DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-81/08
October 1981

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R. Kammerer, J. Barth and F. Gerken
II. Institut für Experimentalphysik der Universität Hamburg

A. Flodstrøm and L.I. Johansson
Department of Physics and Measurement Technology, Linköping University, S-58183 Linköping, Sweden

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R. Kammerer, J. Barth and F. Gerken

II. Institut für Experimentalphysik, Universität Hamburg,

D-2000 Hamburg 50, BRD

and

A. Flodström and L.I. Johansson

Department of Physics and Measurement Technology, Linköping University, S-58183 Linköping, Sweden

Abstract

Synchrotron radiation excited photoemission spectra of Eu and Gd are presented. For Eu a 4f-surface component is resolved with 0.83 eV binding energy shift. For Gd the comparison with XPS data gives strong evidence for a surface shifted 4f-component (ΔE = 0.40 eV). The mean free path of photoelectrons is determined.

to be published in Solid State Communications.

Core level binding energy shifts at the surface of clean metals ("surface shifts") have recently been observed in photoemission spectroscopy for a number of 5d-transition metals[1-3] in quantitative agreement with a relatively simple theory[4]. For rare earth metals the possibility of a change in the 4f-occupation has to be considered: a gain or a loss in binding energy could lead to an exchange of an electron between the valence states and the 4f-shell. This has been established for the surface of Sm metal[5]. For those rare earth elements which remain trivalent up to the surface layer, the theoretical estimate for the surface shift of 0.3 ... 0.4 eV towards higher binding energy has been given[6]. So far, experimental data for surface binding energy shifts on rare earth metals have only been presented for the divalent Yb metal[7,8]. While in Ref. 7 the observed shift of 0.6 eV towards higher binding energy was discussed in terms of surface atoms chemically bound to oxygen, it was later confirmed as an effect of the clean surface[8].

In this letter we present a direct observation of the 4f surface binding energy shift of Eu. The spectra are fitted using the lineshape formula given by Doniach and Sunjic[9]. Strong evidence for a surface shifted 4f-component in Gd is presented by a comparison between our surface sensitive UPS spectra with an XPS spectrum, although a surface shifted 4f-component is not directly observed in our spectra.

The data were taken at the FLIPPER monochromator in the new synchrotron radiation laboratory in Hamburg, HASYLAB. The overall instrumental resolution ranged from 0.19 eV to 0.5 eV. Samples were evaporated onto stainless steel substrates under UHV conditions.

Figure 1 shows the comparison between our UPS spectrum at 40 eV photon energy and an XPS spectrum[10]. Eu atoms are divalent in the metal. Thus we see a weak intensity in the valence band originating from the two 6s electrons.

The $4f^6$ configuration of the ionized f-shell left behind in the photoemission experiment leads to the dominant maximum at 2.1 eV binding energy.

In the LS coupling scheme we find the ^7F as the only possible term. The splitting of the different J-values (J = 0 ..... 6) is too small to be resolved in the spectra[10]. Additionally, the UPS spectrum clearly displays a shoulder at higher binding energy which is not reflected in the XPS data. Because the mean escape depth of photoelectrons has its minimum below 100 eV kinetic energy with only a few Å, the surface sensitivity of the UPS experiment is considerably enhanced over the XPS experiment. Therefore, we explain the shoulder seen in the UPS spectrum as a surface effect. An oxygen contamination of 0.1 L smears out the shoulder, but does not lead to a change in intensity (see Fig. 1). This demonstrates that the shoulder of the clean Eu spectrum is caused by the emission from intrinsic surface states which is partly replaced by the emission from chemically shifted and broadened 4f states after the oxygen exposure. A detailed discussion of the oxidation of Eu is presented elsewhere[11].

In order to extract the surface shifted 4f-level out of the measured curves we compare a series of spectra taken between 30 eV and 220 eV photon energy to theoretical curves generated with the lineshape formula of Doniach and Sunjic . As an example, the fit to the 60 eV spectrum is displayed in Fig. 2. The energy splitting of the multiplet is taken from absorption spectra of Eu^{3+} ions[12] and multiplied with a scaling factor of 0.93[13] as we measured metallic Eu, and the relative intensities of the multiplet lines are taken from Ref. 14. Thus the bulk and surface contributions to the 4f-emission are reproduced by seven Doniach-Sunjic-lineshapes each.

Finally, a background of scattered electrons is generated and added to the curves. This takes account of extrinsic energy losses by inelastic scattering as the photoelectron travels through the solid. Note that these losses occur in addition to the intrinsic losses created at the excitation of the photoelectron which give rise to the asymmetric Doniach-Sunjic lineshape. The influence of extrinsic losses to the measured spectrum becomes more and more important with decreasing kinetic energy of the initially created photoelectron, so that negligence of this effect yields anomalously high asymmetries for the fit of the UPS data compared to the asymmetry determined from XPS data. The resulting fit to the 60 eV spectrum (Fig. 2) resembles the measured curve within the accuracy of the measurement.

The complete series of spectra between 30 eV and 220 eV photon energy agrees well with the theoretical curves generated with fixed parameters for the width, asymmetry and surface binding energy shift. The convolution with a Gaussian profile took the experimental resolution into account.All parameters are summarized in Table 1. The parameters for the bulk contribution deviate from the values determined from XPS data[10] up to a factor of 2. Possibly, this is related to the different scaling factor for the energy splitting of the multiplet. In Ref. 10 a value slightly higher than 1 was used to connect the energy splitting of free Eu^{3+} ions to that of photoionized Eu atoms embedded in the metal. Such a value, however, neglects a possible screening of the nuclear charge by the conduction electrons. We used a scaling factor of 0.93 which we determined independently with high accuracy[13].

The contribution of the surface emission relative to the bulk emission could thus be determined by the peak areas of the generated curves. It is directly related to the mean free path of the photoelectrons. Such an

analysis has already been presented for Yb[7]. The formula, however, after which the data were analyzed, appears not to be appropriate for the collection geometry of the cylindrical mirror analyzer (CMA) which was the same in Ref. 7 as in the experiment presented here.

The axis of the CMA is perpendicular to the incoming photon beam and tilted by 45° against the plane of the electric vector of the radiation. The samples are illuminated under 60° (measured from the surface normal) by s-polarized light. With respect to the axis of the CMA, the collection geometry corresponds to averaging over all azimuthal angles and over polar angles between 36° and 48°. With respect to the surface normal of the sample, however, polar angles between 28° and 90° are accepted[15].

For our analysis of the bulk-surface intensity ratio we assume that the CMA accpets a representative fraction of all photoelectrons emitted from the sample. Within the 3-step model of the photoemission process we calculate the ratio of bulk electrons to surface electrons that can be detected outside the sample under the common additional assumptions[16]: the absorption coefficient μ is constant over the escape depth of photoelectrons ; the sample surface is atomically smooth and perfectly clean; photoelectrons are excited into all polar angles with equal probability. The probability for a bulk electron excited in a distance x from the sample surface to escape into the vacuum without an energy loss is then given by

$$Pr(x) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\theta_{max}} e^{-\frac{x}{\ell(E_{kin})\cos\theta}} \sin\theta \; d\theta \; d\phi$$

where θ_{max} corresponds to the maximum polar angle under which electrons penetrate through the surface without being reflected, and $\ell(E_{kin})$ is the mean free path of the photoelectrons with the kinetic energy E_{kin} given with respect to the Fermi level.

Since the probability for an electron excited in the surface layer to escape into the vacuum is 1/2, we find for the intensity ratio ($E_{kin} > \Phi$):

$$\frac{I_B}{I_S} = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\theta_{max}} \int_0^{\infty} e^{-\frac{x}{\ell(E_{kin})\cos\theta}} \sin\theta \; dx \; d\theta \; d\phi$$

$$= \frac{\sin^2\theta_{max}}{2} \ell(E_{kin}) = \frac{1}{2}\left(1 - \frac{\Phi}{E_{kin}}\right) \ell(E_{kin}) \qquad (1)$$

Φ being the work function of the sample. This expression yields $\ell(E_{kin})$ in terms of the thickness of the surface layer. For $E_{kin} >> \Phi$ (Φ_{EU}=2.5 eV)[17] the mean free path is simply given by twice the bulk-to-surface intensity ratio.

Fig. 3 displays several EDC's taken at different photon energies, the intensity ratios extracted from those measurements and the evaluated mean free path of the photoelectrons. The photon energy scale can be converted to the kinetic energy scale by subtraction of the mean 4f-binding energy in the bulk (2.1 eV). Evidently, the minimum mean free path is reached below 30 eV.

It is interesting to compare the 4f-photoemission of Gd with that of Eu, because of the equal 4f occupation. The binding energy of the 4f-electrons in Gd is about 6 eV higher than in Eu, and Gd is expected to be the most stable trivalent element of the rare earths. Thus the theoretical estimate for a surface shift of 0.3 ... 0.4 eV towards higher binding energy[6] must be applicable. Fig. 4 shows several EDC's of Gd taken at different photon energies. The 4f-emission has its maximum at 8.3 eV binding energy and a FWHM of 1.4 eV. A surface component is not resolved in the spectra. But a comparison with XPS spectra gives interesting information. The XPS spectrum of Eu shows a 4f peak at 2.0 eV binding energy with a FWHM of about 0.7 eV[10] in good agreement with the bulk contribution deconvoluted from our UPS

spectra. We find also for other rare earth metals that apart from surface effects, widths and binding energies of the 4f multiplets measured in UPS agree well with those measured in XPS[18] comprising the case of Yb for which a controversary statement is made in Ref. 7. For Gd, the XPS spectrum shows a 4f peak at 8.0 eV binding energy with a FWHM of about 1.1 eV[10]. Although the resolution of our UPS experiment was even higher, our spectrum reflects a broader peak with its maximum at higher binding energy.

Therefore we applied the same fitting procedure to our Gd spectra as described for Eu. The energy splitting of the multiplet is taken from Ref. 12 and scaled with a factor of 0.97 which was also determined independently[13] and deviates markedly from the value used in Ref. 10 (approx. 1.26). As a result we find that the measured curves agree well with the sum of a bulk and a surface multiplet with a binding energy difference of 0.48 eV (see Fig. 4). The parameters used for the theoretical curves are given in Table 1. The deconvoluted bulk contribution to the 4f emission again is in good agreement with the 4f peak of the XPS spectrum. The evaluation of the mean free path of the photoelectrons after equation (1) gives values approx. 40% lower than those obtained for Eu.

Acknowledgement

The authors are indebted to O. Beimgraben and G. Sprüssel for their help installing the computer program, and to J. Fock for helpful discussions concerning the collection geometry of the CMA.

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Figure Captions

Fig. 1 An XPS spectrum[10] of the 4f-photoemission of Eu is compared to our UPS spectrum at 40 eV photon energy (ΔE = 0.19 eV). The shoulder at higher binding energy is attributed to a surface shifted 4f-level. It smears out on oxygen contamination (dashed curve).

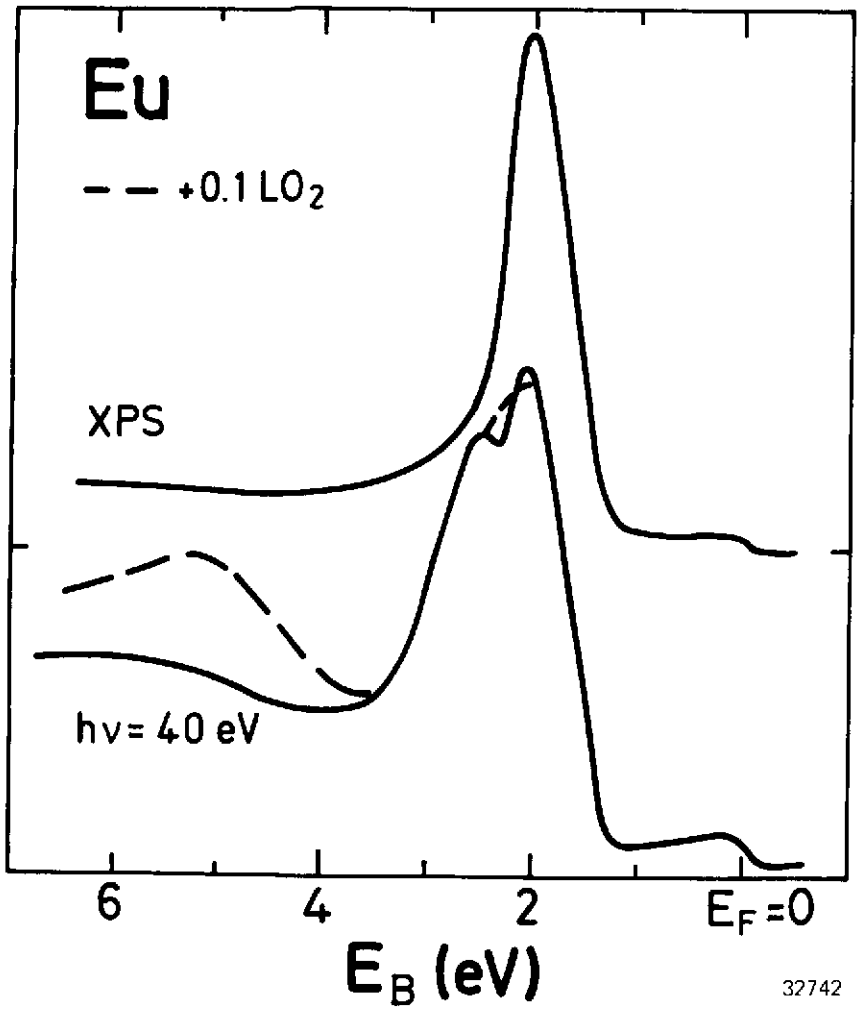
Fig. 2 Fit obtained as described in the text for the ^7F multiplet structure of Eu as measured at 60 eV photon energy (ΔE = 0.19 eV). The single J-components of the surface and bulk contribution are also shown. The measured curve coincides with the fit within the experimental error.

Fig. 3 Valence band spectra of Eu illustrating the decrease of the relative surface contribution to the 4f-photoemission when the photon energy increases from 30 eV to 220 eV (upper part). Dashed curves give the deconvoluted bulk and surface contributions, and the dashed dotted curve represents the background electrons. The lower part displays the ratio of the total bulk-to-surface 4f-emission and the mean free path of the photoelectrons evaluated after equation (1) in terms of the thickness a of the surface layer.

Fig. 4 4f-photoemission of Gd measured at different photon energies, deconvoluted bulk and surface contributions (dashed), and (generated) background of scattered electrons (dashed-dotted).

Table 1: Parameters of the Doniach-Sunjic lineshape analysis of the surface and bulk 4f-photoemission of Eu and Gd (2γ - FWHM, α -asymmetry index, ΔE_{S-B} - surface binding energy shift)

	2γ Bulk	α Bulk	2γ Surface	α Surface	ΔE S-B
Eu	(0.1±0.03)eV	0.2±0.02	(0.13±0.03)eV	0.18±0.02	(0.63±0.02)eV
Gd	(0.3±0.05)eV	0.22±0.02	(0.35±0.05)eV	0.18±0.02	(0.48±0.03)eV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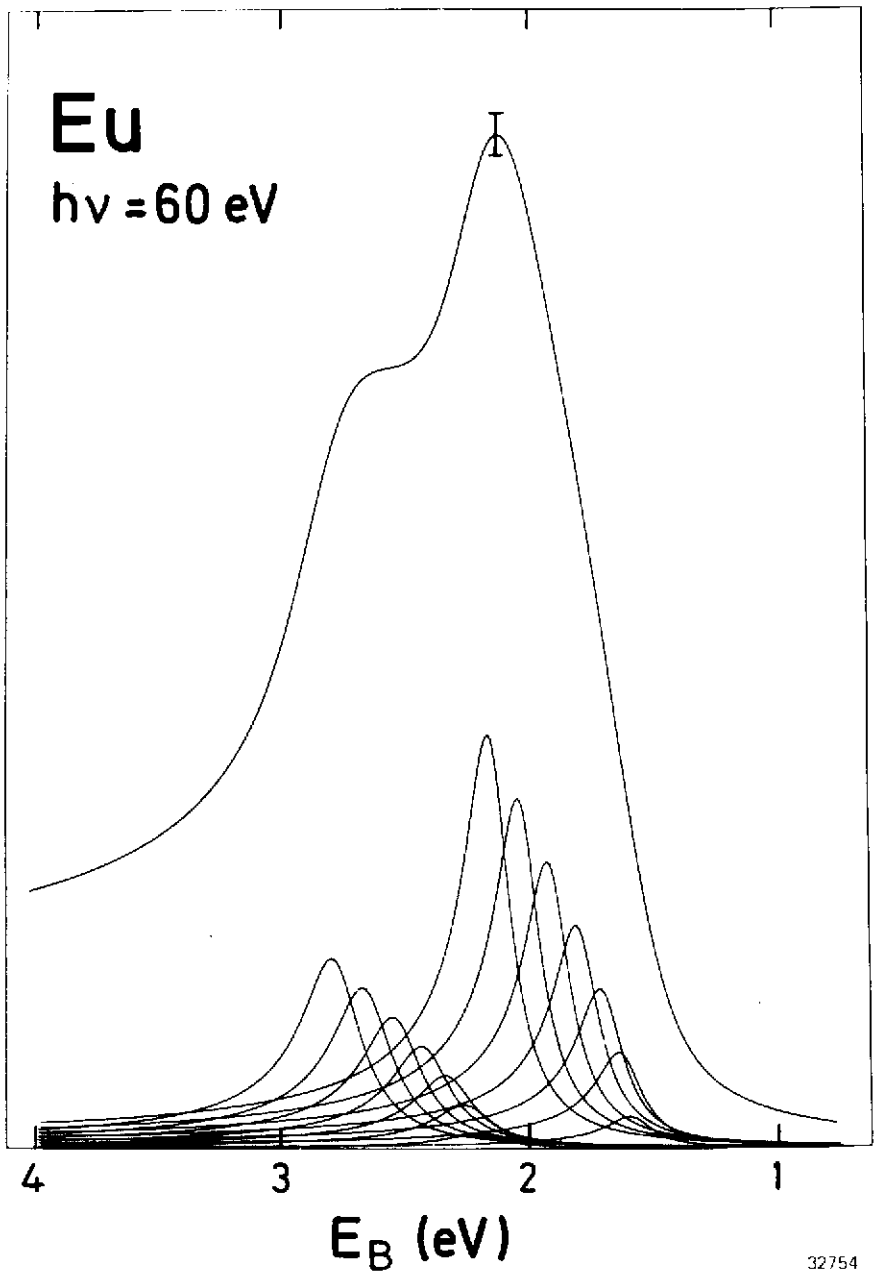
+0.1 LO2
XPS
hν = 40 eV
6
4
2
EF =0
EB (eV)
32742

Fig. 1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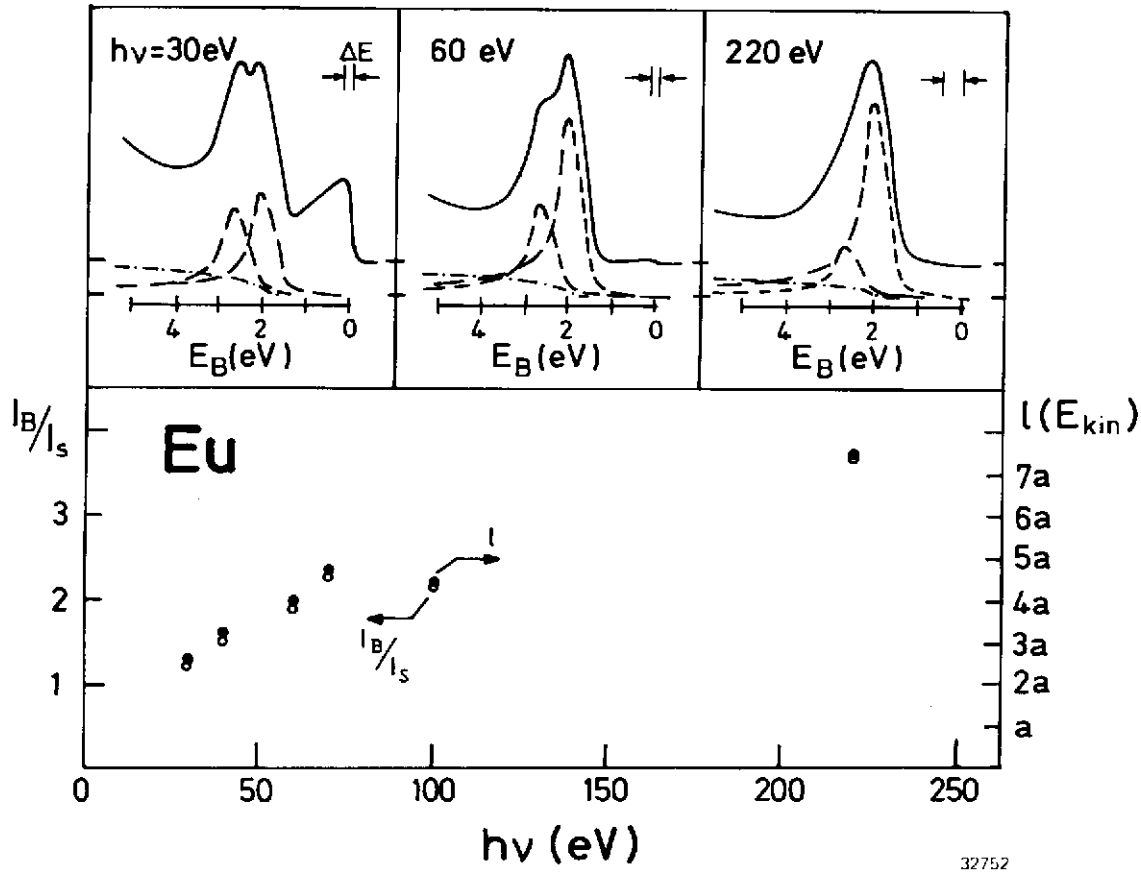
4
3
2
1
EB (eV)
32754

Fig. 2


hν=30eV
ΔE
60 eV
220 eV
4 2 0
E_B(eV)
Eu
I_B/I_s
I(E_kin)
7a
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5a
4a
3a
2a
a
I
0 50 100 150 200 250
hν (eV)
32752

Fig. 3

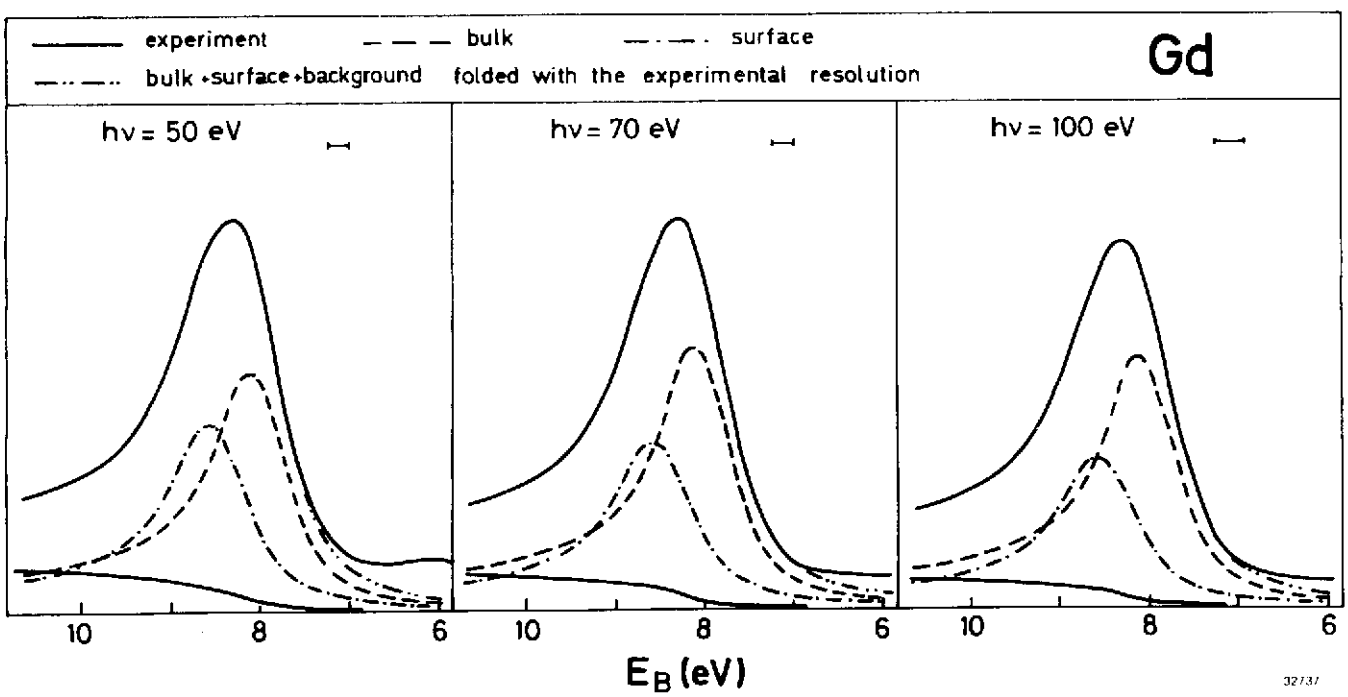
experiment
bulk
surface
bulk+surface+background folded with the experimental resolution
Gd
hν = 50 eV
hν = 70 eV
hν = 100 eV
10 8 6
E_B (eV)
32737

Fig. 4