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4f HOLE LIFETIME AND SURFACE CHEMICAL SHIFT IN Yb METAL

by

S. F. Alvarado, M. Campagna, and W. Gudat
Institut für Festkörperforschung der KFA

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Institut für Festkörperforschung der KFA, Postfach 1913, D-5170 Jülich
W. Germany

Abstract

We report on UHV photoemission studies of Yb metal using synchrotron radiation in the photon energy range $25<h\nu<180$ eV, whereby maximum surface sensitivity can be reached. The 4f photoemission spectrum shows a quadruplet structure due to a superposition of two 4f spin orbit doublets. One doublet has a very symmetric lineshape and an extremely narrow lifetime linewidth $2\gamma=0.013$ eV. We attribute it to bulk emission. The other doublet exhibits almost symmetric lines with a much larger lifetime linewidth $2\gamma=0.43$ eV. It has also a larger binding energy by 0.6 ± 0.03 eV. We attribute this as being due to chemically bound Yb atoms located at the surface. We discuss the implications of these findings for recent high resolution photoemission studies of Rare Earth (RE) metals and their analysis.

The electronic structure of bulk Rare Earth (RE) metals has been recently successfully studied by X-ray photoemission (XPS)$^{(1)}$. It has been established that the relative multiplet positions and intensities as well as absolute 4f binding energies are in good agreement with predictions based on the calculations of the coefficients of fractional parentage$^{(2)}$ and on the renormalized atom scheme$^{(3)}$. On the other hand the lifetime linewidth 2γ and the lineshape of the 4f levels of the RE metals and compounds has not yet received much experimental attention, except for the case of Yb metal$^{(4)}$. Theoretically$^{(5)}$ one expects a rather small linewidth (large 4f hole lifetime); smaller by at least an order of magnitude than the available energy resolution of most XPS apparatus. This is true at least for those RE elements having shallow 4f binding energies (the so called "divalent" metals Eu and Yb) as well as for many Sm-, Eu-, Tm- and Yb compounds.

We present here UHV photoemission spectra of Yb metal obtained using synchrotron radiation in the range $25<h\nu<180$ eV with a total energy resolution ranging down to 0.2 eV. From these spectra we obtain information on both the lifetime linewidth and the lineshape of the 4f levels. As shown in Fig. 1 for photon energies of 40.7 and 99.7 eV the obtained spectra exhibit features not evident in any X-ray photoemission spectra published so far. The 4f contribution appears as a quadruplet structure in contrast to the X-ray results where only one doublet has been observed$^{(1,4)}$. We note that a quadruplet structure in the valence band region of Yb has also been reported by Brodén et al$^{(6)}$ for photoemission experiments performed in the low photon energy range ($6.3<h\nu<10.2$ eV). It was interpreted as due to the spin-orbit split $4f^{13}$ levels with peaks at E_b = 1.25 and E_b = 2.5 eV, and two additional peaks at E_b = 1.7 and E_b = 3 eV attributed to valence band excitations, analogous to those reported for Ca$^{(7)}$. The present analysis leads us however to a different interpretation, namely that the peaks at 1.7 and 3 eV binding energy arise from chemically shifted $4f^{14}$ levels of surface atoms. This shows the need to perform further measurements in the region $h\nu<40$ eV so as to be able to decide whether the mentioned valence band excitations have really been observed.

The experiments were performed at the storage ring DORIS in Hamburg with an experimental set-up already described$^{(8)}$. The samples were prepared in the experimental chamber either by scraping a solid block of Yb metal in situ at a base pressure of $2\text{-}3\times10^{-10}$ Torr with a carbide steel brush or by evaporation onto a polished stainless steel substrate. During evaporation (and after long degassing of the crucible) the pressure in the main chamber still rose to 1.8×10^{-8} Torr. After turning off the evaporator it decreased to 5×10^{-10} Torr within 4 min.

The binding energy and splitting of one of the doublets shown in Fig. 1 coincide with those given for bulk Yb as reported by XPS studies$^{(1,4)}$. The other doublet shifted by 0.6 ± 0.03 eV to higher binding energy has a significantly larger linewidth but it exhibits the same splitting ΔE_{so} = 1.27 ± 0.04 eV. The relative intensity of the two doublets varies with varying photon energy, as it is apparent from Fig. 1. From

the generally known energy dependence of the escape depth of excited electrons$^{(9)}$ we conclude that the doublet located at higher binding energy originates from 4f levels of the topmost layers of the sample. For this reason we choose to call it the "surface doublet". In the energy range $6.3<h\nu<10.2$ eV the surface sensitivity is smaller than for $h\nu\approx40$ eV. The interpretation of the quartet structure we propose here can therefore also account for the photon energy dependence of the relative intensity of the peaks at 2.7 and 3 eV below the Fermi energy reported by Brodén et al.$^{(6)}$. We assign the shifted 4f contribution to Yb atoms chemically bound to contaminants (presumably oxygen) because our data show also two weak broad peaks at $E_B\approx7.5$ and ~12 eV. The latter have previously been observed by W.C. Lang et al.$^{(10)}$ on Yb samples purposely exposed to oxygen and by Brodén et al.$^{(11)}$. For this reason we disregard at present another very tempting possible explanation assigning the surface doublet to an intrinsic property of the clean Yb surface$^{(12)}$. Because no Auger electron spectroscopy facility was available in the chamber we used at DORIS we could not identify the exact chemical nature of the contaminants (adsorbates). A purity analysis of the samples showed that the contributions of the two dominant impurities were smaller than 240 ppm for oxygen and 200 ppm for calcium. We note however that our spectra show clearly that the bonding state of the chemically shifted Yb at the surface is such as to maintain the $4f^{14}$ (divalent) configuration. The possibility of having Yb_2O_3 at the surface is therefore excluded. Whether the oxygen content of the starting material can explain the observed contamination of the samples is not yet clear, especially for the scraped ones!

The 4f doublet we assigned to Yb atoms located in the topmost layer shows some interesting properties. Its relative intensity is approximately the same for evaporated and scraped samples (scraping occurs at pressures of 2×10^{-10} Torr!), and shows little sensitivity to further contamination. Its intensity increases by 5% after 4 hours at 2×10^{-10} Torr in the vacuum chamber.

The analysis of the line shape of the XPS$^{(4)}$ spectra have been performed on data collected under similar sample preparation conditions as ours. Therefore we performed a similar analysis on our data to establish up to which point the reported values for the singularity index$^{(13)}$ (asymmetry parameter) $\alpha_B = 0.15$ and the lifetime linewidth $2\gamma = 0.16$ eV may depend on the unresolved surface doublet. We fitted our data with Doniach-Sunjic lineshapes$^{(13)}$ convoluted with the system's instrument resolution function R(E) given by

$$R(E) = \exp - \left(\frac{E}{EB + B_o}\right)^2 , \text{ with } B = 0.0186\,(\text{eV})^{-1} \text{ as}$$

determined from the analysis of the Ar 3p lines in the gas phase$^{(8)}$. The results of the mean square fits for various photon energies are summarized in the Table I, where we have also displayed the XPS results for comparison. Not unexpectedly we find a lifetime linewidth about an order of magnitude smaller than the value determined from the XPS data. In contrast, the value of α_B is found to be in close agreement. We considered a possible phonon broadening of the 4f lines by treating the gaussian linewidth as a fitting parameter. As expected no appreciable phonon effect was found. The data given in Table I seem to indicate a trend of decreasing linewidth $2\gamma_B$ with hν. We feel however that this point has to be investigated in more detail and if possible with further improved total instrumental resolution. The almost symmetric lines of the surface doublet suggests that the charge density near the Fermi level in this topmost layer has been strongly reduced$^{(13)}$ indicating that the contaminants are chemisorbed at the Yb surface. A 4f doublet with highly symmetric lines has in fact been observed in the semiconductor YbTe (see Fig. 8 of Ref. (14)). By assuming that the chemical shift of the 4f levels be slightly different for atoms in different geometrical sites a further linewidth broadening can result. This could be one important contribution to the broadening of the surface doublet lines.

In Fig. 2 we compare our results with the lifetime linewidth calculated for the atomic elements by McGuire$^{(5)}$. There is a remarkably good agreement. In order to show how well the general trend of the experimental linewidth data versus the atomic number Z is reproduced by the above calculations we added in Fig. 2 further data on Au, Pt, Ir$^{(15-17)}$, and W$^{(18)}$. Certainly it would be worth to examine the 4f levels of other elements with high resolution photoemission.

From Table I it can also be seen that the branching ratio $4f_{7/2}:4f_{5/2}$ shows some dependence on photon energy. A detailed study of this effect has been reported for the 5d levels of lead and lead compounds$^{(19)}$. In the photon energy range studied here the variation in the branching ratio is predominantly due to different excitation cross sections of the $j = 7/2$ and $j = 5/2$ components.

As mentioned earlier the intensity of the surface contribution was found to be well reproducible in different measurements collected at the same photon energy. Thus the thickness of the surface layer responsible for the surface doublet appears to be constant over a period of hours at 2×10^{-10} Torr. We used this fact to determine the energy variation of the photoelectron escape depth $\ell(E\ )$ by assuming that the "surface" component originates from the outermost layer of the sample, and the "bulk" component from the atom layers underneath. Then, with the further assumption of equal cross section behaviour, one can make use of the relation:

$$\frac{I_S}{I_B} = e^{a/\ell\cos\theta} - 1$$

where $I_B(I_S)$ is the bulk (surface) emission intensity and a is the mean distance between neighbouring atomic layers. The angle $\theta \approx 45^{\circ}$ for this particular measurement. The resulting $\ell(E^*)$ is shown in Fig. 3. Note that this rather crude evaluation results in a change of $\ell(E^*)$ by almost a factor 2 between $h\nu = 40$ and 100 eV. Taking $a \approx 2.7$ Å we determine the smallest $\ell(E^*) \sim 4.5$ Å at $h\nu = 40$ eV.

In conclusion we have found that the 4f lifetime linewidth of Yb metal is $2\gamma = 18 \pm 7$ meV (mean value), an order of magnitude smaller than previously determined by XPS studies. This is in better agreement with estimates of McGuire for the atomic elements.

The Doniach-Sunjic asymmetry parameter is on the other hand in agreement with the value previously determined from XPS data.

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Figure Captions

Fig. 1: Energy distribution curves of the valence band region of Yb metal obtained with synchrotron radiation . Dots: experimental data. The fitted envelope (continuous line) represents the superposition of two spin-orbit split doublets of different Doniach—Sunjic-line shapes convoluted with the instrumental resolution function. The first peak of each doublet, 1 "bulk" and 2 "surface", is also shown (dashed line).

Fig. 2: Lifetime line width 2γ of the Yb 4f hole. The available experimental values are compared with the calculations of McGuire for the atomic elements for $70<z<80$. XPS results: ● Ref. 15, ◘ Ref. 16; o Ref. 17; △ Ref. 18.

Fig. 3: Photon energy dependence of the electron escape depth $\ell(E^*)$ in units of a, the mean distance between neighbouring Yb layers ($a \approx 2.7$ Å).

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TABLE I

photon energy hν(eV)	"Bulk" doublet		"Surface"doublet		branching ratio^{+}
	α_B	$2\gamma_B$ (eV)	α_S	$2\gamma_S$ (eV)	$4f_{7/2}:4f_{5/2}$
40.7	0.194	0.0130	~0	0.438	1.49
54.7	0.097	0.0134	~0.006	0.408	1.48
99.7	0.17±0.015	0.029±0.016	~0.015	0.434±0.02	1.36±0.02
1 486 XPS Ref. (15)	0.15	0.160	-	-	4/3

Legend: α_B, α_S : bulk and surface asymmetry parameters.

γ_B, γ_S : 4f hole lifetime linewidth

$^{+}$ found to be approx. equal for both doublets.

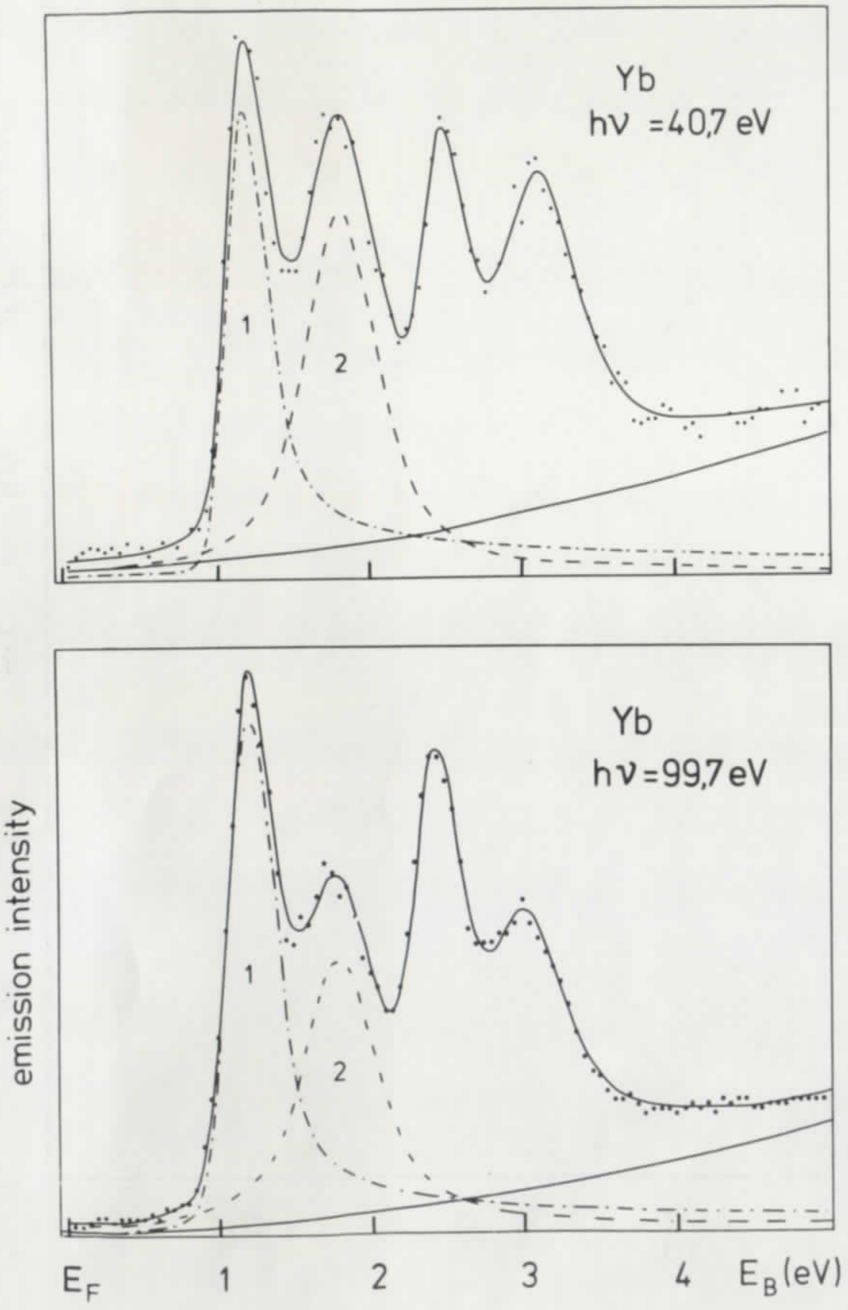
Yb
hν =40,7 eV
1
2
Yb
hν=99,7 eV
1
2
emission intensity
E_F
1
2
3
4
E_B(eV)

Fig. 1

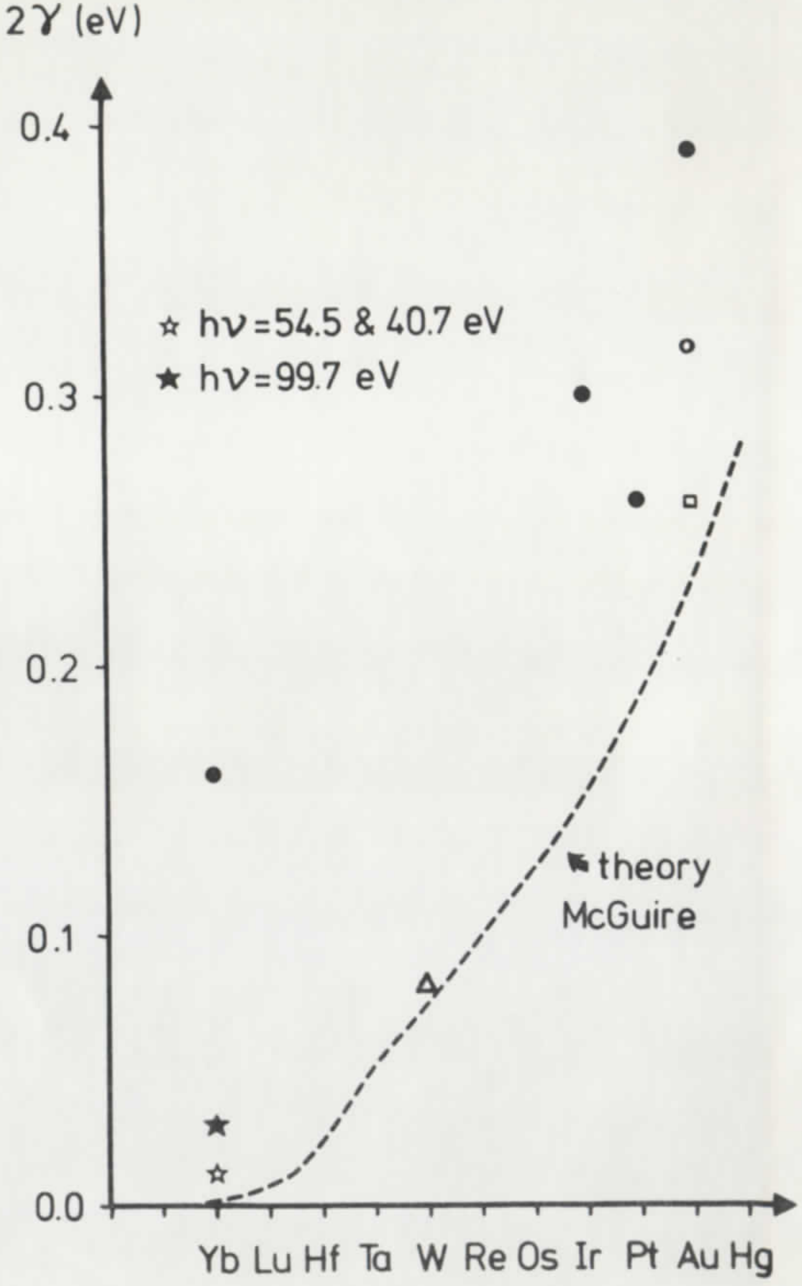
2γ (eV)
0.4
0.3
0.2
0.1
0.0
☆ hν=54.5 & 40.7 eV
★ hν=99.7 eV
theory
McGuire
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg

Fig. 2

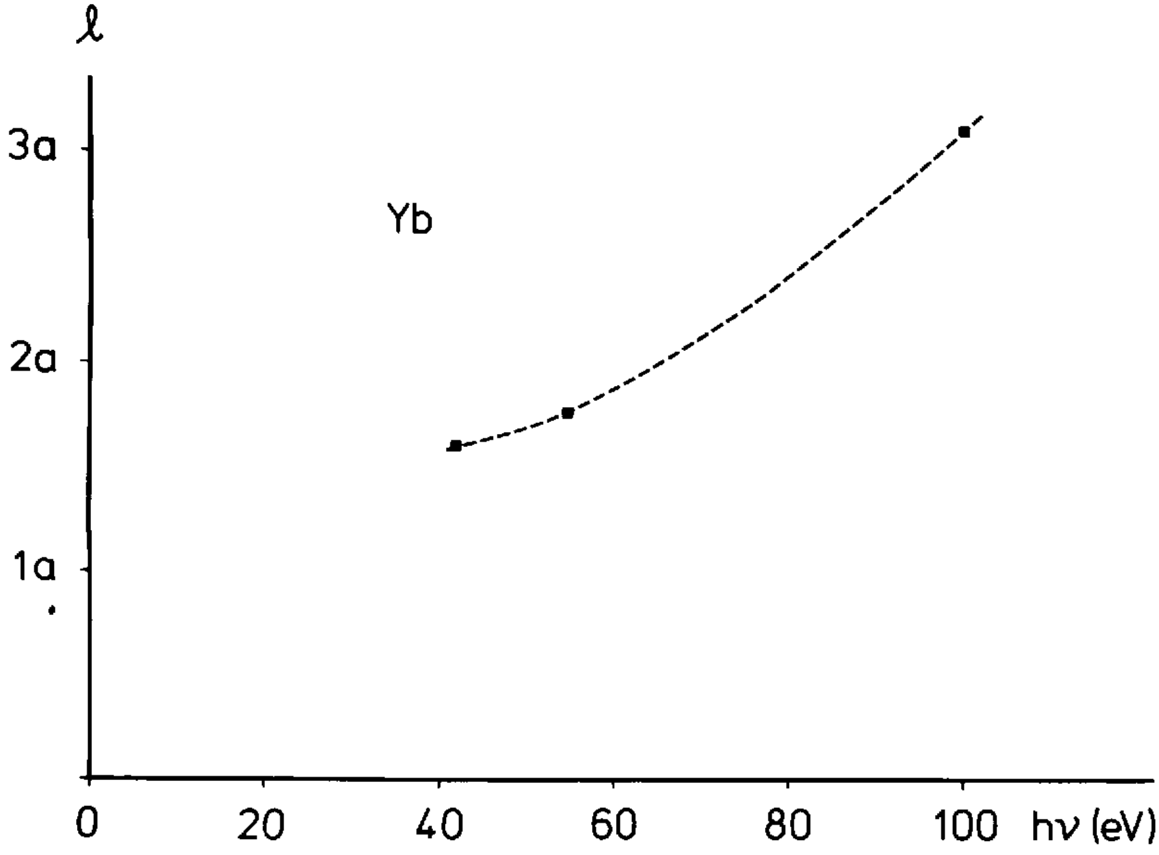

Fig. 3