

# Assignment of the surface core-level shifts to the surface layers of Be(10 $\bar{1}$ 0)

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Photoemission studies and layer resolved Korringa-Kohn-Rostoker (KKR) multiple scattering calculations are used to find the assignment of the surface core-level shifts to the top layers of the Be(10 $\bar{1}$ 0) surface. Striking similarities between experimental and calculated data make it possible to assign the largest shift to layer two, the second largest shift to layers three and four, and the smallest shift to layer one.

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## I. INTRODUCTION

Beryllium has been shown to have unusual electronic properties, which give rise to anomalously large and layer resolved surface shifts of the Be 1s core level.<sup>1-6</sup> For the close packed Be(0001) surface four surface core-level shifts (SCLSs) originating from the four outermost layers have been identified<sup>1</sup> and the assignment of the shifts is in good agreement with the calculations.<sup>2</sup> For Be(10 $\bar{1}$ 0) three surface shifted components have been identified, however there is a controversy over which surface shifted component is to be assigned to which layer. The earliest experimental results<sup>3</sup> were interpreted in a similar way for the (0001) surface, i.e., the largest shift was assigned to the top layer, the second largest shift to the second layer, and the smallest shift to layers three and four. The first calculation<sup>4</sup> for this surface reported that the second layer had the largest shift, and the first layer had a smaller shift than layer three and four for the ideally terminated surface. When allowing for a slight inward relaxation<sup>4</sup> of the outermost layer, the shifts of the first and third layers were found to be fairly similar. Later experimental<sup>5</sup> and calculated<sup>5,6</sup> results assigned the SCLS differently—the largest shift to the second layer, the second largest shift to the first layer, and the smallest shift to layers three and four. In that experimental study,<sup>5</sup> high photon energies were used and an analysis of the photoelectron diffraction effects was done using a single scattering model.

In the present study we have combined new photoemission investigations with multiple scattering calculations of the surface to bulk intensity ratios as a function of electron emission angle and photon energy. The purpose was to see if this allowed us to discriminate among the different assignments made. The results reported below show that the assignment made in the first calculation<sup>4</sup> for the bulk truncated surface agrees best with our findings.

## II. EXPERIMENTAL

The angle resolved experiments were performed at beamline 33 at MAX-lab which is equipped with a spherical

grating monochromator (SGM)<sup>7</sup> and an angle-resolved end station.<sup>8</sup> The electron analyzer was set to have an acceptance angle of  $\pm 2^\circ$  and the total energy resolution was selected to 110 meV at 128 eV. An incidence angle of  $45^\circ$  was selected for the experimental geometry. The normal emission spectra were collected at beamline 311, which is equipped<sup>9</sup> with a modified SX700 monochromator and a Scienta analyzer. A total resolution of  $\leq 50$  meV was selected at photon energies between 120 and 200 eV. This analyzer had an acceptance angle of  $\pm 8^\circ$ .

The Be crystal was cleaned by Ne<sup>+</sup> sputtering and annealing cycles and a clean and well ordered surface was obtained. A distinct rectangular  $1 \times 1$  low energy electron diffraction pattern was observed and recorded core and valence band spectra showed no traces of oxygen or other likely contaminants. All measurements were performed with the crystal cooled to about 100 K.

## III. CALCULATIONS

In order to assign the core-level shifts in the experimental spectra, it is necessary to have a reliable means of calculating photoemission that takes into account:

- (i) the electronic structure in the region of the surface;
- (ii) the matrix elements between the initial hole and final electron states;
- (iii) the scattering and attenuation of the final electron state; and
- (iv) the lifetime of the hole state left in the crystal.

Pendry and co-workers<sup>10</sup> developed a layer KKR scattering code PEOVER1, which included all of these effects in a calculation of photoemission spectra for surfaces of solids with simple structures. The code assumed that the surface could be decomposed into layers of atoms, described by spherically symmetric muffin tin potentials, immersed in a uniform background potential. The surface potential was modeled as a step change to the vacuum potential typically positioned so that it touched the first layer of atomic poten-

tials. The code used a multiple scattering formulation to calculate the decay of the electronic wave field into the surface. It then calculated matrix elements that projected the photoelectron amplitude onto the hole wave field. The hole wave fields emanating from atoms within the layers (the intra-atomic contribution) were allowed to multiply scatter from other atoms within the layer (the intralayer term) and multiply scatter between the layers (the interlayer term). If the initial hole state is a core state, for example as found in many photoelectron diffraction experiments, then the last two terms are small and can be neglected. Once the scattered hole wave field has been calculated, matrix elements enable the calculation of the final coupling back onto the photoelectron state. The intraatomic, interlayer, and intralayer photocurrent contributions from each layer can be accumulated and the total photocurrent calculated.

The PHOTON2<sup>11</sup> code is a generalization of the PEOVER1 code to cope with complicated surface structures. It can deal with an arbitrary number of atoms in the layer unit cell and the atoms within a unit cell need no longer be coplanar. For close packed layers normal to the surface, the artificial separation of atoms into coplanar layers leads to poor, sometimes incorrect, convergence of the interlayer plane wave expansions. Lifting this restriction enables the code to combine atoms closely spaced in the direction normal to the surface into a single layer and allows the use of a plane wave expansion in those regions where it converges best. In the limit the code can deal with a single layer with a surface unit cell that is in essence infinitely deep.

In addition to arbitrary unit cells the code can deal with an arbitrary reconstruction of the surface and an arbitrary stacking of different layer types going into the surface.

On the numerical side the code contains a variable phase package to generate regular and irregular solutions of the electronic Schrödinger equation within the muffin tins—the methodology ensures accurate solutions that obey critical Wronskian relationships.<sup>12</sup>

The code contains a number of scattering options including zero scattering and full multiple scattering for the hole wave field and single scattering, multiple scattering, and renormalized forward scattering perturbation theory for the photoelectron wave field. The code automatically switches between real space summation and Kambe summation for the structure constant calculations as the imaginary part of the energy of either of the two states increases.

A self-consistent muffin tin potential generated<sup>13</sup> for Be was used as the bulk (*B*) potential in the present investigation. The experimentally observed surface shifted Be 1s components were modeled by shifting the bulk potential by 0.700, 0.500, and 0.220 eV for the *S*1, *S*2, and *S*3 components respectively. Note that the labels *S*1 for the largest, *S*2 for the second largest, *S*3 for the smallest shift, and *B* for the bulk component are kept throughout the paper for the potentials. Note also that *L*1, *L*2, and *L*3+*L*4 are used when referring to the surface layers. Using these shifts, each component is well resolved in the calculated spectra, as shown in Fig. 1.

The width of the components in the calculated spectra is determined by the imaginary part of the self energy of the hole state,<sup>11</sup> for which a value of 0.068 eV was used. The larger widths of the components in the experimental spectra

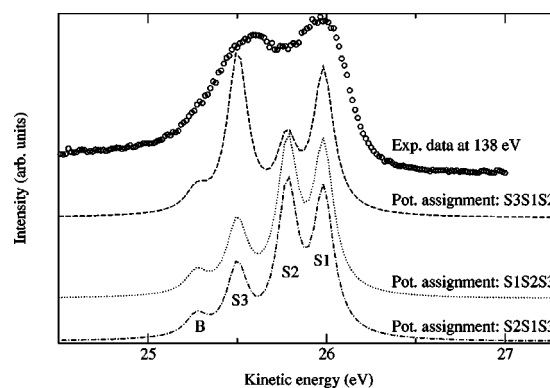


FIG. 1. The top spectrum is the experimental data taken at normal emission using a photon energy of 138 eV. The other three spectra are calculated with three different assignments of the potential shifts. Spectrum two from the top has *S*3 assigned to layer one, *S*1 to layer two, and *S*2 to layers three and four. Spectrum three has *S*1 assigned to layer one, *S*2 to layer two, and *S*3 to layers three and four and the bottom spectrum has *S*2 assigned to layer one, *S*1 to layer two, and *S*3 to layers three and four.

are attributed to Gaussian broadening, mainly due to the experiment resolution and to temperature broadening effects. It is not necessary to take these effects into account to be able to see that the assignment of the surface core-level shifts to the surface layers of Be(10 $\bar{1}$ 0) that gives the best agreement with experimental data is the first calculated curve from the top. However, more evidence for this is needed. The intensities of the components in both the calculated<sup>14</sup> and experimental<sup>15</sup> spectra were extracted using a curve fitting procedure.<sup>16</sup> This allowed the surface to bulk intensity ratios (peak area ratios) to be extracted in a straight forward manner. The calculated ratios are specified by the atomic layer to bulk ratios [*L*1/*B*, *L*2/*B*, and (*L*3+*L*4)/*B*] while the experimental ratios are given by the surface shift to bulk ratios (*S*1/*B*, *S*2/*B*, and *S*3/*B*).

The calculations showed that the intensity ratios were very sensitive to different photon energies and different values of the imaginary part of the self energy of the electron state,<sup>11</sup>  $\text{Im}(\Sigma)$  (see Fig. 2). The peak at  $\theta \approx 25^\circ$  is the photoelectron diffraction peak, which has been used to find the offset between the photon energies used for the calculated and experimental spectra. A comparison is done for the *S*3/*B* intensity ratio because here we saw the most structure in the experimental data. The assignment used in the calculations for these spectra was surface shift *S*1 to *L*1, *S*2 to *L*2, and *S*3 to *L*3+*L*4. Since the result of our investigation is another assignment scheme, spectra similar to the ones in Fig. 2 were recalculated with the new assignment, but this changed neither the energy offset nor the choice of  $\text{Im}(\Sigma)$ .  $\text{Im}(\Sigma)$  is inversely proportional to the mean free path according to<sup>17</sup>

$$\lambda = \frac{C}{\text{Im}(\Sigma)}. \quad (1)$$

The calculated intensity ratios were, on the other hand, found to be sensitive neither to the actual potential shift assigned to the respective atomic layer nor to relaxations (not shown).

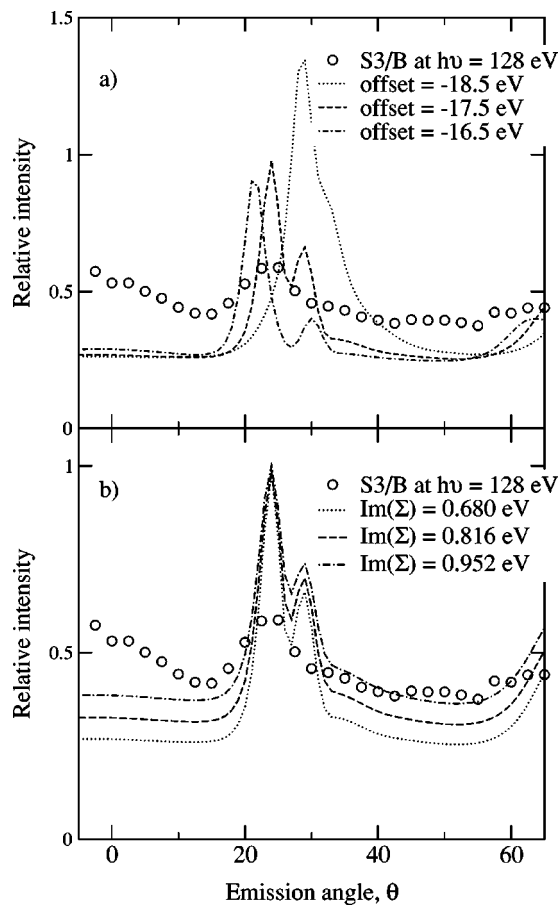


FIG. 2. Two panels to show how the relationship between experimental and calculated energies. Both the experimental and the calculated spectra were taken in the  $\Gamma$ -A direction. In (a), it is shown how sensitive angle resolved emission spectra are to the photon energy. This has been used to find the energy offset needed to make the calculated spectra correspond to the experimental spectra. In (b) it is shown how the spectra changes when  $\text{Im}(\Sigma)$  is changed. The photon energy offset used for these calculations was -17.5 eV.

All the initial calculations were therefore done with S1 assigned to L1, S2 to L2, and S3 to (L3+L4) on the ideally terminated surface.

The calculations were angle averaged to partly emulate the acceptance angle of the analyzer used.

#### IV. RESULTS AND DISCUSSION

The sensitivity in the angular resolved emission spectra to the photon energy was used, as shown in Fig. 2(a), to set the energy scale for the calculations. The difference between the calculated spectra shown is about 1 eV. The photon energy scale was locked in this way for 128 and 138 eV. In Fig. 2(b) the photon energy used was the corrected value for 128 eV and the value of  $\text{Im}(\Sigma)$  was varied. Here the correct value is less apparent, so a least square method was used. The value found for  $\text{Im}(\Sigma)$ , 0.816 eV, at  $h\nu = 128$  eV was then substituted into Eq. (1) and an analytic function that modeled the mean free path in Ref. 17 was then used to calculate the

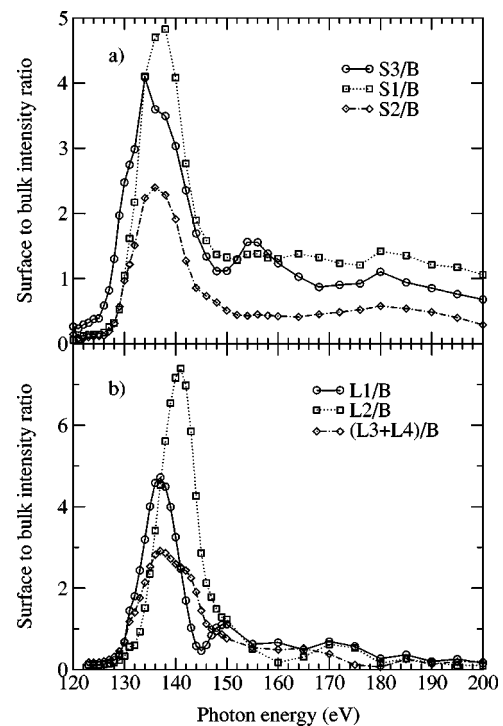


FIG. 3. (a) Experimental and (b) calculated surface to bulk intensity ratios as a function of photon energy. From the similarities between these curves it is evident that S3 is to be assigned to L1, S1 to L2, and S2 to (L3+L4). Both the experimental and calculated data were taken in the direction normal to the surface. See text for further details.

values for  $\text{Im}(\Sigma)$  for the photon energies used. The experimental and calculated surface to bulk intensity ratios as a function of photon energy are shown in Figs. 3(a) and 3(b), respectively. Calculations were also performed using  $\text{Im}(\Sigma) = 0.952$  eV at  $h\nu = 128$  eV, which resulted in very similar curves as those shown in Fig. 3(b).

It is easy to compare the characterizing features in Fig. 3. The most striking similarity is the strength of the intensity ratios, where it is clear that the highest ratio, L2/B, in the calculations is matched by the experimental S1/B ratio. The second highest, L1/B, is matched by S3/B and the lowest, (L3+L4)/B, is matched by S2/B. Next we should notice that the maximum of L1/B is at a lower photon energy compared to L2/B, which is similar to the way the maximum of S3/B is positioned in relation to S1/B. Also, L1/B has a local maximum at 150 eV, which is matched by a local maximum at 155 eV for S3/B. Putting all this together, it is clear that the assignment of the SCLS to the surface layers of Be(1010) should be S1 to L2, S2 to (L3+L4), and S3 to L1.

The potential assignment used in the production of Fig. 3 was S1 to L1, S2 to L2, and S3 to (L3+L4). The fact that the result, in spite of this, points to another assignment only proves a stronger case. The calculations were repeated using the two other assignments indicated in Fig. 1, S2 to L1, S1 to L2, and S3 to (L3+L4) as proposed earlier<sup>5,6</sup> and finally, S3 to L1, S1 to L2, and S2 to (L3+L4) as the present result indicate. The differences between these calculations were minimal—all of the characteristic features in the calculated

intensity ratios were the same and thus point towards the same assignment of the SCLS to the atomic surface layers. The calculations were also repeated with the relaxations reported by Hofmann *et al.*<sup>18</sup> giving the same result.

## V. CONCLUSION

In summary, the combined results of the photoemission experiments and the layer resolved KKR multiple scattering calculations have allowed an assignment of the surface core-level shifts to the top layers of the Be(10 $\bar{1}$ 0) surface. A comparison between calculated and experimental surface to bulk intensity ratios unambiguously shows that the largest shift  $S1$  should be assigned to the second layer,  $L2$ , the next

largest shift  $S2$  to layers three and four  $L3+L4$ , and the smallest shift,  $S3$ , to layer one  $L1$ .

This assignment disagrees with the one initially proposed.<sup>3</sup> It agrees partly with more recent findings<sup>5,6</sup> in which the largest shift was assigned to the second layer, but disagrees concerning the assignment of the two other surface components. Our assignment agrees best with the first calculated<sup>4</sup> surface core-level shifts for the bulk terminated surface.

## ACKNOWLEDGMENT

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<sup>11</sup>The code is being written up and will be submitted to Computer Physics Communications for publication in the near future. The code will also be available through the CCP3 library. For further details and access to a beta release version of the code please

contact the CCP3 Secretary, Dr. A. Wander, at Daresbury Laboratory. The code is currently being evaluated and validated over a wide range of structures and structural combinations. The original code has been further developed by R. J. Blake.

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<sup>13</sup>The Be bulk potential was supplied by the Condensed matter physics theory group at Uppsala University. When using it in the PHOTON2 code it gave the same bulk band structure as previously published by other authors.

<sup>14</sup>The Lorentzian width was kept at 0.14 eV and a Gaussian width of 0.015 eV was used since the program would not allow a zero width.

<sup>15</sup>The Lorentzian width was kept around 0.10 eV for all components and the Gaussian width was held around 0.20 eV. A different Gaussian width for the bulk component was needed (0.25 eV) for the angle resolved data. The asymmetry parameter was kept between 0.01 and 0.02 for all the components. A polynomial background was used.

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