# Theoretical 2*p*-core-level shift and crystal-field splitting at the Al(001) surface

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(Received 26 May 1981)

Core-energy shifts and crystal-field splittings of the Al(001)-2*p* levels are determined theoretically using our recently developed full-potential self-consistent linearized-augmented-plane-wave (FLAPW) method. From the electronic structure of a nine-layer Al(001) single slab, we find a 2*p*-core-level shift of 120 meV to reduced binding energies for the surface and 50 meV for the subsurface layers and a crystal-field splitting of 38 meV for the $2p_{3/2}$ state in the surface layer. Thus these theoretical results emphasize that both effects are important for a proper analysis of experimental data.

Recent developments in surface-sensitive photoemission experiments using synchrotron radiation have stimulated the theoretical investigation of the electronic structure of surfaces. Al is of particular interest since it provides the classical case of a nearly free-electron metal and the study of surface-induced effects on the 2*p* core level gives insight into the effective screening near the metal-vacuum interface. Eberhardt *et al.*[1] found from x-ray photoemission spectroscopy (XPS) measurements on an Al(001) surface that, quite surprisingly, the 2*p* line from the surface layers was not shifted within an experimental uncertainty of $\pm 40$ meV compared to the bulk signal, but the line for the surface signal was markedly broadened by 100–200 meV. These authors attributed the broadening to a crystal-field splitting of the initial states in the surface layer and supported this idea by a simple atomic model calculation.

Although a comprehensive interpretation of photoemission spectra has to take into account the complicated scattering mechanisms of the photoelectron, electron-hole interactions, secondary processes like Auger transitions, and many-body relaxation effects, the starting point of a theoretical investigation has to be an accurate calculation of the initial ground state. As it turns out in many cases, the electronic structure of the initial ground state alone determines the main features of the photoemission spectrum. We have carried out a self-consistent calculation for a nine-layer Al(001) film using our recently developed full-potential linearized-augmented-plane-wave (FLAPW) method.[2] We find for the Al 2*p* states in the surface layer a shift to smaller binding energies of 120 meV accompanied by a crystal-field splitting of 38 meV for the $2p_{3/2}$ states. The core-level shift in the subsurface layer is decreased to 50 mRy and vanishes in the third layer. A pronounced crystal-field splitting is found only for the surface layer. Very recently, Chiang and Eastman[3] derived from surface-sensitive photoelectron partial yield spectra a 2*p* core-level shift of $\sim -57$ meV and a much smaller surface-sensitive broadening than did Eberhardt *et al.* Our layer-decomposed results indicate that both effects (shift and splitting) are important in analyzing the experimental data.

In the FLAPW method, no shape approximation is made to the potential of the valence states. In particular, the nonspherical potential inside the muffin-tin spheres is crucial for describing the crystal-field splitting of the Al 2*p* levels, which are almost completely localized within the atomic spheres. This feature of a general potential also inside the muffin-tin spheres distinguishes the FLAPW calculation from earlier LAPW results[4] for a nine-layer Al(001) film where a spherical average of the potential inside the muffin-tin spheres was employed. Hence this earlier calculation was not conclusive for determining the crystal-field splitting of the 2*p* level.

In the present study we have used the same geometrical parameters as in the earlier work[4] (i.e., the bulk value of 5.3984 a.u. for the Al-Al distance). We have chosen the Gáspár-Kohn-Sham form for the exchange and the Wigner interpolation formula[5] for the correlation potential since these potentials are known[4] to give a good description of the work function. During the self-consistency procedure all core states including the 2*p* states were treated fully relativistically. Self-consistency was assumed when the input and output potential differed, on the average, by less than 2.7 mRy; at this point the eigenvalues are stable to better than 0.1 mRy.

Using the self-consistent full potential inside the muffin-tin spheres, the crystal-field splitting of the $2p_{3/2}$ levels is treated perturbatively by considering

 

TABLE I. FLAPW one-electron energy eigenvalues for the core levels in a nine-layer Al(001) film. The values are given in eV with respect to the vacuum. The last column lists the crystal-field splitting of the $2p_{3/2}$ levels.

| | $1s_{1/2}$ | $2s_{1/2}$ | $2p_{1/2}$ | $2p_{3/2}$ | Splitting |
|---|---|---|---|---|---|
| Surface | −1502.792 | −106.758 | −69.262 | −68.822 | −0.038 |
| $s-1$ | −1502.846 | −106.829 | −69.331 | −68.892 | 0.0008 |
| $s-2$ | −1502.889 | −106.877 | −69.379 | −68.939 | 0.006 |
| $s-3$ | −1502.882 | −106.863 | −69.366 | −68.927 | 0.004 |
| Center | −1502.886 | −106.880 | −69.381 | −68.942 | 0.010 |

the first-order shifts in the eigenvalues due to the nonspherical terms in the potential. We have used fully relativistic four-component spinors which transform[6] as the irreducible representations $\Delta_6$ and $\Delta_7$ of the double group $C_{4v}$ to obtain the shifts

$$\Delta_6\colon\ \Delta E = \tfrac{1}{2}V_2\ ,\quad \Delta_7\colon\ \Delta E = -\tfrac{1}{2}V_2\ ,$$

relative to the unperturbed $p_{3/2}$ eigenvalues where

$$V_2 = \frac{1}{\sqrt{5\pi}} \int [\,|f(r)|^2 + |g(r)|^2\,]\, V_{20}(r) r^2\, dr$$

and

$$\int [\,|f(r)|^2 + |g(r)|^2\,] r^2\, dr = 1\ .$$

$V_{20}(r)$ is the $(l=2,\ m=0)$ term of the lattice harmonic expansion of the potential in the muffin-tin spheres and $f(g)$ is the radial function of the large (small) component of the $2p_{3/2}$ level. The term $V_{20}(r)$ gives the only symmetry-allowed nonspherical contribution for the $p_{3/2}$ level, while the $p_{1/2}$ level is unaffected by the nonspherical potential.

The FLAPW one-electron energy eigenvalues for the $2p$ core states including the crystal-field splitting are listed in Table I and plotted in Fig. 1. We observe for the $2p_{1/2}$ and $2p_{3/2}$ levels in the surface layer compared to the central (bulklike) layer a shift of ~120 meV to smaller binding energies. A similar shift, although reduced to 50 meV, is also found for the subsurface layer $(s-1)$. In the layer $s-2$ the surface induced shift is almost completely screened but we notice a slight oscillation in the layers $s-2$, $s-3$, and the central layer. The $1s$ and $2s$ core states (cf. Table I) show essentially the same shifts as the $2p$ levels. As expected, the crystal-field splitting is localized to the surface layer and almost no splitting is found for the subsurface layers.

The accuracy of the present calculation is indicated by the calculated work function of 4.53 eV which is in very good agreement with the experimental value of 4.41 ±0.03 eV.[7] By contrast, Krakauer *et al.*[4] obtained a value of 4.7 eV using the LAPW method for films with a spherically averaged charge density and potential inside the muffin-tin spheres. Also, no core-level shifts were found in this earlier calculation. Thus, the results obtained here demonstrate the importance of a general charge density and potential inside the muffin-tin spheres even for a nearly-free-electron metal surface like the Al(001) surface.

The study of such small effects as the $2p$ core-level shift and the crystal-field splitting of the $2p$ levels at the Al(001) surface provides a sensitive and challenging test of both experiment and theory. Eberhardt *et al.*[1] observed a pronounced broadening (~100–200 meV) which they attributed to crystal-field splitting, but, to their surprise, there was no $2p$ shift within an error of ±40 meV. From an atomic model calculation, Eberhardt *et al.*[1] estimated the crystal-field splitting to be ~65 meV. Independently of our work, Chiang and Eastman[3] have very recently derived from their photoemission partial yield experiments a $2p$ core-level shift for Al(001) of ~−57

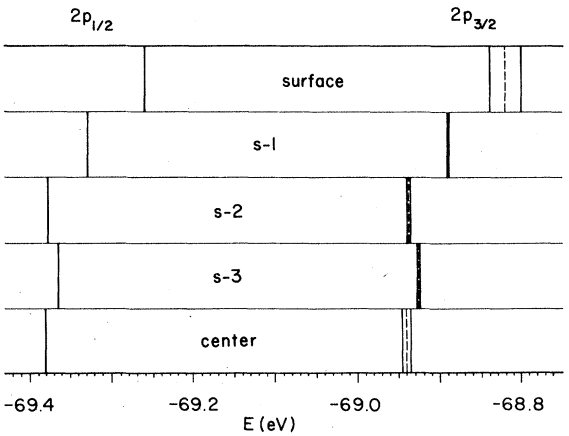


FIG. 1. FLAPW one-electron energy eigenvalues for the $2p$ core states in a nine-layer Al(001) film. The values are given with respect to the vacuum. The dashed lines are the values for the $2p_{3/2}$ states without crystal-field splitting.

meV and a much smaller surface-sensitive broadening than did Eberhardt *et al.*[1]

Our theoretical results, which show both a shift and a crystal-field splitting, permit some comparison and discussion of these experiments. Whereas Eberhardt *et al.*[1] overemphasized crystal-field effects and did not find a $2p$ shift, Chiang and Eastman did not take into account crystal-field effects in their fitting procedure. We find that both effects are important for a proper analysis of the experimental data. Further, since only the $2p_{3/2}$ states show a crystal-field splitting, one should be able, in principle, to isolate crystal-field effects in the experimental spectra by comparing the $2p_{1/2}$ and the $2p_{3/2}$ spectra. Thus, it will be illuminating to reexamine the experimental data using our layer-decomposed theoretical results.

This work was supported by the National Science Foundation Grant No. DMR 77-23776 and under the NSF-MRL program through the Materials Research Center of Northwestern University, Grant No. DMR 79-23573.

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