shift for the Al(111) surface by fitting the (111) spectrum using as model line shapes the bulk and surface line shapes from the (100) surface. Assuming, as a worst case, that the surface intensity is only one third of the bulk intensity [for

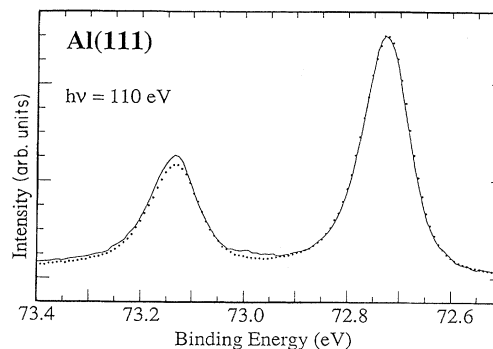


FIG. 3. Al $2p$ spectrum from Al(100) (dots). Sample temperature is 100 K. Also shown is the bulk spectrum decomposed from the (100) surface (solid line), see text and Fig. 2. The later spectrum is shifted by 9 meV towards lower binding energy.

the (100) surface the surface intensity is around 70% of the bulk at similar photon energies] the largest shift which we find compatible with the (111) spectra is 15 meV. Any increase of the surface intensity will decrease this value.

As already pointed out in Ref. 4, using arguments based on surface energies, it is expected that the Al(111) surface should have a much smaller shift than the (100) surface. The value estimated in Ref. 4 is close to zero, in excellent agreement with the present result. It would, nevertheless, be most interesting if *ab initio* calculations as those for the (100) surface⁶ were also performed for the (111) surface to test the structural sensitivity of this type of calculations.

Finally, we should comment on a recent paper¹⁵ on the surface core-level shift for Al(100). Using x-ray photoelectron spectroscopy (excitation energy 1487 eV and medium resolution 0.35 eV), the authors claim they find a surface core-level shift of $+0.2$ eV (note positive sign). This is completely incompatible with all previous results, theoretical and experimental (Ref. 2–6), and also with the present results (see Fig. 1).

To summarize, we find that the surface core-level shift of the Al(100) is (-96 ± 5) meV, in very good agreement with theoretical predictions based on *ab initio* total-energy calculations. For the (111) surface, the shift is close to zero and an upper limit of 15 meV was estimated. Finally, we find no signs of any significant crystal-field splitting of the surface core levels. We believe that the present results should settle the discussion on the surface core-level shifts of the Al(100) and Al(111) surfaces, at least regarding experimental values.

The present work was financially supported by the Swedish Natural Science Research Council and the TPÖBR Foundation.

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