Fourth-layer surface core-level shift on Be(0001)

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(Received 20 January 1998)

Three surface shifted Be 1*s* components were identified in an earlier investigation of Be(0001). The theoretical results indicated, however, that also the fourth atomic layer may exhibit a shift large enough to make it separable from the bulk component. A photoemission investigation was therefore made and the results indeed show the presence of a fourth surface shifted component. Due to the size of the shift and the number and widths of the components involved the fourth-layer contribution does not appear as a resolved peak in recorded spectra. Utilizing curve fits of recorded and difference spectra the presence of a fourth shifted component is clearly demonstrated by the present data. Surface core-level shifts of -870 ± 25, -605 ± 25, -335 ± 25, and -160 ± 50 meV are extracted for layers 1–4. A refit of the old data assuming four surface components yielded shifts in agreement with the present values and fits of better quality, i.e., having smaller residuals.
[S0163-1829(98)08131-4]

The electronic properties of the Be(0001) surface is quite unusual, giant surface Friedel oscillations[1] and a surface electron-phonon coupling parameter four times the bulk value[2] were recently observed. Anomalously large surface core-level shifts[3–5] have been reported earlier and have been explained[4,6,7] as having originated from the unique electronic properties of Be metal. For the close-packed (0001) surface three surface shifted components were clearly resolved[3] and interpreted[3,4] as having originated from the three outermost atomic layers. The theoretical results[4,6,7] suggested, however, that also the fourth layer could have a shift large enough to make it separable from the bulk component. This is the subject of the present investigation. An angle-resolved photoemission study of Be(0001) was conducted at a slightly higher energy resolution than previously obtained. The presence of a fourth surface shifted component is demonstrated using a curve fitting procedure. The fourth-layer contribution does not appear as a clear peak in the recorded spectra since it overlaps strongly with both the bulk and third-layer components. A curve fit procedure is therefore required and the results show unambiguously the presence of a fourth component with a shift in good agreement with theoretical predictions.[4,6,7] In view of these findings the old data[3] were refitted assuming four surface shifted components and fits of better quality (smaller residuals) and values for the layer resolved shifts in agreement with the values reported below were obtained.

The experiments were performed at beamline 33, at the MAX I storage ring, which is equipped with a SGM monochromator[8] and an angle-resolved end station.[9] The monochromator was set to give an energy resolution of 35–40 meV in the photon energy range 125–136 eV. For the electron analyzer an acceptance angle of $\pm2°$ and an energy resolution of 33 meV was selected. A total energy resolution of 48–52 meV was thus obtained in this photon energy range. An incidence angle of 45° was selected in the investigation.

The Be(0001) crystal was cleaned by Ne^+ sputtering and annealing cycles. In the final cleaning cycles the sample was sputtered about 5 min at 550–600 °C and then annealed for about 1 min at that temperature. A 1×1 low-energy electron diffraction pattern with sharp diffraction spots and a low background intensity was obtained. Recorded valence-band spectra showed only the expected bulk and surface state contributions[2,10] and no signal from likely contaminants. A total width [full width at half-maximum (FWHM)] of 400 meV was obtained for the surface state at Γ at room temperature using a photon energy of 15 eV, which indicates a clean and well-ordered surface.[2] Core-level spectra were collected after LN cooling, i.e., at a sample temperature of about 100 K. The temperature was monitored with a thermocouple mounted on the sample holder.

Be 1*s* photoemission spectra recorded from Be(0001) using three different photon energies are shown in Fig. 1. At each energy both a spectrum recorded at normal emission and at an electron emission angle of 36°, along the Γ-*K* azimuthal direction, is presented. Three surface shifted components (labeled $S1$, $S2$, and $S3$) are directly observable, most prominent in the 134-eV spectra, and the bulk component (labeled *B*) is seen to be dominant only in the 126- and 130-eV normal emission spectra. Four peaks (local maxima) are discernible in the 126- and 130-eV spectra and of special interest to notice is the apparent shift in energy location of the local maximum at the largest binding energy when varying the emission angle from 0° to 36°. The position of the bulk component will of course not shift upon changing the emission angle but there are two plausible reasons why it may appear to shift. One is that when the relative intensity of the bulk component becomes smaller the strong overlap with the neighboring third-layer component ($S3$) may give rise to an apparent shift. The other reason is that there actually exists a fourth unresolved surface component ($S4$), located in between the bulk component and the third-layer component. If the relative intensity of this fourth component increases while that of the bulk decreases a shift in the location of the maximum of their combined contributions is expected. To distinguish between these two cases a curve-fitting procedure has to be utilized and we have applied the same method as used earlier.[11] It deserves to be noticed that in the analysis we have utilized also Be 1*s* spectra recorded, at a total in-

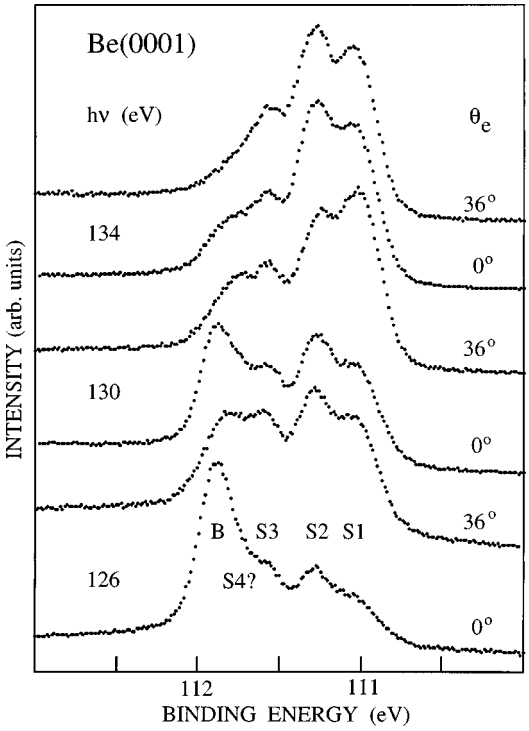

FIG. 1. Be 1*s* photoemission spectra recorded from Be(0001) using three different photon energies. At each photon energy a spectrum recorded at normal emission and one at an electron emission angle of 36°, along the Γ-*K* azimuthal direction, are shown. Contribution from the bulk, *B*, and three surface, $S1-S3$, components are clearly resolved. Whether or not a fourth unresolved surface component, $S4$, exists is the subject of this investigation.

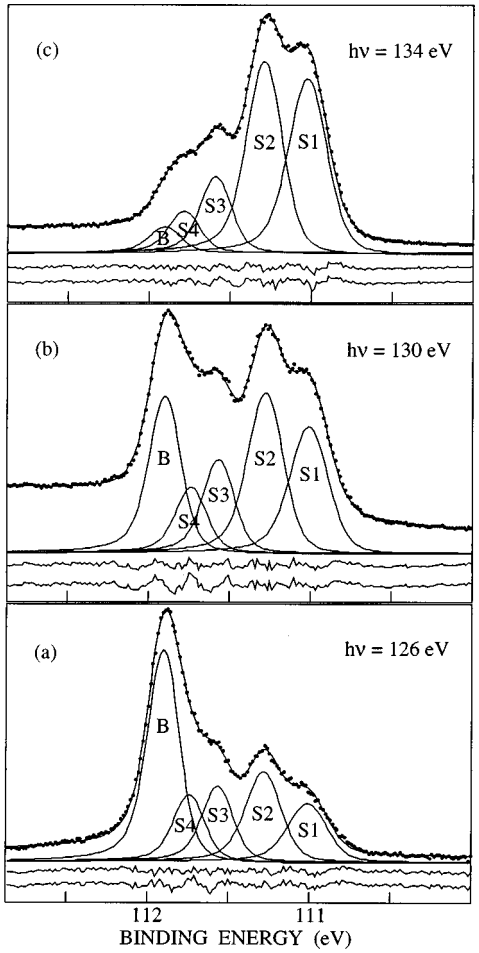

FIG. 2. Normal emission Be 1*s* spectrum (dots) recorded from Be(0001) using a photon energy of (a) 126, (b) 130, and (c) 134 eV. The solid curves through the data points show the results of applying the fit procedure, assuming one bulk and four surface components. The two bottom curves in each panel show the residual obtained in this fit (upper curve) and the residual obtained (Ref. 14) when assuming one bulk and three surface components (lower curve).

strumental resolution of 100 meV, at emission angles from 0° to 50° along both the Γ-*M* and Γ-*K* azimuthal direction at $h\nu=127$ eV as well as normal emission spectra at photon energies from 123 to 150 eV. Here we only present spectra recorded using the higher-energy resolution (48–52 meV) since applying the fit procedure gave identical results concerning the number of components and layer resolved shift values for the two different data sets. Only larger Gaussian width parameters were required for obtaining best fits to the data set collected using a lower total instrumental resolution.

In the fit procedure utilized[11] peaks of Doniach-Sunjic line shapes are convoluted with Gaussian broadening functions and different background models can be selected. The line shape is determined by the Lorentzian width and the asymmetry parameter and the broadening function by the Gaussian width. For the background we have used a linear model in the fits presented below. We have also applied the earlier utilized Shirley model and obtained essentially identical results.[12] When fitting four or five components having significant overlap it is necessary to put some constraints on the line-shape parameters in order to get physically meaningful results. We could not make an independent determination of all parameters involved, which is difficult and has so far only been tried in a few cases.[13] Initially we applied the procedure chosen earlier,[3,5] i.e., to keep the asymmetry parameter and the Lorentzian width the same for all components and the Gaussian width the same for all except the surface layer component ($S1$). Using this approach we made fits assuming three surface components and one bulk component.[14] What we found was that the separation obtained between the bulk and the surface components consistently became somewhat smaller in spectra recorded at higher surface sensitivity. However, the values extracted for the layer resolved shifts agreed within the error bars given with the earlier published values.[3] Referring to the spectra shown in Fig. 1, we found that the energy locations of the surface components remained constant but that the fitted bulk component appeared at a smaller (30–50 meV) binding energy both in the 126- and 130-eV spectra collected at 36° compared to that at normal emission and in the 134 eV spectra compared to the normal emission spectra taken at 126 and 130 eV. However, since core-level shifts cannot depend on photon energy or electron emission angle this apparent shift of the bulk component suggests that it is worthwhile to include a fourth surface shifted component $S4$ in the analysis. Again, the asymmetry parameter and the Lorentzian width were kept the same for all components but this time we found that best fits were obtained if also the second-layer component ($S2$) was allowed to have a different Gaussian width than the bulk, $S3$, and $S4$ components.[15] Using this

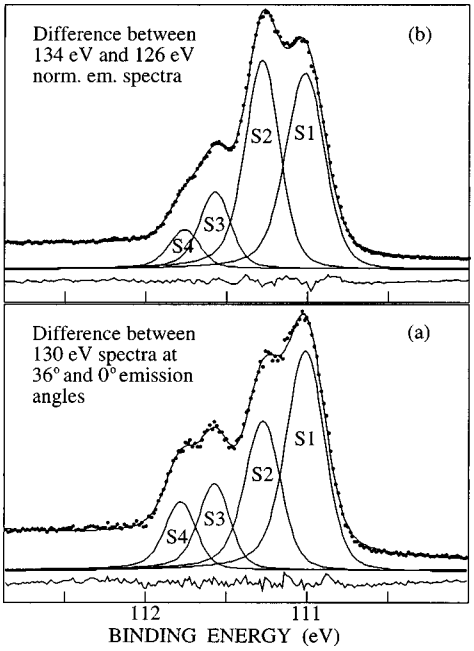

FIG. 3. Difference spectrum (dots) constructed (a) between 130-eV spectra recorded at emission angles of 36° and 0° and (b) between normal emission spectra collected at 134 and 126 eV. The solid curves through the data points show the results of applying the fit procedure, the four surface components used, and the residual obtained in the fit.

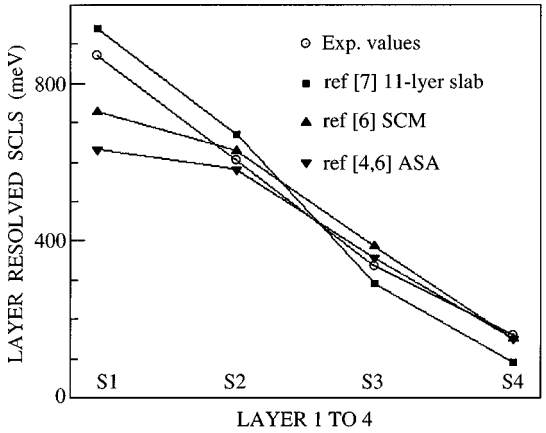

FIG. 4. Extracted layer resolved surface core-level shifts and values predicted in earlier calculations (Refs. 4, 6, and 7).

procedure fits of better quality, having smaller residuals, and giving no systematic variation in the values extracted for the layer resolved shifts were obtained. This is illustrated in Fig. 2.

An additional way of demonstrating that a fourth surface component is required seemed desirable since using a larger number of components in general will result in fits of better quality. For that purpose we constructed difference spectra between spectra collected at high and low surface sensitivity. Those considered as low surface sensitive spectra in Fig. 1 are the 126 and 130 eV recorded at normal emission while the others are considered as high surface sensitive spectra. The idea was to subtract a proper bulk contribution, essentially, from a surface sensitive spectrum and investigate whether the difference spectrum obtained could be adequately modeled using three surface shifted components or if a fourth component was required. Two such examples are shown in Fig. 3. The difference spectrum obtained between the 130-eV spectra recorded at emission angles of 36° and 0° is shown in Fig. 3(a) and the difference spectrum obtained between the 134- and 126-eV normal emission spectra in Fig. 3(b). In both cases a shoulder is clearly observed on the high-binding-energy side of the peak corresponding to the $S3$ component. A fourth surface shifted component is therefore required to model these difference spectra unless the $S3$ component is allowed to have a considerably larger Gaussian width[16] than both the $S1$ and $S2$ components. The latter is, however, not reasonable in view of recent electron loss results.[17] Results obtained by applying the fit procedure to the recorded and the difference spectra and by assuming four surface shifted components are shown in Figs. 2 and 3. Surface core-level shifts of -870 ± 25, -605 ± 25, -335 ± 25, and -160 ± 50 meV were extracted for layers 1–4, where the uncertainty represents the maximum spread obtained from 30 independent determinations. These values are plotted in Fig. 4 together with the layer resolved shifts predicted by calculations.[4,6,7] For layers 1–3 the experimental values lie within the range spanned by the different calculations while for layer 4 the experimental value of -160 ± 50 meV lies on the high-energy side. Considering the large uncertainty obtained in this value, which reflects the difficulty of determining the energy location of a component that is not visually resolved in recorded spectra, the agreement is good.

In the previous analysis[3] or normal emission spectra collected from Be(0001) we assumed the existence of only three surface shifted components and one bulk component although a surface shift in the fourth layer of Be(0001) was predicted in the first calculation.[4] With the limited set of normal emission data we then had recorded we could not safely conclude that a fourth-layer component actually existed although fits of better quality were obtained when using four surface components instead of three. An angle-resolved data set was needed to conclusively show that a fourth surface component actually does contribute. We have now refitted the old data[3] using four surface components and we have also utilized difference spectra similar to the one shown in Fig. 3(b). Surface core-level shift values that agreed, within error bars, with those specified above were extracted.

In summary, an angle-resolved photoemission investigation of Be(0001) has been reported and presence of a fourth surface shifted component in the Be 1s spectra has been demonstrated. Since the fourth-layer component is not visibly resolved in the recorded spectra, we had to utilize a curve fit analysis to demonstrate its presence. Surface core-level shifts of -870 ± 25, -605 ± 25, -335 ± 25, and -160 ± 50 meV were extracted for layers 1–4. A refit of the old data[3] assuming four surface components yielded shifts in agreement with the present values and fits of better quality. These values agree well with the layer resolved shifts predicted by different calculations.[4,6,7]

Financial support by the Swedish Natural Research Council is gratefully acknowledged.

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[12] Identical results were obtained concerning the layer resolved shifts and the number of components needed but slightly different Gaussian width and asymmetry values gave best fits when using a Shirley background.
[13] See, for example, D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **63**, 1976 (1989), and references given therein.
[14] The parameters giving best fits when assuming three surface components and one bulk component were an asymmetry parameter of 0.04 and a Lorentzian width of 0.07 eV for all components and a Gaussian width of 0.21 eV for all components except $S1$ where a width of 0.24 eV was found to be needed.
[15] The parameters giving best fits when assuming four surface and one bulk component were an asymmetry parameter of 0.04 and a Lorentzian width of 0.07 eV for all components and a Gaussian width of 0.19 eV for all components except $S2$ and $S1$ where widths of, respectively, 0.21 and 0.24 eV were found to be needed.
[16] A Gaussian width of 0.32–0.38 eV was required for component $S3$ in order to give reasonable fits to the difference spectra when assuming only three surface components. Surface phonon modes can be expected to give rise to additional broadening of surface layer components but not to be considerably larger for the third layer than for the first and second layers.
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