

DESY SR-81/11
October 1981

SURFACE SHIFTS ON RARE EARTH METALS

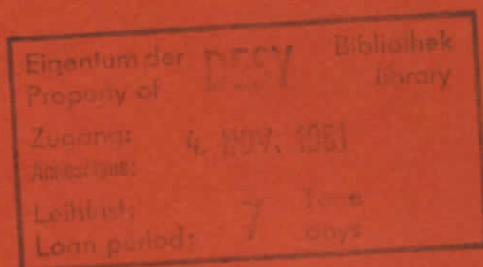
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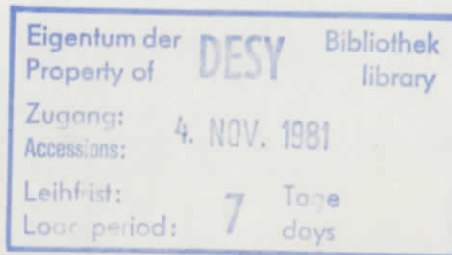
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ABSTRACT

Surface shifts on various rare earth metals are determined using high resolution synchrotron radiation induced photoelectron spectroscopy. The mean free path of the photoelectrons is evaluated. The surface of Sm metal is confirmed to be completely divalent.



Contributed paper IV. Europ. Conf. on Surface Science,
to be published in Surface Science.

Binding energy shifts for core levels at clean metal surfaces are by now a well established effect (see, e.g., Ref. 1 and references cited therein) which is now applied to study the surface structure of metals² and surface segregation in alloys³. Investigations are mainly focussed on the 5d transition metals where the emission from the sharp, shallowly bound 4f core levels is well suited to detect surface shifts. However, also for the rare earth (RE) metals the partly filled 4f shell is well localized, core-like, and hardly affected by the band structure.

We have initiated a program to study the UPS spectra of all RE metals at photon energies ranging from 30 eV to 200 eV with high resolution ($\Delta E = 0.1 \dots 0.2$ eV). Our spectra can be compared with recently published high resolution ($\Delta E = 0.25$ eV) XPS data by Lang et al.⁴. The mean free path of the photoelectrons excited in the solid is in the order of 20 Å for kinetic energies around 1 keV (at XPS excitation) and reaches its minimum for kinetic energies below 100 eV with only a few Å. Thus, our UPS spectra are extremely surface sensitive, and in fact the detection of surface shifts emerges as one fundamental result from our measurements.

Data are taken at the new Hamburger Synchrotronstrahlungslabor HASYLAB. Synchrotron radiation from the storage ring DORIS is monochromatized by the FLIPPER monochromator. The photoelectrons are analyzed by a double pass cylindrical mirror analyzer. High purity samples (99.99%) are evaporated from tungsten filaments onto stainless steel substrates under UHV conditions (base pressure of the system ca. $1 \cdot 10^{-10}$ Torr). The cleanliness of the sample surfaces can be checked with high sensitivity by monitoring the Oxygen 2p signal at 40 eV photon energy.

Our results for the surface shift of Eu and Gd are already presented elsewhere together with a detailed description of the data analysis applied to detect the surface shift⁵. The intensities of the different multiplet lines of the ionized f-shell are calculated in the fractional parentage scheme and convoluted with a Doniach-Sunjic lineshape⁶ with parameters for width and asymmetry for which XPS data⁴ serve as a reference. This is done for each J-value. All contributions are added up and folded with a Gaussian lineshape to account for the instrumental resolution. For the surface emission the multiplet lines are rigidly shifted in energy, the magnitude of the displacement being the surface shift, and convoluted with a Doniach-

Sun'ic lineshape with another set of parameters. All parameters including the surface shift are obtained by comparison of the generated curve with the measured spectra.

The data analysis is not yet complete. Here we present our results for some heavier RE metals with a relatively simple multiplet structure. For Tb and Dy the analysis could be confined to the multiplet lines with the higher multiplicity which form a group well separated from the others. These data are connected to our results for Eu and Gd⁵, and for Yb which confirm earlier measurements⁷. The surface shift of Sm which leads to a surface valence change^{8, 9} is also discussed in the light of our measurements.

The situation for the heavier RE's is illustrated by Dy (Fig. 1) and Ho (Fig. 2). Both elements exhibit rich multiplet structure in their photoemission spectra containing two different multiplicities. For Dy, however, a small group of lines at 4 eV binding energy form a structure well separated from the rest. Here, a component shifted towards higher binding energy by ca. 0.5 eV is clearly discernable by the comparison with the XPS spectrum. For the rest of the spectrum, this shifted component always overlaps with other structure and thus rather manifests itself in different relative intensities of the multiplet structure compared to the XPS spectrum. This situation is likely met with in Ho (Fig. 2) which we show as an example for the complexity of the determination of surface shifts in many heavy RE metals.

In order to prove that the shifted component of the 4f emission is an intrinsic effect of the clean surface, we took spectra at various photon energies. By tuning the photon energy we also tune the kinetic energy of the photoelectrons which leads to a variation of the mean free path of the photoelectrons inside the solid and thus to a variation of the surface sensitivity. Fig. 3 displays two spectra of Dy taken at 40 eV and 80 eV photon energy. Note that the different cross-section dependence of the s-d-valence electrons and the 4f-electrons leads to the dramatic intensity variation of the valence band near the Fermi energy. Note further that the cross-section for oxygen 2p electrons is highest at ca. 40 eV photon energy. Thus the complete absence of structure around 6 eV binding energy, where the O 2p emission is to be expected, indicates that the sample surface is of high purity. This fact proves, together with the intensity increase of the high binding energy shoulder of the 4 eV-structure when the photon energy decreases from 100 eV

(Fig. 1) to 40 eV (Fig. 3), that the shifted 4f emission originates from the clean surface.

All values obtained so far for the surface shifts of the RE metals are compiled in Fig. 4. For the surface shift of the trivalent metals, the theoretical estimate of 0.3 ... 0.4 eV towards higher binding energies is given¹⁰. Neglecting Sm in this context we find the surface shifts of the trivalent metals Gd, Tb and Dy with 0.48 eV, 0.51 eV and 0.53 eV being significantly different but not far from this estimate. Though not significant, the surface shift has a tendency to increase from Gd to Dy. The divalent metals Eu and Yb show the same surface shift of 0.63 eV.

The mean free path of the photoelectrons inside the solid can be extracted from our data by the determination of the surface-to-bulk intensity ratio of the 4f emission. This extremely valuable quantity is hardly accessible by other techniques in this energy range where it is assumed to pass a minimum of only a few λ . An evaluation of the mean free path can be carried out on the basis of a model which depends on the collection geometry of the analyzer. Our model is described in detail in Ref. 5 yielding the equation:

$$\lambda(E_{kin}) = 2 \left(1 - \frac{\phi}{E_{kin}}\right)^{-1} \frac{I_B}{I_S}$$

which gives the mean free path λ in terms of the thickness a of the surface layer as a function of the kinetic energy E_{kin} of the photoelectrons (referenced to the Fermi level). ϕ stands for the work function of the sample, and I_B and I_S are the intensities of the surface and bulk components.

The resulting values of the mean free path covering the range of energies between 30 eV and 220 eV are displayed in Fig. 5. For all investigated metals we find decreasing values of the mean free path towards lower energies, the minimum being apparently reached at 30 eV or even below. Differences between trivalent and divalent metals are not yet significant, although the data points for the trivalent ones tend to lie at lower values, especially at higher energies.

For Sm a surface valence change has been detected by XPS⁸ and UPS⁹ measurements both yielding a mean surface valence of 2.6. Combined measurements¹¹ of Bremsstrahlungs-Isochromat-Spectroscopy (BIS) and surface sensitive XPS spectra related this valence change to a surface shift that pulls the lowest

states of the divalent f^6 configuration which are unoccupied in the trivalent bulk below the Fermi level. For the integral surface shift the value of 1.23 eV was determined¹¹. It should, however, be kept in mind that the valence change requires a minimum surface shift of only 0.46 eV¹¹ which is in fact lower than our values obtained for other trivalent RE metals. Additional energy may be set free by the valence change itself resulting in the anomalously high total value for the surface shift.

From the energy separation of the Fermi level and either the unoccupied f^6 state of the bulk and the occupied f^6 state at the surface, it was concluded in Ref. 11 that the surface must be completely divalent as the bulk is completely trivalent. This statement being in contradiction to the earlier determinations^{8, 9} of the Sm surface valence gains strong support by our measurements. Any trivalent contribution at the surface must experience at least the minimum surface shift that is sufficient to drive the valence change (0.46 eV). If this contribution makes up a substantial fraction (> 10%) a displaced multiplet structure should accompany the 4f bulk emission. Our spectra show no indication for a shifted emission from the trivalent f^5 ground state (compare Fig. 6). In fact the emission from the f^5 configuration is in perfect agreement with XPS results⁴. We note that also the intensity ratio between the 4f-surface emission and bulk emission is estimated to be compatible with a completely divalent surface.

We conclude that synchrotron radiation induced UPS spectroscopy is best suited for the investigation of surface effects, if a monochromator is used that covers the energy range from 20 eV to 200 eV with high resolution. In conventional XPS experiments the surface sensitivity is varied by choosing different take-off angles for the photoelectrons^{8, 11}. Our results indicate that a comparison of He II- and XPS- induced spectra is likely to disentangle surface and bulk emission much easier.

Acknowledgment

The authors are indebted to Y. Baer for generously providing the XPS spectra.

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Figure Captions

- Fig. 1 Comparison of our UPS spectrum and an XPS spectrum⁴ of Dy.
- Fig. 2 Comparison of our UPS spectrum and an XPS spectrum⁴ of Ho.
- Fig. 3 UPS spectra of Dy showing the increased contribution of the surface emission at 40 eV photon energy.
- Fig. 4 Magnitude of the surface shift of the RE metals.
*) Theoretical estimate for the trivalent metals from Ref. 10,
**) value taken from Ref. 11.
- Fig. 5 Mean free path λ of the photoelectrons in terms of the thickness a of the surface layer plotted versus the kinetic energy of the photoelectrons. The solid line drawn as a visual aid connects the data points for Yb.
- Fig. 6 Comparison of our UPS spectra and an XPS spectrum⁴ of Sm. Vertical bars give the energy positions and calculated intensities of the bulk emission ($4f^5 \rightarrow 4f^4$), surface emission ($4f^6 \rightarrow 4f^5$), and Bremsstrahlungs-Isochromat-spectrum ($4f^5 \rightarrow 4f^6$).

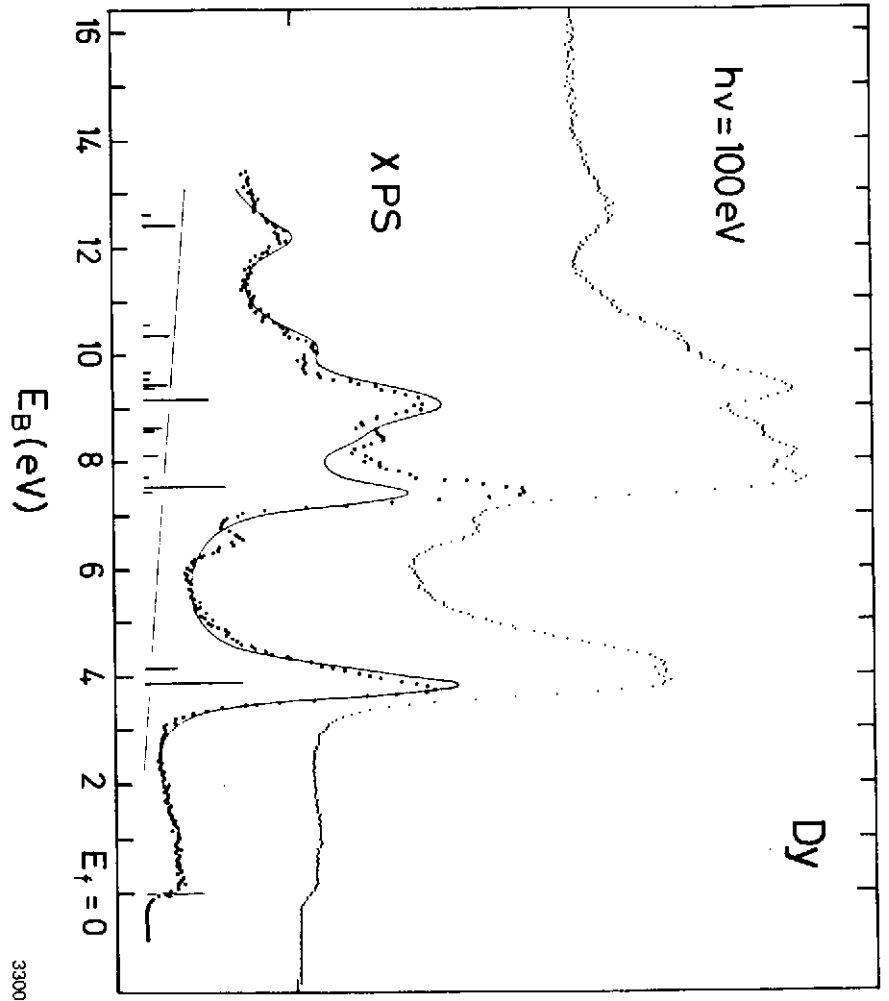


Fig. 1

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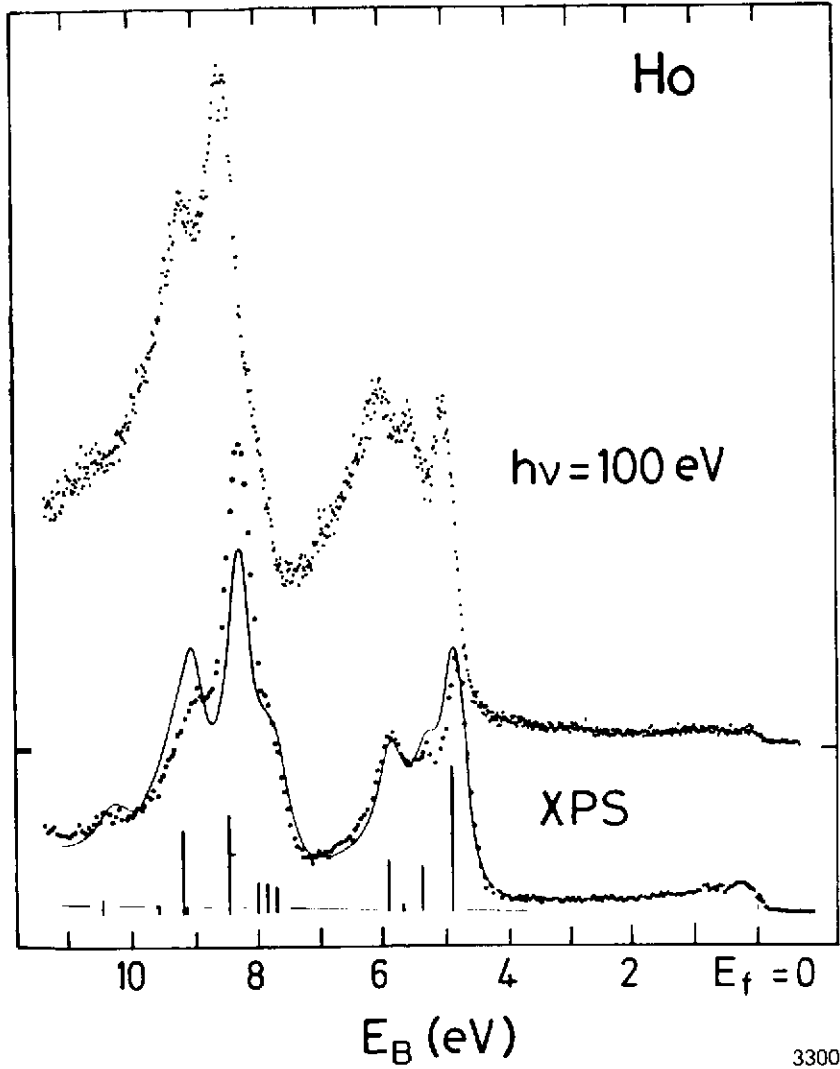


Fig. 2

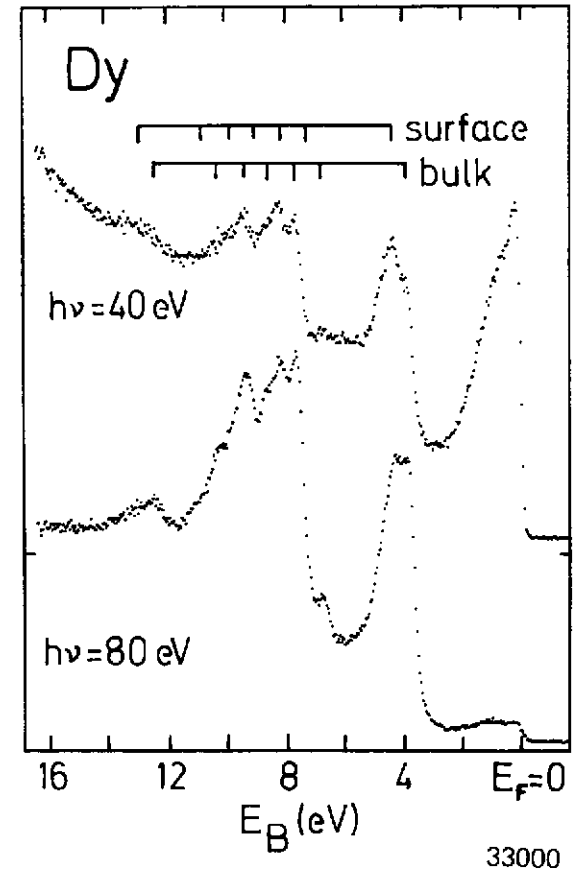


Fig. 3

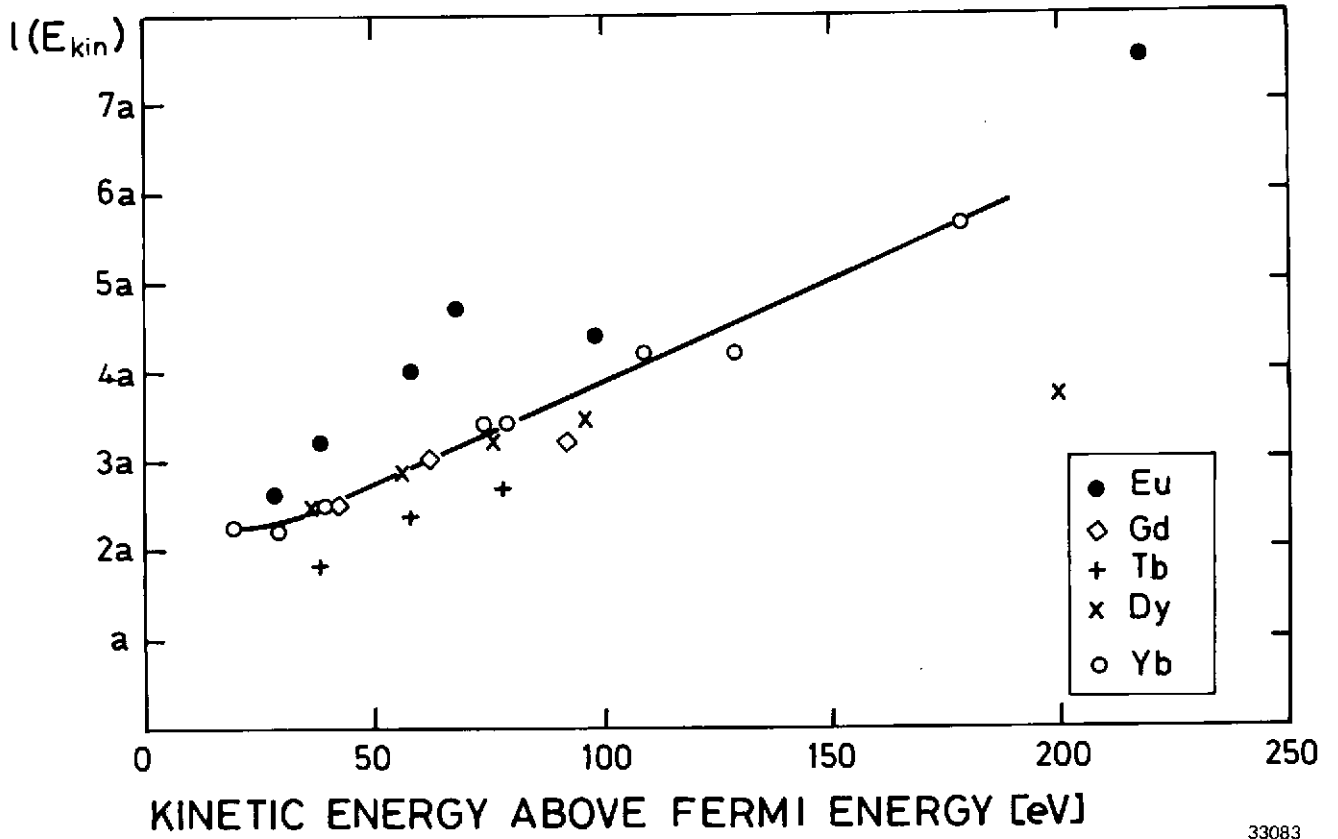


Fig. 5

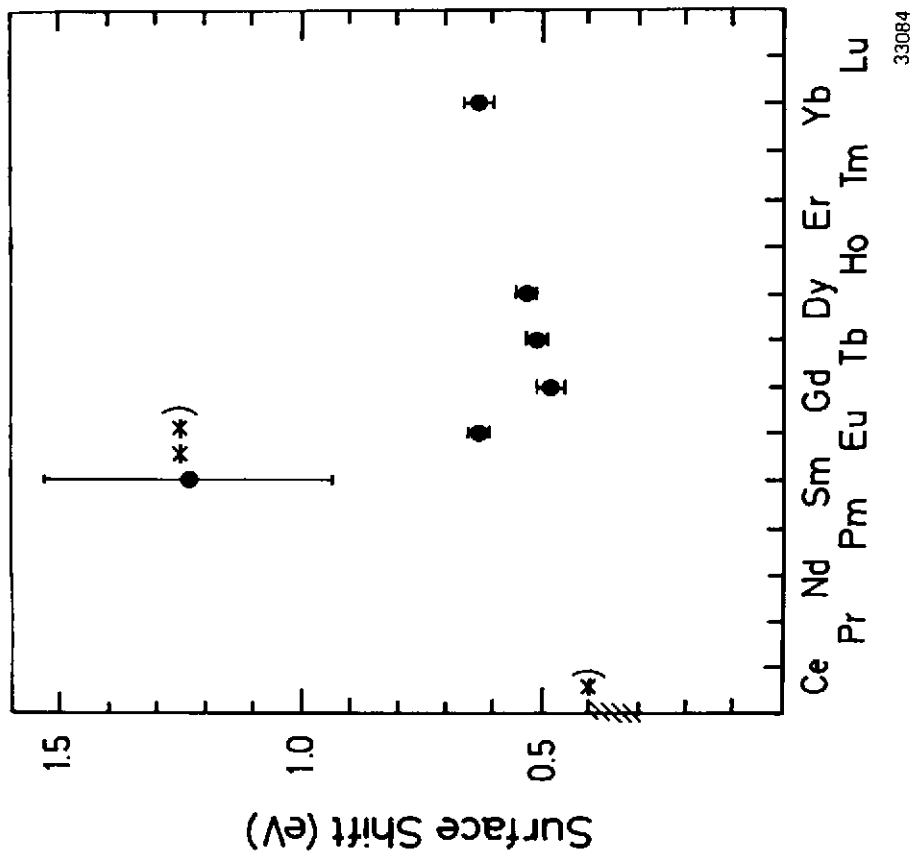


Fig. 4

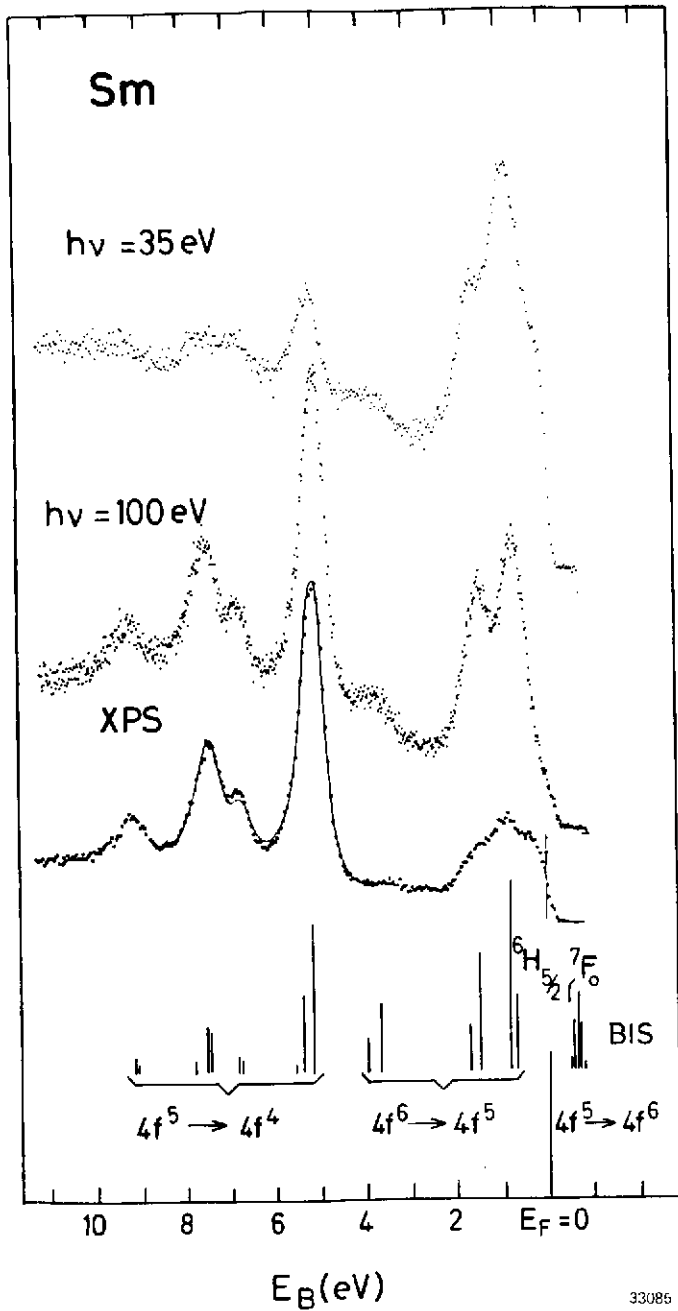


Fig. 6