

Surface state on clean Tb(0001)

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Angle-resolved photoemission experiments on clean Tb(0001) reveal the existence of a state 0.5 eV below the Fermi level which has the properties of a surface state. It exhibits no dispersion with respect to the momentum component perpendicular to the surface in the photon-energy range between 15 and 55 eV; it is located in a band gap of the projected band structure at $\bar{\Gamma}$; and it is very sensitive to oxygen contamination of the surface. The wave function of this surface state has Δ_1 symmetry, as the intensity of the photoemission peak decreases when the p component of the exciting radiation is reduced. Both the very weak energy dispersion with respect to the parallel component k_{\parallel} of the momentum and the photon-energy dependence of the photoionization cross section indicate that the surface state has $5d_{z^2}$ orbital character. The existence of this surface state can be explained by the same theory of surface core-level shifts that is related to the narrowing of the surface density of d states in transition metals.

I. INTRODUCTION

The surfaces of the rare-earth metals are of great scientific interest because of their unusual magnetic properties, their valence-charge effects, and their structure reconstructions. Their study, however, presents a strong challenge to the experimentalist owing to the pronounced chemical reactivity of the rare-earth elements, which makes it very difficult to produce and maintain atomically clean surfaces.¹

Some recent experiments revealing novel surface effects in rare-earth metals have been done on thin films of the rare earths grown epitaxially on suitable substrates. Thus, Weller *et al.*² grew epitaxial Gd(0001) films on W{110} to observe a so-called "magnetic surface reconstruction" of the $4f$ spins which are antiferromagnetically coupled to the underlying ferromagnetic bulk. Stenborg *et al.*³ grew epitaxial Sm(0001) films on Mo{110} to demonstrate a valence-transition-induced 5×5 reconstruction of the topmost surface layer that corresponds to a 25% expansion of the interatomic distances.

Epitaxial films have the advantage over bulk crystals that their surfaces are not contaminated by bulk impurities (if the source material is suitably pure), but have the disadvantage that surface orientation is limited to that which can be grown on appropriate substrates. By contrast, bulk crystals do not suffer from the latter limitation, but present instead the problem of bulk impurities segregating onto the surface. In spite of this problem, a few studies of bulk-crystal surfaces have been reported in the recent literature. Thus, Blyth *et al.*⁴ made qualitative observations by low-energy electron diffraction (LEED) on (0001) and $(1\bar{1}\bar{2}0)$ surfaces of Y, Pr, Gd, Ho, and Er, while Barrett *et al.*⁵ described angle-resolved photoemission experiments on the $(1\bar{1}\bar{2}0)$ surfaces of Ho and Er. These studies revealed the remarkable fact that the

$(1\bar{1}\bar{2}0)$ surfaces produce the same LEED patterns and the same photoemission spectra as the corresponding basal-plane terminated surfaces.

An investigation of the electronic structure of Tb by means of angle-resolved experiments on Tb(0001) was recently reported by our group,⁶ but the sample used in that investigation was found to contain Fe impurities which segregated in substantial amounts on the (0001) surface. The use of a purer sample allowed a quantitative LEED study of a clean Tb(0001) surface,⁷ which found a first-interlayer contraction of 3.9% and a second-interlayer expansion of 1.4% with respect to bulk spacing.

The availability of purer samples has made it possible to develop appropriate cleaning procedures which can indeed eliminate the impurities from the surface region of Tb(0001). New angle-resolved photoemission experiments on a clean Tb(0001) surface (to be reported elsewhere⁸) show that the presence of Fe impurities on the surface of less-pure crystals causes the top portion of the $6s-5d_{3z^2-1}$ Δ_1 -type band to shift toward higher binding energies. In the present paper we report the observation of a surface state on clean Tb(0001) at the center of the Brillouin zone $\bar{\Gamma}$ in an energy gap of the projected band structure. Since this surface state can only be observed on a clean surface, its observation is in fact proof of the cleanness of the surface studied.

We give some experimental details in Sec. II, describe the cleaning procedures in Sec. III, present the results in Sec. IV, and draw the conclusions in Sec. V.

II. EXPERIMENT

The photoemission experiments were carried out on beamline U7B at the National Synchrotron Light Source in the Brookhaven National Laboratory. The synchro-

tron radiation was dispersed by means of a plane-grating monochromator and the photoelectron energies were measured by means of an angle-resolved cylindrical mirror analyzer (CMA) with an angular resolution of 4° . A three-axes manipulator⁹ allowed variations of the polar, azimuthal, and tilt axis of the sample under study in such a way that photoemission experiments could be done either with *s*- or ($75\%s + 25\%p$)-polarized radiation.

Two different samples were used in the present investigations. Since one of the major difficulties in the study of bulk and surface properties of the rare earths is experimental and consists, in particular, in obtaining pure and atomically clean samples, we devote below a separate section to the description of the procedures that were adopted in this work in order to prepare a clean surface and found to be successful.

III. CLEANING PROCEDURES

It is well known to surface scientists that the impurities found on a surface originate from two different sources: the surroundings and the interior of the surface (usually referred to as the bulk). In most "clean" experimental chambers the impurities that originate from the surroundings are predominantly hydrogen, carbon, and oxygen. They can be reduced by thorough outgassing of all exposed parts in the experimental chamber and then by frequent cleaning of the surface *in situ*. The impurities that originate from the bulk depend on the nature and the purity of the material whose surfaces are under study. In the present case of Tb, and to a large extent, we presume, in the case of most rare-earth metals, these impurities are H, N, O, F, Cl, Pd, and Fe, but the first four do not seem to diffuse to the surface as much and as rapidly as the last three. With present-day samples it is unlikely that all these impurities can be completely drained out of the bulk, but appropriate procedures can indeed eliminate all or almost all of them from the surface region. We describe in the following one such procedure that was successful with Tb(0001).

The experiments described herein were done on two Tb samples, both present in the experimental chamber in the same run: they were mounted on a special manipulator that allowed either one to be moved in the proper position for LEED or photoemission experiments.⁹ The two samples had different origins. Sample *A* was purchased from the Materials Preparation Center of the Iowa State University in Ames, Iowa, was cut from the same ingot, and was prepared in the same manner as the sample that we studied earlier (this sample was found to contain substantial amounts of Fe impurity⁶). In particular, the sample was electropolished in a bath that passivated the surface with a Cl layer (see details in Ref. 6). It was therefore expected that sample *A* would contain at least Cl and Fe impurities in the surface region, according to our previous experience.⁶ Sample *B* stemmed from a single crystal that was grown and purified by the electromigration process in the School of Metallurgy and Materials of the University of Birmingham (U.K.). This sample was mechanically polished as described elsewhere⁷ and was expected to contain less Fe impurity than sample *A*.

The base pressure in our experimental chamber was $(1-2) \times 10^{-10}$ Torr; cleaning was done throughout by means of Ar-ion bombardments (5×10^{-5} Torr, $2-3 \mu\text{A}$, $200-800$ eV) followed by anneals. The chemical state of the surface was monitored by Auger-electron spectroscopy (AES) with a double-pass cylindrical mirror analyzer (CMA) and 3000-eV primary electron energy. The atomic order on the surface was monitored by low-energy electron diffraction (LEED).

In the process of searching for the most efficient cleaning procedures both samples were subjected to many hours of Ar-ion bombardments (with the target either at room temperature or at elevated temperature) and were then annealed at different temperatures for different times. For brevity, we summarize our experiments by giving below the final cleaning recipe adopted in this work, which we hope may be useful to other workers.

We assume that after the surface-polishing process the sample is never heated to temperatures higher than 450°C . In this case there is a good probability that the surface region can be cleaned with the following procedure. Bombard the surface heated to $450^\circ\text{C}-500^\circ\text{C}$ with Ar ions and anneal the sample at 450°C . The ion bombardment usually extends to periods of several hours (sample *A* required more than 40 h), while the annealing

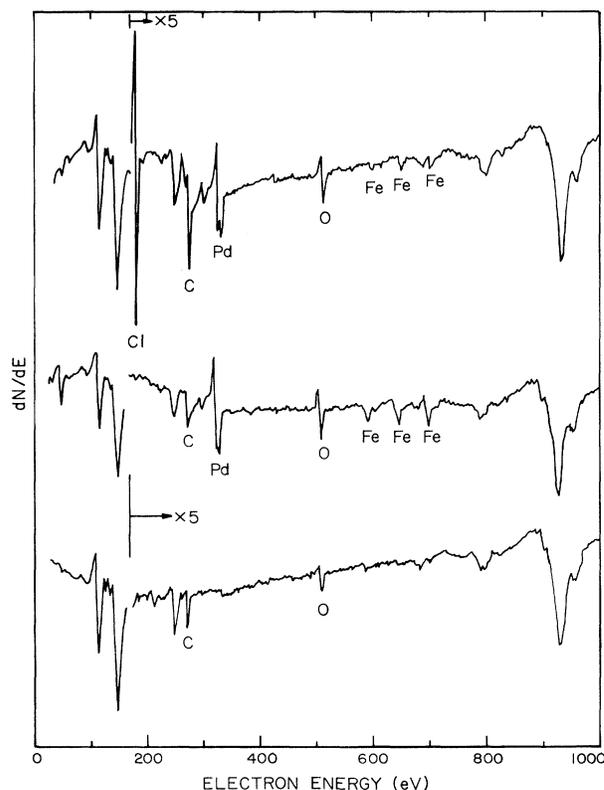


FIG. 1. AES scans from Tb(0001) surfaces. Top: after heat treatments at $700^\circ\text{C}-750^\circ\text{C}$ (dominant impurities are Cl, C, O, and Fe). Middle: after elimination of Cl (see text). Bottom: after prolonged ion bombardments at $450^\circ\text{C}-500^\circ\text{C}$ (see text).

treatment may last only 20–30 min. These low-temperature anneals do *not* produce very sharp LEED patterns, but we found that the $I(V)$ spectra obtained under these conditions were essentially the same as those measured on surfaces annealed at 600°C–700°C and producing very sharp LEED patterns.

The trouble with high-temperature anneals is that several impurities segregate on the surface, namely, in our case, Cl, Pd, and Fe. Figure 1 (top) depicts a typical AES scan obtained from sample *B* after about 4 h of anneals at 700°C–750°C. For LEED work, moderate amounts of Cl (but note, six or seven times *less* than in Fig. 1, top) are acceptable [as tested by means of $I(V)$ spectra, see Ref. 7], but for photoemission the Cl AES signal must be reduced to at least one-tenth of that shown in Fig. 1 (top). Unfortunately, depletion of Cl from the surface region required very long (about 60 h) Ar-ion bombardments of the *hot* surface (about 750°C–800°C), but these treatments did not reduce, and in fact increased, the Pd and the Fe signals (see Fig. 1, middle).

Figure 1 (bottom) is a typical AES scan from a surface depleted of Cl, Pd, and Fe. For photoemission work, the C and O signals must be further reduced: this goal can be achieved by frequent recleaning of the surface (approximately every 40 min in our chamber). Recleaning involves Ar-ion bombardment of the surface at 450°C–500°C for 20 min and subsequent anneal at 450°C for 10 min. It may be useful to point out that in our experience the C and O contaminations were substantially reduced if the surface, after cleaning, was *not* exposed either to high-energy electrons (for AES) or high-intensity photons (for “zero-order” alignment).

The importance of having a purified sample such as sample *B* should not be underestimated. It was because of the lesser Fe content in the bulk that the surface of sample *B* could be cleaned by 450°C–500°C bombardments in a reasonable number of hours (about 20 in this work) even after prolonged anneals at 750°C–800°C. Under the same conditions, the surface of sample *A* could not be depleted of Fe. Although the actual atomic concentrations of Fe on the two surfaces are difficult to estimate with confidence, a comparison of the ratios R_A between the intensity of the AES line of Fe at 703 eV and the intensity of the Tb line at 146 eV. The largest values of R_A measured in this work were 0.28 for sample *A* and 0.12 for sample *B*; the smallest R_A values were 0.01 for sample *A* and essentially 0 for sample *B*.

IV. RESULTS

The results described below were found to be reproducible with either sample *A* or sample *B* in their clean conditions. For brevity, we show only the results obtained with sample *B*.

Figure 2 depicts angle-resolved normal-emission spectra from clean Tb(0001) as measured with 25%*p*-polarized radiation in the photon-energy range between 15 and 90 eV. We note the presence of five peaks, denoted by *A*, *B*, *C*, *D*, and *S* in Fig. 2, which we discuss in the following.

Peaks *A* and *D*, located at 2.6 and 7.7 eV, respectively, below the Fermi level E_F , are due to the 4*f* electrons of Tb. The energy positions of these two peaks are very close to those reported by Gerken *et al.*¹⁰ These peaks can be seen only with photon energies larger than about 30 eV because below 30 eV the photoionization cross section of the 4*f* electrons is very small.¹¹

Peak *B*, weak and identifiable only at low photon energies, disperses from –6.1 eV at 15 eV to –3.0 eV at 18 eV, and is due to direct transitions from the 6*s*-5*d*_{3z²-1} Δ₁-type band. This peak is the object of a detailed study to be reported elsewhere⁸ and will not be discussed further here.

Peak *C*, nondispersive at about 6 eV below the Fermi level, grew rather rapidly with time after cleaning of the surface. It is associated with increasing oxygen contam-

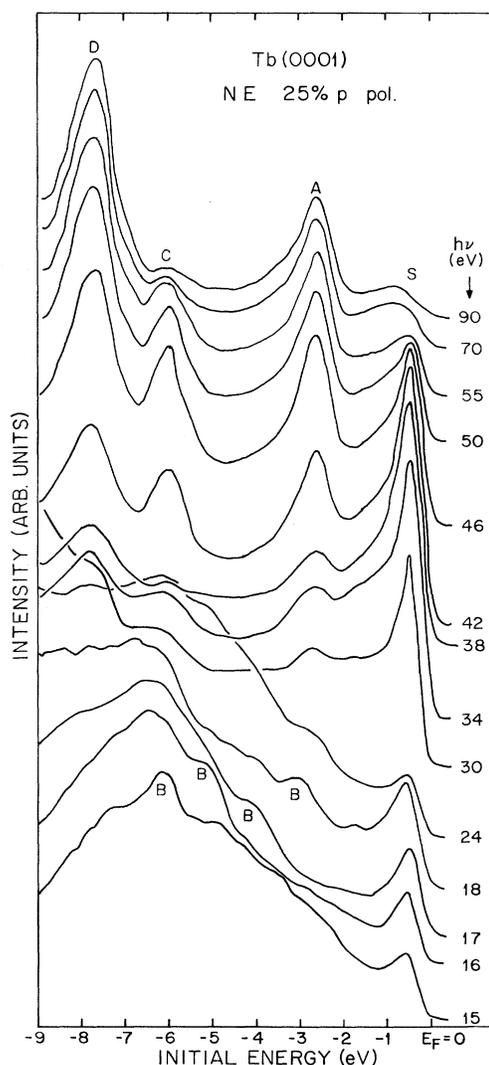


FIG. 2. Angle-resolved electron distribution curves measured on clean Tb(0001) at normal emission with (75%*s*+25%*p*)-polarized radiation.

ination, as proven by AES spectra.

Peak *S*, located about 0.5 eV below the Fermi level, varies in intensity but not in position in the photon-energy range from 15 to 55 eV. We identify this peak with the emission from a surface state as described in the following.

The experimental identification of a surface state is based on the verification of recognized properties of surface states, namely (1) absence of energy dispersion with respect to the perpendicular component k_{\perp} of the momentum; (2) energy location in band gaps of the projected band structure; and (3) intensity sensitivity to the presence of foreign atoms on the surface.

Property (1) is exhibited by peak *S* in Fig. 2. Since the curves depicted in the figure were collected at normal emission, the fact that peak *S* does not disperse with photon energy means that it is independent of k_{\perp} . Property (2) is also exhibited by peak *S* because its energy location (0.5 eV below E_F) is inside the energy-band gap of the band structure projected at $\bar{\Gamma}$ on the (0001) surface. Both the band calculation with the relativistic augmented-plane-wave method of Jackson¹² and the band calculation with relativistic linear muffin-tin orbitals of Christensen⁶ show that there is an energy gap between 0 (the Fermi level) and -2 eV along the $\Gamma\Delta A$ line. Property (3), sen-

sitivity to the presence of foreign atoms, is also exhibited by peak *S* as demonstrated in Fig. 3(a). In this figure, the solid curve is an electron distribution curve (EDC) measured with 38-eV 25%*p*-polarized photons at normal emission from clean Tb(0001), while the dashed curve is an EDC measured under the same conditions from a surface that was exposed to oxygen and was shown by AES to be contaminated with about 0.3 layers of oxygen.¹³ The strong -6-eV peak *C* in the dashed EDC is in fact caused by the oxygen 2*p* electrons. The figure shows that the intensity of peak *S* decreased much faster, as a consequence of the oxygen contamination, than the intensities of the bulk 4*f* peaks *A* and *D*.

Having proven the existence of the surface state, we now discuss its origin. We show below that our experimental results are useful for the purpose of choosing among the 4*f*, 5*d*, 6*s*, or 6*p* as possible parents of the *S* state.

Figure 3(b) determines the polarization dependence of peak *S*. The two curves depicted in Fig. 3(b) (solid and dashed) were measured with 25%*p*- and *s*-polarized radiation, respectively. Comparison of the ratios of intensities of peak *S* to the corelike *A* and *D* peaks shows that these ratios decrease when the *p* component of the radiation is reduced. Hence, according to the dipole selection rules, the wave function of the surface state *S* has Δ_1 symmetry.

We also note in Fig. 2 that the intensity ratios of peak *S* to the bulk 4*f* peaks (*A* and *D*) are functions of photon

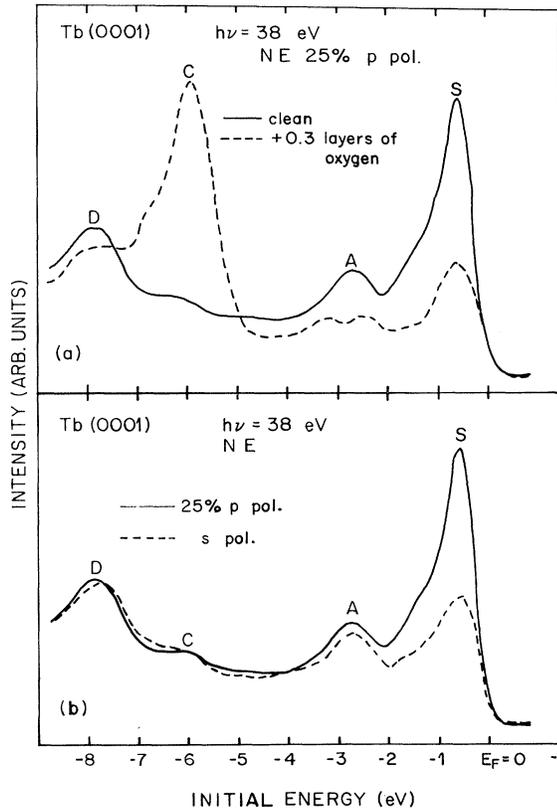


FIG. 3. (a) Effect of oxygen impurity (dashed curve) on the EDC of a clean Tb(0001) surface (solid curve). (b) Dependence of the photoemission spectra from clean Tb(0001) upon the polarization of the exciting radiation.

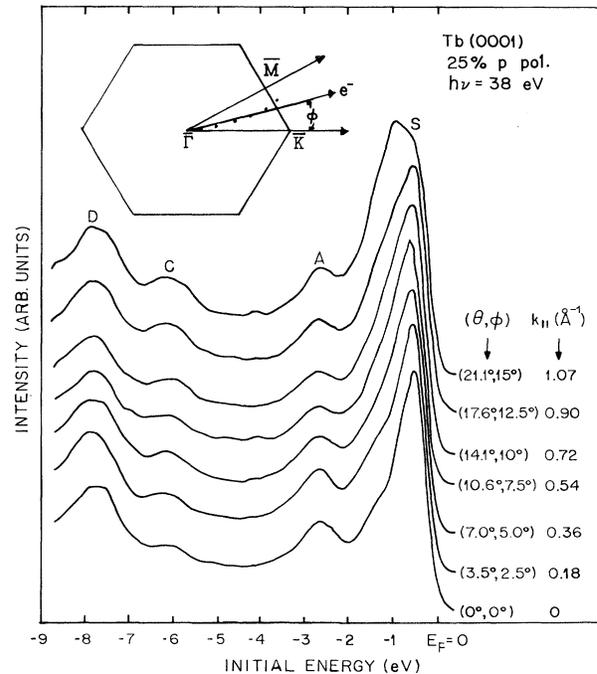


FIG. 4. Study of the dependence of surface state *S* upon the parallel component k_{\parallel} of the momentum. θ is the polar angle; ϕ is the azimuthal angle (defined in the inset). The dots in the inset define the path in the surface Brillouin zone along which the EDC's have been measured.

energy $h\nu$, i.e., increase with $h\nu$, reach a maximum at $h\nu \approx 38$ eV, and finally vanish for $h\nu > 55$ eV. If we compare this photon-energy dependence of peak S with the photon-energy dependence of the photoionization cross sections of the $4f$, $5d$, and $6s$ electrons in Tb (Ref. 11), we conclude that the surface state S does *not* originate from the $4f$ electrons.

Further information may be gathered from the dispersion of state S with the parallel component k_{\parallel} of the momentum. Unfortunately, our experimental facilities did not allow us to measure the dispersion along major symmetry lines such as $\bar{\Gamma}\bar{K}$ or $\bar{\Gamma}\bar{M}$, but we could measure the k_{\parallel} dependence of peak S along a path in the Brillouin zone that is defined by the values of polar angle θ and azimuthal angle ϕ given in Fig. 4. The inset in Fig. 4 defines the azimuthal angle ϕ . From the lattice constants of Tb ($a = 3.60$ Å, $c = 5.69$ Å) we calculate $k_{\bar{\Gamma}\bar{K}} = 1.16$ Å⁻¹ and $k_{\bar{\Gamma}\bar{M}} = 1.00$ Å⁻¹. The solid circles in the inset show the momentum component parallel to the surface (k_{\parallel}) of the photoelectrons from the surface state with different take-off angles θ and ϕ as given near the corresponding EDC's in Fig. 4. The results indicate a very weak dispersion with k_{\parallel} and therefore we conclude that the surface state has $5d_{3z^2-1}$ orbital character, *not* $6s$ or $6p_z$ orbital character.

The existence of surface state S can then be explained by the theory of surface core-level shifts in transition metals.¹⁴ We recall first that in rare-earth metals the $4f$ electrons, although quite weakly bound with respect to the Fermi level, are highly localized and have strong atomic-like character. Hence the valence band has only three valence electrons¹⁵ with $(5d6s)^3$ configuration. Now, on the surface, the width of the valence band is narrower than in the bulk, because the coordination number is smaller than in the bulk. Hence, in the absence of any

electron-charge transfer between surface and bulk, and because there are only three electrons in the $(5d6s)$ band, the position of the Fermi level is higher for the surface than for the bulk. There will therefore be charge transfer from the surface to the bulk in order to align the Fermi levels. As a consequence, the valence band of the surface is shifted toward higher binding energies with respect to the bulk. The bulk band-structure calculations along the $\Gamma\Delta A$ line^{6,12} exhibit two bands located about 1 eV above the Fermi level. Furthermore, the band-structure calculation done by Freeman and co-workers¹⁶ for Gd(0001) shows a bulk nonbonding $5d_{z^2}$ state 1 eV above the Fermi level which drops sharply below E_F at $\bar{\Gamma}$, resulting in a flat band dispersion near the edge of the Brillouin zone. We conclude therefore that the surface state that we have observed on clean Tb(0001) originates from the $(5d6s)$ band above the Fermi level and is indeed very similar in character to the surface state calculated by Freeman and co-workers on Gd(0001).

V. CONCLUSION

Angle-resolved photoemission experiments on clean Tb(0001) revealed the existence of a surface state 0.5 eV below the Fermi level. This state is located in the band gap of the projected band structure at $\bar{\Gamma}$ and has $5d_{3z^2-1}$ character.

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¹³The oxygen coverage of the surface was determined from the measured ratio $R = I_{O(510 \text{ eV})} / I_{Tb(146 \text{ eV})} = 0.54$ between the intensities of the O and Tb AES lines at 510 and 146 eV, respectively, with the formula $R = R_{\infty} [1 - \exp(-d/\lambda_{O(510 \text{ eV})})] / \exp(-d/\lambda_{Tb(146 \text{ eV})})$. The quantity $R_{\infty} = 5$ was obtained from the AES sensitivities given in the AES Handbook [L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronic Industries, Inc., Eden Prairie, MN, 1978)], and the electron mean free paths λ were calculated to be $\lambda_{O(510 \text{ eV})} = 12.2$ Å and $\lambda_{Tb(146 \text{ eV})} = 6.59$ Å from the formula given by Seah and Dench [M. P. Seah and W. A. Dench, Surf. Interf. Anal. **1**, 2 (1979)].

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