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# Core-level shift at a jelliumlike surface: Al(001)

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The shift of $2p$ core-level binding energies associated with surface atoms relative to bulk atoms for an Al(001) surface has been determined using photoemission partial-yield techniques. The observed shift is −57 meV. A possible mechanism for the core-level shift is discussed using a simple jellium model; i.e., the shift is related to the variation in the electrostatic potential associated with the conduction-electron response to the jelliumlike surface potential step.

Core-level binding energies associated with surface atoms are generally shifted relative to bulk atoms. This phenomenon has been observed using photoemission techiques in several transition or noble metals[1,2] and semiconductors.[3] Such surface core-level shifts are due to potential variations and differential relaxation effects near the surfaces, and are sensitive to the surface electronic and atomic structures.[2,4] Thus, measured shifts can provide tests for various surface model calculations. For $5d$ transition metals, the observed shifts have been explained very well using a tight-binding approach[2] which is appropriate for $5d$ electrons. For semiconductors such as GaAs, the shifts have been attributed to charge transfer involving the surface atoms within a chemical-bond picture.[3] It is interesting to determine core shifts for free-electron-like metals for which the crystal bonding is mainly due to delocalized *sp* electrons.

In this paper, we report a measured surface $2p$ core-level shift for Al(001) which is a simple surface for a free-electron-like metal. We have observed a shift of −57 meV; i.e., core-level binding energies are decreased for surface atoms relative to bulk atoms. This shift is very small. For comparison, measured values for surface Ga and As atoms of GaAs(110) are +280 and −370 meV, respectively[3]; the values for Ir(100) and Ir(111) are about −500 to −700 meV (Ref. 1); and the value for W(110) is −300 meV (Ref. 1), etc. Previously, Eberhardt *et al.*[5] observed a surface-sensitive effect for Al(001) which was interpreted as a surface broadening due to crystal-field-splitting effects. In contrast, we find a net surface core-level shift with much smaller surface-sensitive broadening. Krakauer *et al.*[6] recently performed a self-consistent thin-film calculation for a nine-layer Al(001) slab, and found no surface core-level shift within the accuracy of their calculation. In this paper, we discuss a possible mechanism for the core shift using a jellium model; the shift is related to the conduction-electron response to a jelliumlike surface potential.

The experiment was done at the Synchrotron Radiation Center at Stoughton, Wisconsin. An Al(001) surface was prepared by repeated Ne ion sputtering and annealing. The sample was kept at 40 K during the measurement to minimize thermal-broadening effects. Angle-integrated spectra were taken with a double-pass cylindrical-mirror analyzer. In order to optimize the experimental system resolution, partial-yield spectra were taken instead of direct photoemission spectra. In this case, the system resolution involves only the monochromator resolution (~0.07 eV).

Results are shown in Fig. 1. The long-dashed curve was obtained by collecting secondary electrons with kinetic energies of 3 ±0.3 eV while scanning the incident photon energy. Within the small photon energy range scanned, the partial-yield spectrum is proportional to the optical absorption to a very good approximation. Since the electron escape depth at these kinetic energies is greater than 50 Å,[5] the spectrum essentially represents a bulk absorption spectrum. The two edges at 72.73 and 73.15 eV correspond to transitions from the $2p_{3/2}$ and $2p_{1/2}$ core levels to the Fermi level. The solid curve in Fig. 1 was obtained by collecting secondary electrons with kinetic energies of 48 ±0.5 eV. Since the electron escape depth at these energies is about 4 Å,[5] the spectrum contains a substantial surface contribution. Clearly, the two edges are shifted to lower energies. With a reasonable estimate of the backgrounds (short-dashed lines in Fig. 1), the half-amplitude points of the edges for the two curves are indicated by crosses. The shifts are about 21 meV. These shifts are much smaller than the actual surface core-level shift, since the bulk contribution to the surface-sensitive spectrum (solid

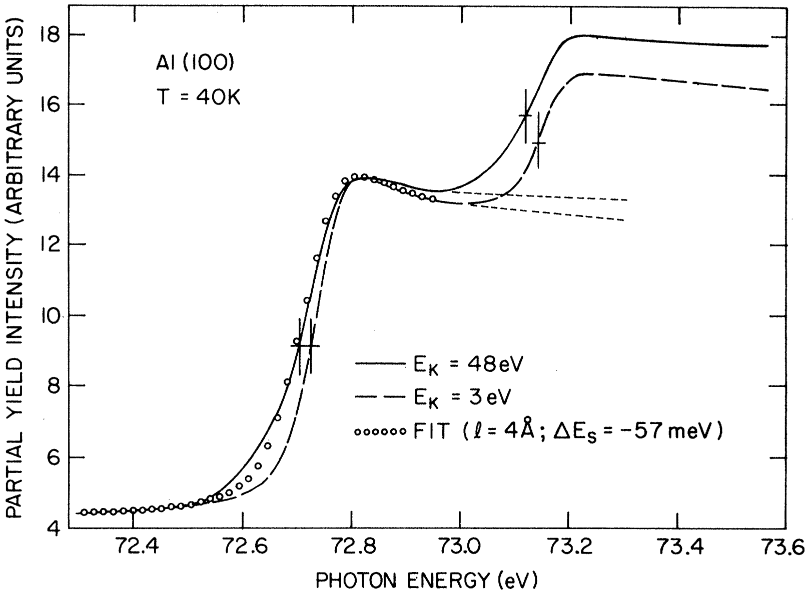

FIG. 1. Photoemission partial-yield spectra for an Al(001) surface at 40 K. Solid and long-dashed curves were obtained by collecting secondary electrons with kinetic energies around 48 and 3 eV, respectively. The half-amplitude points for the $2p_{1/2,3/2}$ edges are indicated by crosses, with the estimated backgrounds indicated by short-dashed lines. The circles are a least-squares fit to the surface-senstive spectrum (solid curve) for the $2p_{3/2}$ edge; with the assumed electron escape depth $1 = 4$ Å, the surface core-level shift $\Delta E_S$ is found to be −57 meV.

curve) is still larger than the surface-layer contribution. By assuming that the mean electron escape depth is 4 Å for electron kinetic energies $E_K \simeq 48$ eV,[5] we obtain the surface-to-bulk intensity ratio for the solid curve to be 0.659.[3] The circles in Fig. 1 are a least-squares fit to the surface sensitive spectrum for the $2p_{3/2}$ edge in the range $h\nu = 72.3$ to 72.82 eV. This fit is obtained using a linear combination of the bulk spectrum (long-dashed curve) and its replica, with the latter being shifted by the core-level shift (fitting parameter) and having the intensity ratio determined above. The surface core-level shift determined in this way is −57 meV, and the resultant fit shown in Fig. 1 is quite good. If different electron escape depths are assumed (3.5 or 4.5 Å), somewhat different shifts are obtained (−50 or −62 meV, respectively), and the quality of the fit is roughly the same. Therefore, we obtain a surface core-level shift of $-57 \pm 7$ meV in view of the uncertainty ($\sim 0.5$ Å) in the electron escape depth. In the above analysis, we have ignored possible small subsurface core-level shifts (see below) and crystal-field splitting effects; inclusion of these effects would broaden the edges. In fact, such a broadening is seen for the surface-sensitive spectrum (solid curve in Fig. 1).

The two curves in Fig. 1 have apparently different spin-orbit branching ratios. The spectra are produced by collecting secondary electrons which are due to direct photoemission of the valence bands, direct recombination of the core holes, and $LVV$ Auger transitions, etc.[5] These secondary emission processes have different relative cross sections at different kinetic energies. The spin-orbit branching ratios can be also different for these processes since the matrix elements are different. Therefore, the above effects can account for the apparently different spin-orbit branching ratios for the two curves in Fig. 1.

We next discuss a possible mechanism for the surface core-level shift. Using a jellium model to describe the electronic structure of the Al(001) surface, screening of the jellium surface-potential-step results in potential variation in the conduction-electron sea near the surface.[7] The electrostatic potential rises smoothly near the jellium surface potential step and shows characteristic Friedel oscillations inside the jellium. The resultant electrostatic potential energy of an electron at the surface atomic plane is higher than in the bulk by approximately 120 meV from a self-consistent local-density-functional calculation.[7] Since the screening is very effective with the high electron density in aluminum ($r_s = 2.07$), the potential variation at the subsurface atomic planes is small and will be ignored in our discussion (the variation at the second atomic plane is estimated to be <15% for that at the surface atomic plane). Thus, the surface core-level binding energy is shifted by about −120 meV relative to the bulk in the initial state just due to the potential variation. We have ignored in the above the atomistic effect by treating the crystal as jellium, because the difference is potential at two atomic locations in unchanged to first order by including the atomic part in the crystal potential.[8]

The initial-state shift according to the above model (−120 meV) correctly accounts for the sign of the observed shift (−57 meV), yet the magnitude is too large. The discrepancy may exist for two reasons: (1) It is known from other studies that the potential variation amplitude is likely overestimated in the self-consistent local-density-functional calculation.[9] (2) The residual discrepancy is most likely due to final-state (relaxation) shift. A reliable estimate of the final-state shift within our model is difficult, and is not attempted here. However, previous experiments for transition metals and semiconductors[1-3,10] indicate that initial-state shifts alone generally account for the experimental results well; i.e., final-state shifts are smaller than initial-state shifts. The question of the magnitude of the final-state shift is open in the present case; a detailed theoretical study is desirable.

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[1] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. Lett. 41, 1425 (1978); T. M. Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and J. C. Vedrine, *ibid.* 43, 789 (1979); J. F. Van der Veen, F. J. Himpsel, and D. E. Eastman, *ibid.* 44, 189 (1980).

[2] Anders Rosengren and Börje Johansson, Phys. Rev. B 22, 3706 (1980).

[3] D. E. Eastman, T.-C. Chiang, P. Heimann, and F. J. Himpsel, Phys. Rev. Lett. 45, 656 (1980); F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, *ibid.* 45, 1112 (1980); S. Brennan, J. Stöhr, R. Jaeger, and J. E. Rowe, *ibid.* 45, 1414 (1980).

[4] D. E. Eastman, M. Aono, T.-C. Chiang, G. Landgren, and R. Ludeke, Bull. Am. Phys. Soc. 26, 352 (1981); and unpublished results.

[5] W. Eberhardt, G. Kalkoffen, and C. Kunz, Solid State Commun. 32, 901 (1979).

[6] H. Krakauer, M. Posternak, A. J. Freeman, and D. D. Koelling, Phys. Rev. B (in press).

[7] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970). N. D. Lang has performed the calculation (unpublished) for *A*l ($r_s = 2.07$).

[8] E. Caruthers, L. Kleiman, and G. P. Alldredge, Phys. Rev. B 8, 4570 (1973).

[9] J. D. Dow and R. E. Allen (private communications).

[10] P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B 20, 1433 (1979).