Physics of the Be$(10\bar{1}0)$ Surface Core Level Spectrum

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Photoelectron diffraction has been utilized to confirm the theoretical prediction that the surface core level shifts observed for Be$(10\bar{1}0)$ have been improperly assigned. The original assignment based upon the relative intensity of the shifted components was intuitively obvious: the peak with the largest shift of -0.7 eV with respect to the bulk was associated with the surface plane, the next peak shifted by -0.5 eV stems from the second layer, and the third peak at -0.22 eV from the third and fourth layers. First-principles theory and our experimental data show that the largest shift is associated with the second plane, not the first plane. [S0031-9007(98)07350-5]

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The measurement of core level binding energies is a commonly used technique to probe the chemical environment of the emitting atoms. In free molecules the shift between the binding energies of identical elements in a different bonding configuration can be rather large, on the order of one electron volt. On solid surfaces a smaller but similar effect is often observed: the core level binding energies of the atoms in the outermost layer(s) differ slightly from those in the bulk due to the different electronic environment, a phenomenon referred to as surface core level shift (SCLS). One expects this SCLS to be largest for the first atomic layer. On most metals this is fulfilled and the SCLS for the deeper layers are unmeasurably small. In this Letter we show that an intuitively obvious assignment which is furthermore supported by the relative intensity of the core level lines may fail even in rather simple cases such as a clean metal surface. We show how to find or verify an assignment in a straightforward experiment.

The surfaces of beryllium provide an excellent test case for the quantitative understanding of SCLS. Both the (0001) and the $(10\bar{1}0)$ surface show three unusually large surface related $1s$ core level shifts [1,2]. The number of shifted components and the size of the shifts are caused by the unusual electronic structure of Be. While the bulk has a low density of states at the Fermi level the surface electronic structure is dominated by the presence of metallic surface states [3]. In this sense Be is closer to a semiconductor than to a simple metal. Johansson and co-workers have assigned the SCLS such that the component with the largest shift originates in the first layer, the component with the second largest shift in the second layer, and the component with the smallest shift in the third and third plus fourth layers for Be(0001) and Be$(10\bar{1}0)$

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[1,2], respectively. This assignment was not only based on intuition but also supported by the relative intensity of the lines: the SCLS lines from the deeper layers were lower in intensity, consistent with the expectation that the electrons from these layers are more likely to suffer inelastic scattering processes. For Be(0001) four different calculations gave more or less satisfactory agreement with the measured shifts [4–7]. All calculations confirm the basic assignment of the experimental data.

On the $(10\bar{1}0)$ surface doubt over the initial assignment of the shifted components in the core level spectrum was created by a calculation which predicted the second layer to have a larger shift than the first layer [8]. We have now investigated this issue by high energy-resolution angle-scan photoelectron diffraction. In the following we will describe the experimental idea and the results which, indeed, confirm the unusual assignment predicted by theory. Then we will use the results of our first-principles calculation to discuss the physics of the Be$(10\bar{1}0)$ core level spectrum.

The basic idea of the experiment is to use the high atomic forward scattering factor and small scattering phase shift of the ion cores for electrons with kinetic energies greater than about 400 eV [9]. In the so-called forward scattering geometry, where an atom of the first layer lies on a straight line between a second layer atom and the detector (see Fig. 1) [10], this strong forward scattering ensures an enhancement of the core level component from the second layer. An inspection of the spectra taken in an angular scan around this forward scattering geometry then reveals the identity of the second layer peak which shows the pronounced forward scattering enhancement while the intensity from the first layer stays more or less constant. While this experiment is conceptually simple the small cross section for the Be 1s excitation at higher energies combined with the requirement of high resolution render it difficult, even at a third generation synchrotron radiation source.

All the experiments were carried out at the Super-ESCA beam line of the synchrotron radiation source ELETTRA in Trieste. A clean Be$(10\bar{1}0)$ sample was prepared using methods described elsewhere [8]. Be 1s core level spectra were taken for two photon energies: $h\nu = 180$ and $h\nu = 500$ eV. The combined resolution of the beam line and the electron energy analyzer was 70 and 250 meV, respectively. The sample temperature was around 120 K.

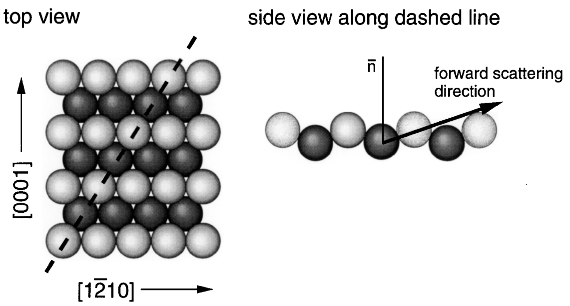

FIG. 1. Sketch of the forward scattering geometry. A first layer atom has to lie on a straight line between a second layer atom and the electron detector.

Figure 2 shows a spectrum taken at $h\nu = 180$ eV. We have fitted these data to four Doniach-Sunjic lines convoluted with Gaussian distributions and a linear background. This resulted in shifts and line shape parameters very similar to those found by Johansson *et al.* [2] except for higher asymmetries of 0.09 and 0.14 for bulk and surface components, respectively. Our SCLS are -0.71, -0.50, and -0.24 eV for $S1$, $S2$, and $S3$, respectively. Note that we use the same nomenclature as Johansson *et al.,* i.e., $S1$ is the component with the largest shift.

At $h\nu = 500$ eV we have performed an azimuthal scan at a polar emission angle of 75° off the surface normal. Figure 3 shows three spectra taken at azimuthal emission directions $[1\bar{2}10]$, [0001], and in the forward scattering direction. In the latter spectrum a very clear increase in the intensity on the low binding energy side is observed. From an inspection of the raw data, however, it is not possible to judge if this increase is due to the $S1$ or $S2$ component.

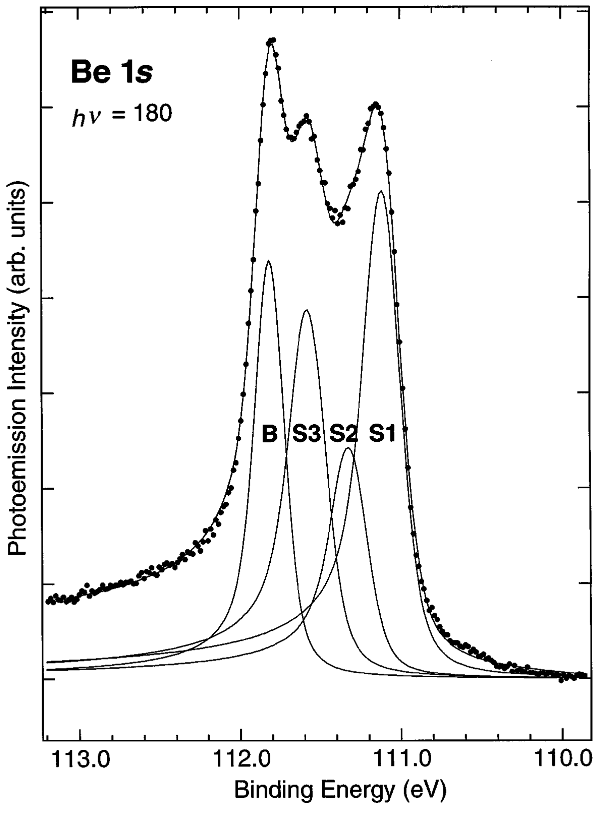

FIG. 2. Be 1s core level spectrum taken at $T = 120$ K and $h\nu = 180$ eV in normal emission. An inspection of the raw data reveals that four lines are necessary to obtain a satisfactory fit. The solid lines represent the fitted components for the bulk (B) and the surface layers ($S1, S2, S3$). Note that we use the nomenclature of Johansson *et al.* (Ref. [2]) where $S1$ is the component with the largest shift.

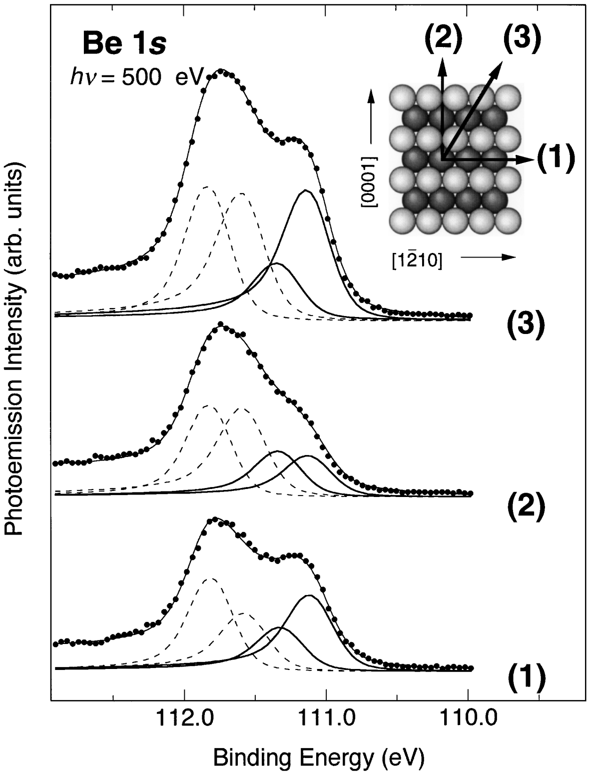

FIG. 3. Three Be $1s$ core level spectra taken at $T = 120$ K and $h\nu = 500$ eV taken at a polar emission angle of 75° off normal and an azimuthal emission direction of (1) $[1\bar{2}10]$, (2) [0001], and (3) 57.5° off $[1\bar{2}10]$, i.e., in the forward scattering geometry. The latter spectrum shows a clear enhancement of the intensity on the low binding energy side. A fit shows that this is due to the intensity increase of $S1$. The inset shows a sketch of the measurement geometry.

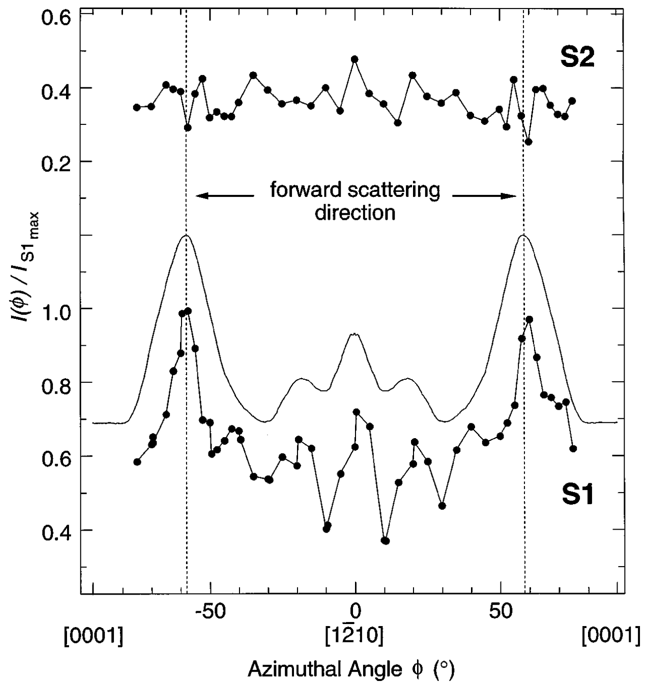

FIG. 4. Angular dependence of $S1$ and $S2$, i.e., for the core level component with the largest and second largest shift. The $S1$ signal shows a clear peak in the forward scattering direction, indicating that $S1$ is due to emission from the second layer. The solid line represents the result of a multiple-scattering cluster calculation for the diffracted intensities.

We have fitted all of the data taken at $h\nu = 500$ eV using the fit parameters obtained at $h\nu = 180$ eV allowing only for a different Gaussian width in order to account for the lower resolution. Figure 4 shows the intensities of the $S1$ and $S2$ components as a function of azimuthal emission angle ϕ, normalized to the maximum intensity of the $S1$ component. It can be clearly seen that $S1$, i.e., the peak with the largest shift, shows the forward scattering enhancement at the expected angle ($\phi = 57.5°$) whereas $S2$ does not change very much as a function of ϕ. Furthermore, the solid line in Fig. 4 represents the result of a multiple-scattering calculation of the diffracted intensity [11] of the photoelectrons emitted in the second layer which agrees remarkably well with the observed modulations of the $S1$ component.

While experiment and theory clearly show that the second layer gives a larger shift than the first layer it remains to be explained. We have performed first-principles calculations where we break down the total core level shifts for each layer into two initial state contributions (electrostatic and exchange/correlation) and the final state contribution (screening).

Our calculations [7] rely on density functional theory within the local density approximation (LDA) for exchange and correlation (XC) [12]. To calculate SCLS one has to compare the total energy of a Be atom with a $1s$ core hole in the bulk and in different surface layers, without allowing structural relaxation in response to the core hole. For this purpose we construct a Be pseudopotential with a core hole. To analyze the origin of the SCLS we calculate the initial state contribution. It is the difference of bulk and surface electrostatic and XC potential at the atomic cores of relaxed Be$(10\bar{1}0)$. The final state or screening contribution is the difference between initial state and full SCLS.

The Be$(10\bar{1}0)$ surface is represented by fully relaxed 18 layer slabs. Ideally a single core hole should be used to calculate the SCLS. However, using a core hole concentration of 1/4 monolayer gives SCLS a better than 0.05 eV accuracy. Tests performed for **k** sampling, slab thickness, impurity concentration, and plane-wave cutoff indicate that the calculated SCLS are converged to better than 0.1 eV within LDA.

Table I gives the resulting SCLS which agree qualitatively with the experiment. The unusual ordering of the SCLS is mainly caused by the anomalous electrostatic initial state shift for the first and second layers. The initial state shift for the first layer is very small. This is surprising keeping in mind the high contribution of surface states to the density of states in this layer [8]. It should create an electrostatic potential to keep the surface layer charge neutral causing an electrostatic shift of the core

TABLE I. Calculated and measured SCLS of Be$(10\bar{1}0)$ in eV. Negative SCLS indicate a lower binding energy of the core electron as compared to the bulk. The calculated full SCLS is broken up into the initial state and final state components. The former is composed of a shift of the electrostatic and the XC potential. The final state or screening contribution to the SCLS is the difference between the full and the initial state SCLS.

				Layer		
		1	2	3	4	5
Full SCLS	calculation	−0.57	−0.80	−0.39	−0.19	−0.18
	experiment	−0.50	−0.71	−0.24		
Initial state		−0.10	−0.62	−0.11	−0.11	0.01
	electrostatic	0.0	−0.59	−0.11	−0.11	0.01
	XC	−0.10	−0.03	0.0	0.0	0.0
Final state		−0.47	−0.18	−0.28	−0.08	−0.19

level [5,6]. In this case, however, our calculation of the density of states projected on the top layer atoms (PDOS) shows a significant band narrowing due to the reduced coordination of the atoms. This reduction of the occupied PDOS almost compensates the surface state without a shift in the electrostatic potential of the first layer. The second layer atoms, on the other hand, are almost fully coordinated, which reduces the band narrowing. Furthermore, we find a p_z-like peak in the PDOS which is cut by E_F and mostly empty in the first layer and moved below E_F in the second layer [13]. This increases the surface state contribution in the second layer [14]. Thus, the surface state is not compensated in the second layer and this leads to the large initial state shift.

The final state contribution reflects the ability of the electrons to screen the core hole. A good measure for this ability is the PDOS at the E_F. In the first layer this PDOS is very high due to the p_z-like PDOS peak which is cut by E_F. In the second layer the p_z peak in the PDOS shifts below the Fermi energy and thus contributes little to the screening.

In summary, we have shown how a seemingly obvious assignment of the chemical shifts in x-ray photoelectron spectroscopy may fail even for a simple case such as a clean metal surface. The reason is that the physics leading to the core level shifts is an involved interplay between initial and final state effects. In any experiment dealing with surface core level shifts caution should be taken as to the assignment. The situation should be more severe in the case of semiconductors were we expect that many more examples of a counter intuitive assignment can be found. On the other hand, the experimental procedure outlined here can be used to find or verify an assignment once the geometric structure of the surface is known.

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