Three Surface-Shifted Core Levels on Be(0001)

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The results of a high resolution photoemission study of the Be(0001) surface carried out at temperatures between 100 and 450 K are reported. At 100 K, three distinctly shifted Be $1s$ levels, exhibiting shifts of -825, -570, and -265 meV, are revealed and interpreted to originate from the three outermost atomic layers. Identification of two subsurface core level shifts and a first layer surface shift of -825 meV is unique among close-packed metal surfaces. Temperature dependent broadening effects observed in the bulk and surface Be $1s$ peaks are also reported.

For close-packed metal surfaces only the atoms in the outermost layer are in general found to exhibit surface core level shifts large enough to allow an unambiguous separation of surface and bulk contributions [1–5]. The influence of the surface is thus effectively felt only by the first-layer atoms, which has been attributed to the short screening length typical for metals. In this Letter we report observations for the Be(0001) surface that are very different compared to earlier findings [1–5] on close-packed metal surfaces. Three shifted Be $1s$ core levels are clearly resolved, in photoemission spectra recorded at 100 K, and interpreted to originate from the three outermost layers of this simple-metal surface. The Be(0001) surface is thus unique since two subsurface peaks can be unambiguously identified and the first layer shows the largest surface shift observed so far on any close-packed metal surface.

Recent investigations [6,7] of the Be(0001) surface showed an anomalous relaxation behavior. A low-energy electron diffraction analysis [6] showed the first interplanar spacing, i.e., between the outer two layers, to be expanded by 5.8% but the second and third interplanar spacings to have almost no relaxation. Linearized-augmented-plane-wave calculations for a nine-layer slab [7] agreed with this unusual finding of a large outer layer expansion relative to the truncated bulk lattice. The calculated results implied an expansion of 3.9% in the first interplanar spacing but moreover an expansion of 2.2% in the second interplanar spacing. These calculations [7] also showed the charge distribution in subsurface layers to be substantially affected by this relaxation. The p_σ population of the muffin tins in the outer layers was shown to be significantly reduced while the s and p_π occupations only showed small changes. Since core level binding energies are sensitive to the charge distribution [1,2], charge rearrangement could possibly give rise to substantial energy shifts also for subsurface layer atoms. This is indeed also what our experimental results indicate. The surface shifts are, however, not interpreted as a consequence of the anomalous lattice expansion at the surface.

A surface core level shift calculation [8] for the unrelaxed surface gives shifts for the three outermost layers not far off the values observed experimentally. It is shown in that paper (the following in this issue) that instead it is the unique electronic properties of beryllium metal that give rise to these anomalous surface shifts.

A core level study of the Be(0001) surface has been reported earlier [9]. That study was performed at room temperature and the results were interpreted in terms of a single surface-shifted component, shifted by -0.50 eV relative to the bulk peak. The surface peak was found to be considerably broader than the bulk peak and to contain additional structure. The main broadening in both the bulk and surface peaks, as well as the additional structure in the surface peak, was attributed to phonon shakeup. Our results agree with the suggestion that vibrational effects contribute strongly to the width of the Be $1s$ level but show that the additional structure is not due to such effects. Instead additional surface-shifted components are revealed, which cannot be resolved at room temperature.

The experiments were performed at beam line 22 at the MAX I storage ring in Lund, Sweden [10]. The total resolution varied from 70 meV at 123 eV photon energy to 110 meV at 170 eV. The analyzer accepts a cone of angular width $\pm 8°$. Normal emission and an incidence angle of 40° was chosen as the experimental geometry in the investigations. The Be(0001) crystal [11] was cleaned by Ar$^+$ sputtering at elevated temperature and annealing cycles. In the final cleaning cycles the sample was sputtered about 10 min at 550 °C and then annealed at 450 °C for about 20 sec. A distinct low-energy electron diffraction pattern with sharp diffraction spots and a low background intensity was obtained after cleaning. The pattern showed a sixfold symmetry which indicates averaging over the two possible terminations of Be(0001). The cleanliness of the surface was checked by monitoring the core levels of likely contaminants (O, C, and S) and by measurements of the valence band region at a photon energy of 80 eV. No oxygen or sulphur signal could be

detected in the final cleaning stages but a very weak carbon signal was discernible, which by using tabulated cross section values [12], was estimated to correspond to an amount of less than 1% of a monolayer. The temperature of the sample was monitored with a thermocouple spot welded to the side of the crystal.

Be 1s photoemission spectra from the Be(0001) surface recorded at different photon energies and at a temperature of 100 K are shown by the dotted curves in Fig. 1. Four distinct structures are clearly resolved, having energy differences so large that shifts can be extracted without using curve fitting procedures. Pronounced variations in the relative intensity of these structures are observed when the kinetic energy of the photoelectrons is varied around the minimum of the escape depth curve [13,14]. The high binding energy peak is seen to be very weak in the 136 and 140 eV spectra, i.e., close to the expected minimum in the escape depth curve, and to gain in relative intensity for lower as well as higher photon energies where the escape depth increases. This energy dependence allows us to conclude that this component (labeled B in Fig. 1) is due to emission from bulk atoms.
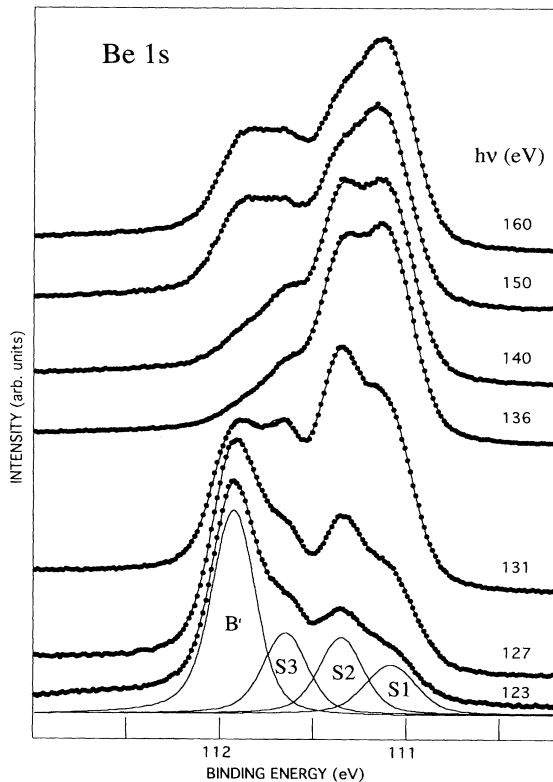

FIG. 1. Be 1s photoemission spectra from Be(0001) recorded at 100 K using different photon energies (dotted curves). The results of a curve fitting procedure are shown by the solid curves through the data points. The four solid curves in the bottom part of the figure show the four components fitted to the 123 eV spectrum.

The other three components (labeled S1, S2, and S3 in Fig. 1) are all interpreted as surface related since they all give dominant contributions at energies where the escape depth is expected to be small [13,14]. Based on the relative intensities and their photon energy dependence we interpret these components to originate from the first (S1), second (S2), and third (S3) layers of the Be(0001) surface (see below for a more quantitative description). Shifts of approximately −800, −550, and −250 meV are obtained for, respectively, the S1, S2, and S3 components by simply reading the peak positions in the spectra.

In order to extract the relative intensity and refine the shifts of the components a curve fitting procedure was utilized [15]. When fitting four components having significant overlap we found it necessary to put constraints on the line shapes in order to get physically meaningful results. After having tested various approaches [16] we chose a simple procedure in which the asymmetry parameter and the Lorentzian width were kept the same for all four components and the Gaussian width was kept the same for all except component S1. A Lorentzian width (FWHM) of 90 meV and an asymmetry parameter of 0.02 was found to result in good fits to the spectra at all photon energies. The Gaussian width (FWHM) depends on the photon energy and, as discussed below, on the temperature of the sample. At 100 K the Gaussian width of the bulk peak varied from 215 meV at 122 eV to 235 meV at 170 eV, a variation that is consistent with the variation of the monochromator resolution in this energy range. The extracted shift relative to the bulk component was −265 ± 25 meV for S3, −570 ± 20 meV for S2, and −825 ± 30 meV for S1, where the uncertainties represent the maximum spread obtained in 25 independent determinations. These values are insensitive to the exact fitting procedure used [15]. The surface to bulk intensity ratios extracted for the three shifted
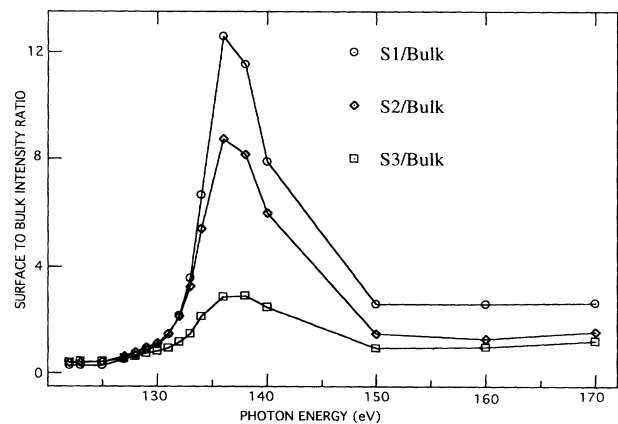

FIG. 2. Surface to bulk intensity ratios extracted versus photon energy for the three components labeled S1, S2, and S3 in Fig. 1.
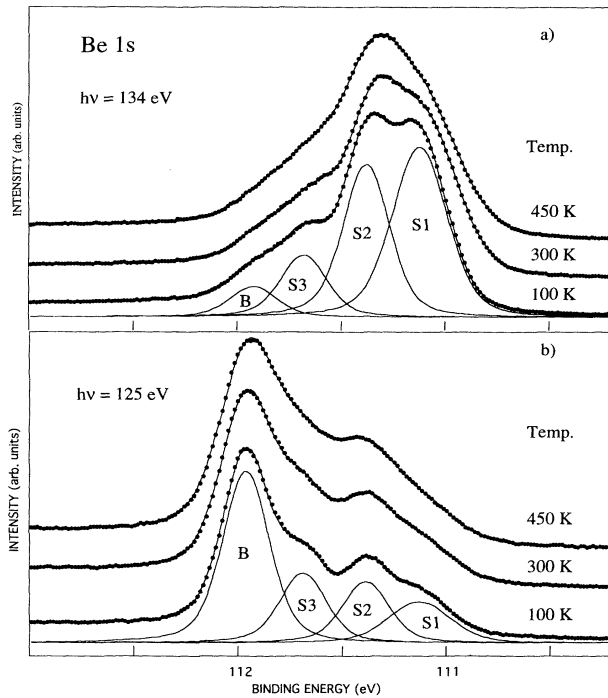
FIG. 3. Be $1s$ spectra recorded (dotted curves) at three temperatures using a photon energy of (a) 134 eV and (b) 125 eV. The solid curves through the data points show the results of the curve fitting procedure and the four solid curves shown in the bottom part of each figure show the four components fitted to the 100 K spectrum.

FIG. 4. Variation in Guassian width (FWHM) with temperature, determined for the surface layer peak (S1) and for the other three components (B, S3, and S2), when an instrumental broadening of 80 meV has been removed by quadratic subtraction.

components are plotted in Fig. 2 versus photon energy. This plot shows clearly that these three components give the strongest contribution when the escape depth is expected to be smallest, i.e., at a photon energy of ca. 135 eV. The energy dependence of these ratios is fairly similar but their maximum values differ significantly. The behavior strongly suggests that peaks S1, S2, and S3 can be assigned to contributions from respectively the first, second, and third layers of the Be(0001) surface.

Be $1s$ spectra recorded at temperatures between 100 and 450 K are shown by dotted curves in Figs. 3(a) and 3(b). The 134 eV spectra have a dominant contribution from the surface shifted components, the bulk contribution represents less than 10% of the total signal. In the spectra recorded at 125 eV, however, the bulk contribution represents about 50% of the total signal. When fitting these spectra assuming that all peaks except S1 have the same Gaussian width we obtain a variation in widths with temperature as shown in Fig. 4. An experimental broadening of 80 meV has been removed by standard quadratic subtraction. The Gaussian widths are observed to be large, showing that vibrational broadening is strong in Be metal. It may of course be argued that the use of a larger Lorentzian width would lead to smaller Gaussians. It is, however, not possible, without deteri-
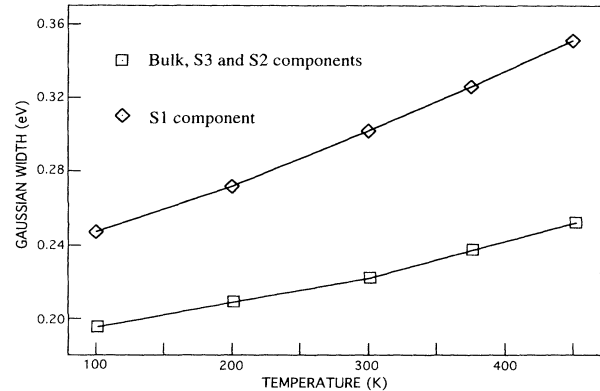
orating the quality of the fits, to increase the Lorentzian width so much that the Gaussian widths decrease significantly. The vibrational broadening contribution arises from the dynamical displacement following phonon excitations. This displacement, the root mean square vibrational amplitude, is known to increase with temperature. An analytic expression, derived using the Debye model, was utilized recently to describe the temperature dependent vibrational broadening in Na and Ta [3,4]. In our case a rather large increase in Gaussian width with temperature is observed and the surface layer peak S1 shows, as expected [4,17], the strongest variation. The increased width at the surface comes most likely from the softer phonon modes, associated with motion of the core-excited atom perpendicular to the surface plane, observed earlier on the Be surface [6,7]. The strong temperature dependence we observe explains why only a single surface component, containing additional structure, could be revealed in the earlier study [9] of Be(0001) carried out at room temperature.

Calculated results [8] for the unrelaxed Be(0001) surface give negative shifts for the three outermost layers with magnitudes close to the values observed experimentally. These theoretical results strongly support our interpretation and also provide an explanation that it is the unique electronic properties of beryllium metal that make this surface anomalous compared to other close-packed metal surfaces. It is, however, worthwhile to consider other possibilities to the existence of three distinct surface-shifted levels. That two terminations, A or B termination in the AB stacking sequence, do exist on this close-packed surface is evident [6] from the observed sixfold symmetry in the low energy electron diffraction (LEED) pattern. These two terminations should, however, yield identical surface shifts since the bonding geometry of the surface and subsurface atoms would be identical in these two cases. The possibility of face cen-

tered cubic types of terminations (involving *ABC* stacking sequences) has previously been considered in LEED investigations of the (0001) surface of hexagonal crystals, but has been ruled out [18-20]. The recent LEED results [6] also show that different terminations are not a plausible explanation. In the earlier core level study [9] of Be(0001) the additional structure in the surface peak was attributed to phonon shakeup. We observe an increase in the Gaussian width for all four components when increasing the temperature from 100 to 450 K but the relative intensities are found to be fairly constant and no large effect is observed in the extracted surface shifts. When changing the kinetic energy of the photoelectrons, however, the relative intensities showed pronounced variations; see Fig. 2. Vibrational effects can therefore not provide an explanation to the three shifted core levels observed. Neither can contamination effects since the three shifted levels were clearly resolved also at an earlier stage in the cleaning process, when a considerably larger carbon signal and a weak oxygen signal were detected.

In summary, we have revealed the presence of three surface shifted Be $1s$ components on the Be(0001) surface. These components, having surface shifts of -265, -570, and -825 meV are interpreted to originate from the three outermost layers. Calculated results for the unrelaxed [8] surface strongly support this interpretation and provide also an explanation, that it is the unique electronic properties of beryllium metal that make this surface anomalous compared to other close-packed metal surfaces, where only one surface shifted component has been possible to identify unambiguously [1-5]. Temperature dependent studies revealed a larger temperature dependent broadening of the surface layer component compared to the other components, which was expected.

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