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EXCITED MULTIPLET LINES IN RESONANT PHOTOEMISSION SPECTRA OF Gd

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Excited Multiplet Lines in Resonant Photoemission Spectra of Gd

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Abstract

Resonant photoemission spectra of Gd metal in the photon energy range of the 4d → 4f excitation show previously unobserved 4f multiplet structure. This structure is identified as excited quintet lines by showing that a calculation in the fractional parentage scheme yields an excellent agreement with the experimental curve. Our result provides new insight into the resonance interaction; it also implies an explanation of an unidentified resonance structure in SmS.

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The understanding of correlation effects in rare earths has gained considerably by resonant photoemission in the last years. The decay processes of the excited states in the region of the 4d → 4f "giant absorption resonance" influence the photoionization cross-sections of the 4f multiplets in the rare earths (see e.g. Ref. 1-4). In this paper, we report the first observation of additional 4f multiplet structure in the electron distribution curves (EDC) of Gd in the region of the 4d → 4f excitation. It is well established that ordinary 4f photoemission spectra are well described by the fractional parentage scheme[5] which for Gd only allows the septet configuration. We proove that the additional structure originates from excited quintet configurations of the $4f^6$ state reached by the Auger decay of the resonantly excited $4d^9 4f^8$ configurations. Our finding sheds new light on the mechanism of the resonance interaction.

Our measurements were performed in the HASYLAB with the FLIPPER monochromator using the synchrotron radiation of the storage ring DORIS in Hamburg. The photoelectrons were collected with a commercial double pass cylindrical mirror analyser. The geometry of the experiment is described in Ref.6 . The Gd samples were evaporated in situ on stainless steel substrates under UHV conditions.

Three EDC's of Gd measured in the region of the giant resonance, are shown in Fig. 1. Since the ground state of Gd is $(4f^7)\ ^8S_{7/2}$, for photon energies below the resonance the only final state for photoemission from the f-shell is $(4f^6)\ ^7F_J$ which leads to the dominant structure at 8.3 eV binding energy. The different J-components cannot be resolved. The intensity of this peak is correlated with the absorption structure and can be well fitted with a single Fano profile[4]. In addition, curve 2 in Fig. 1 shows new structure in the binding energy region of 10 to 20 eV. In Fig. 2 the intensity of this structure versus photon energy is given by the dotted curve. For photon energies in the maximum

of the absorption the structures are dominated by the giant resonance of the ^7F line, and the intensity could not be determined. For Eu metal, which has the same 4f configuration as Gd, we find equivalent results. This suggests that the details of the effect are dependent on the occupation of the 4f-shell.

We assign this structure to excited quintet configurations of the $4f^6$ state which are accessible by the Auger decay of the resonantly excited $4f^8$ configuration as illustrated in Fig. 3. In the ground state Gd has seven 4f electrons with parallel spins which form the configuration $^8S_{7/2}$. In a "normal photoemission process" just one electron is kicked out and we get the final state $(4f^6)\ ^7F$. For photon energies in the giant resonance a $4d \rightarrow 4f$ excitation leads to the configuration $4d^9\ 4f^8$. Following the Pauli principle the eighth electron must have opposite spin. The excited configuration can decay by direct recombination in two different channels:

1. The excited electron fills the 4d-hole and the energy is transferred to another 4f-electron or vice versa. This leads to the same final state as in "normal photoemission". This process is responsible for the intensity variation of the ^7F-peak in the giant resonance.

2. The electron with "spin down" stays in the 4f shell and two other 4f electrons take part in the Auger process. This leads to the final state ^5X where X stands for all possible angular momentum quantum numbers. To reach these final states a spin flip of one electron is required either in the excitation of a 4d electron to the 4f-shell or in the decay of the $4d^9\ 4f^8$ configuration. It is obvious from Fig. 2 that the intensity variation of the quintet lines does not follow the shape of the absorption curve but is mainly correlated with the fine structure indicated by number 2 in Fig. 2.

Following Sugar's[7] calculation for Gd a strong absorption line involving a spin flip appears at the onset of the giant resonance. Since the absorption fine structure is not too well reproduced, a refined calculation would be worthwhile.

In order to verify our assignment for the additional 4f multiplet structure we compare the spectrum with a calculation in the fractional parentage scheme[8] for the relative intensities of the quintet lines. Since the $4d \rightarrow 4f$ absorption even at a fixed photon energy may contain different excitations which do not all lead to quintet states we cannot expect to reproduce the correct septet to quintet intensity ratio with our calculation. We calculate the following processes:

1. Excitation from $(f^7)\ ^8S_{7/2}$ to $(f^8)\ ^7F_J$

2. Decay from $(f^8)\ ^7F_J$ to $(f^7)\ ^8S_{7/2}$ and ^6Y_J; and
   decay from $(f^7)\ ^8S_{7/2}$ (or ^6Y_J) to $(f^6)\ ^7F_J$ (or ^5X_J)

X and Y again stand for all possible angular momentum quantum numbers. This calculation was done for every possible J-value of the different configurations using a formula given by Cox[9]. In this approximation the influence of the 4d hole is neglected.

The energy positions of the different levels of the f^6 configurations up to 5 eV above the ground state ^7F_o were taken from optical data of Eu^{3+} and a calculation in intermediate coupling[10]. We calculated the higher lying levels in LS coupling approximation. A scaling factor is applied in order to account for the different nuclear charge of Eu^{3+} and Gd and for the screening of the valence electrons in the metal (Fig. 4). We then fold the calculated lines with asymmetric Doniach-Sunjic curves[11] to account for the fact that the atomic lines occur in a metallic sample. The experimental resolution was considered by a convolution with a Gaussian curve of 0.35 eV FWHM (lower

curve in Fig. 5). Since we have strong evidence that the binding energy of the 4f levels in Gd is lower in the bulk than at the surface[6] this curve consists of two sets of lines with an energy difference of 0.48 eV and a bulk to surface peak height ratio of 1/0.4.

Because the calculation does not give the correct ratio between the ^7F and the ^5X contribution we add a ^7F part to the curve with a 4.25 times higher amplitude. Finally, we generate a background for the bulk contribution of the theoretical curve with a computer program which simulates the travel of the photoelectrons through the sample. The upper curve in Fig. 5 shows the sum of all discussed contributions in comparison with the measured curve.

As a result we see an excellent agreement between theory and experiment particularly in the first part of the spectrum where the energy positions of these lines are available from intermediate coupling calculations. For the scaling factor we determined the value of 0.97. The equivalent results from Eu metal were analysed in the same way as described for Gd. We determined a scaling factor of 0.93. These values are much lower than published by Lang et al.[5] (1 for Eu and 1.26 for Gd). While Lang et al. could only use the ^7F-peak from XPS measurements with a FWHM of about 1.1 eV we can use the large ^7F and ^5X multiplet splitting of about 10 eV to fit the scaling factor. Our scaling factor for Eu metal shows that the influence of the 6s valence electrons in the screening of the nuclear charge is not negligible. In Gd the valence band contains a localized 5d electron which obviously leads to a very effective screening of the additional nuclear charge compared with Eu.

The excitation of new multiplet structure via resonant photoemission possibly provides also the explanation for a resonance structure reported for SmS[19] for which a satisfactory understanding is still lacking. The photoemission spectra of divalent Sm in SmS contain three maxima which are assigned to ^6H, ^6F and ^6P. For a photon energy in the region of the fine structure preceding

the giant resonance, Ref. 12 reported a very sharp resonance enhancement of the photoemission intensity at the ^6P line only. This was interpreted as a Fano resonance of the ^6P line. At the same time, the FWHM of the EDC structure at the ^6P line goes through a maximum which was argued to reflect a minimum lifetime of the excited state.

This explanation must be strongly questioned since the FWHM of an EDC structure taking part in a resonance remains essentially unchanged because it reflects the lifetime of the final hole state, not that of the intermediately excited configuration. On the contrary, these observations quite naturally fit into the framework of new multiplet structure with lower multiplicity created by the Auger decay of an intermediately excited configuration as we outlined for Gd. Indeed, the energy positions of all quartet lines of Sm^{3+} are reported to coincide with the ^6P state covering a range of 2.5 eV[13]. The intensity profile obtained in Ref. 12 is similar to our finding for Gd (see Fig. 2 dashed curve).

We have shown that in the region of the giant resonances all details in the photoemission spectra are generated by the Auger decay of $4d^9\ 4f^{N+1}$ configurations. Our calculations within the fractional parentage scheme are a first step towards a quantitative theoretical description of the photoemission resonances. The inclusion of Auger matrix elements and the other parameters entering the Fano formalism now appears to be feasible also in the rare earth quite along the lines of the successful theory of the Mn 3p absorption resonance by Davis and Feldkamp[14].

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Figure Captions

Fig. 1 Energy distribution curves of Gd taken at photon energies of 130 eV (1), 142.44 eV (2), and 149 eV (3) (compare Fig. 2).

Fig. 2 Yield spectrum of Gd in the region of the 4d → 4f excitation. The numbers refer to the EDC's of Fig. 1. The dashed curve gives the intensity of the quintet lines.

Fig. 3 Illustration of the 4f photoemission process and the decay channels of the resonantly excited $4d^9\ 4f^8$ configuration in Gd.

Fig. 4 Cut of curve 2 in Fig. 1 showing the quintet states of $4f^6$ on an enlarged scale (zero suppression !). The vertical lines indicate the result of our calculation.

Fig. 5 Theoretical lines from Fig. 4 folded with asymmetric Doniach-Sunjic line shapes (solid curve) and compared to the measured EDC (points) as described in the text. The fit parameters are given in Ref. 6.

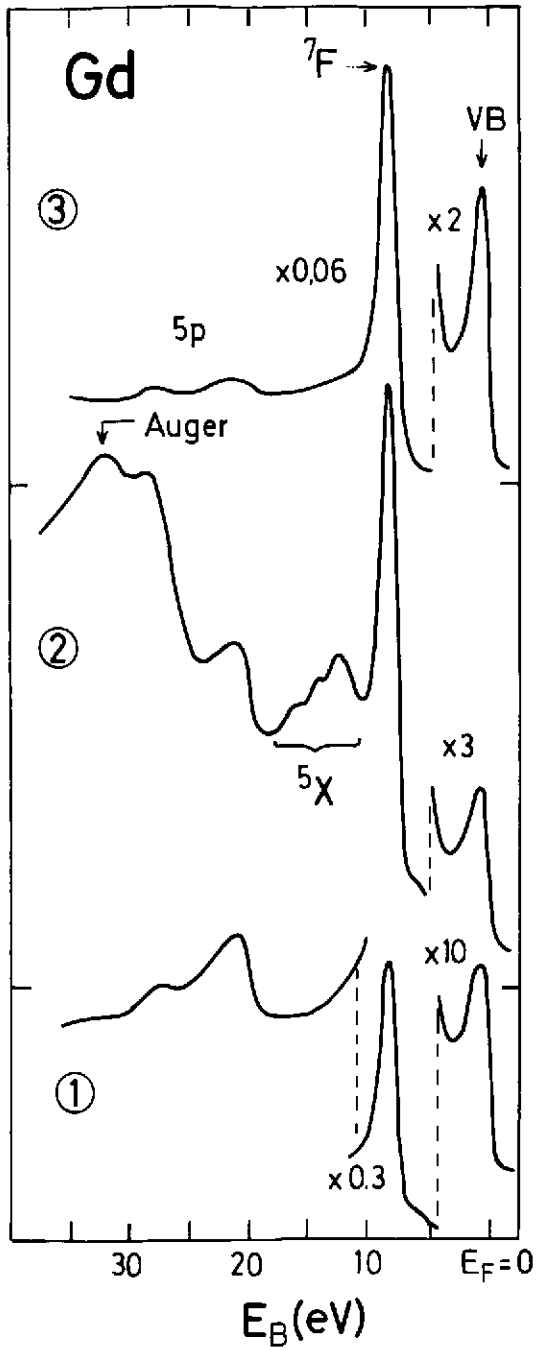

Fig. 1

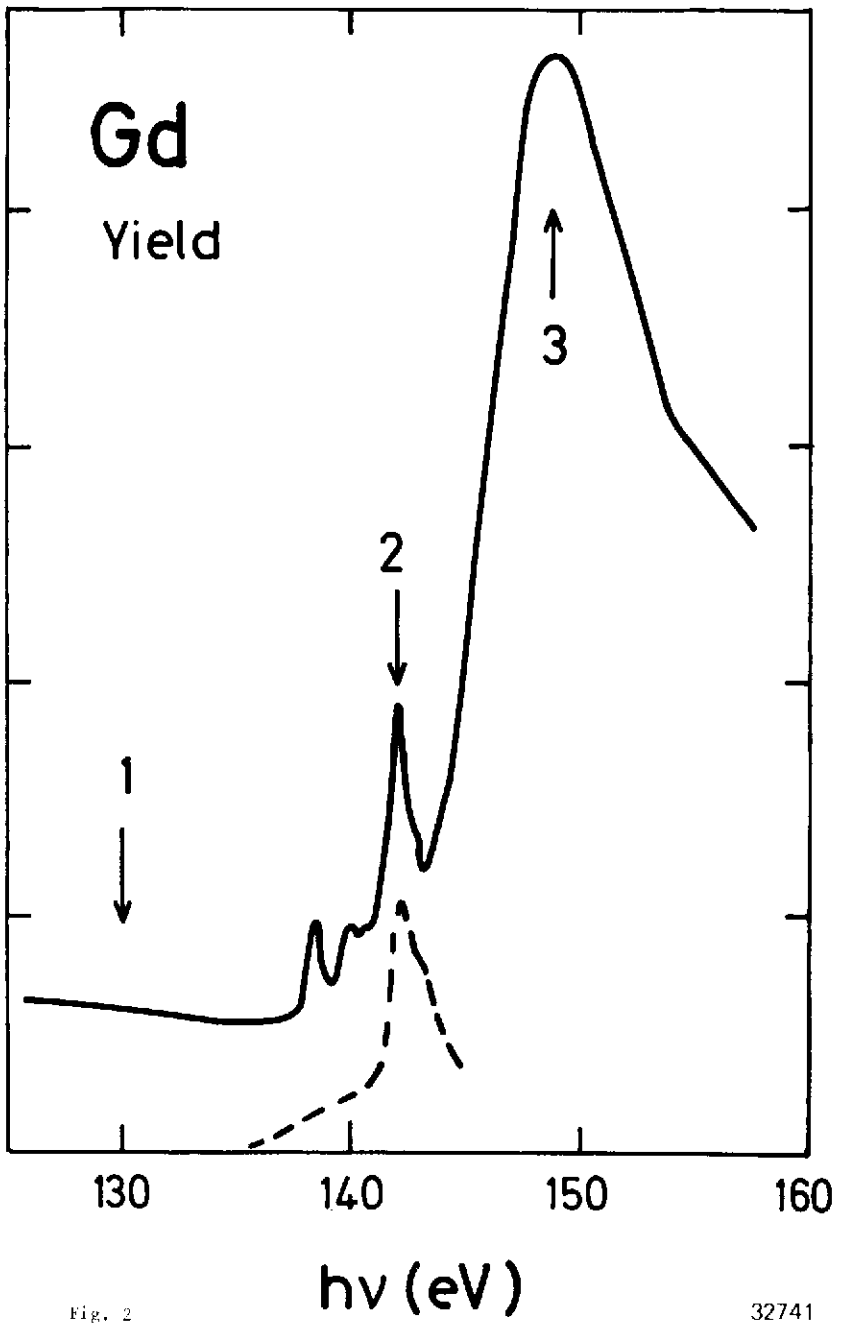

Fig. 2

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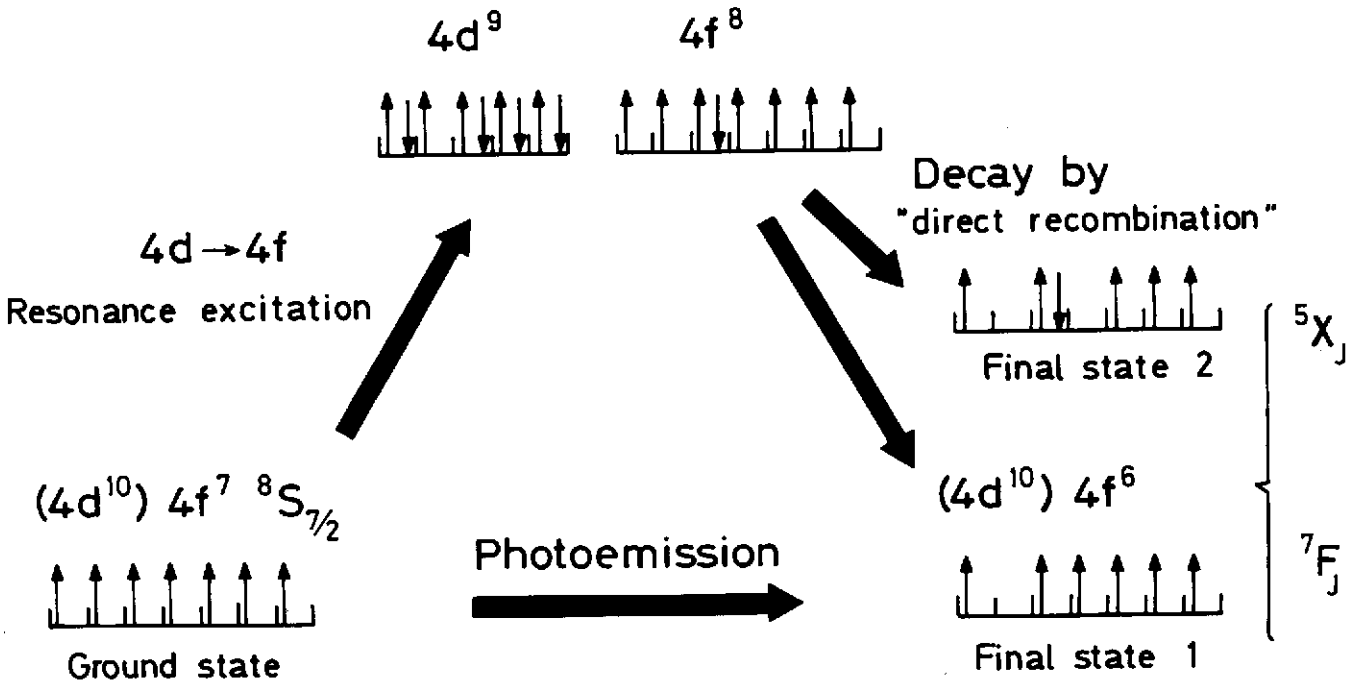
4d⁹
4f⁸
Decay by
"direct recombination"
4d→4f
Resonance excitation
Final state 2
⁵X_J
(4d¹⁰) 4f⁷ ⁸S₇/₂
Photoemission
(4d¹⁰) 4f⁶
⁷F_J
Ground state
Final state 1
32736

Fig. 3

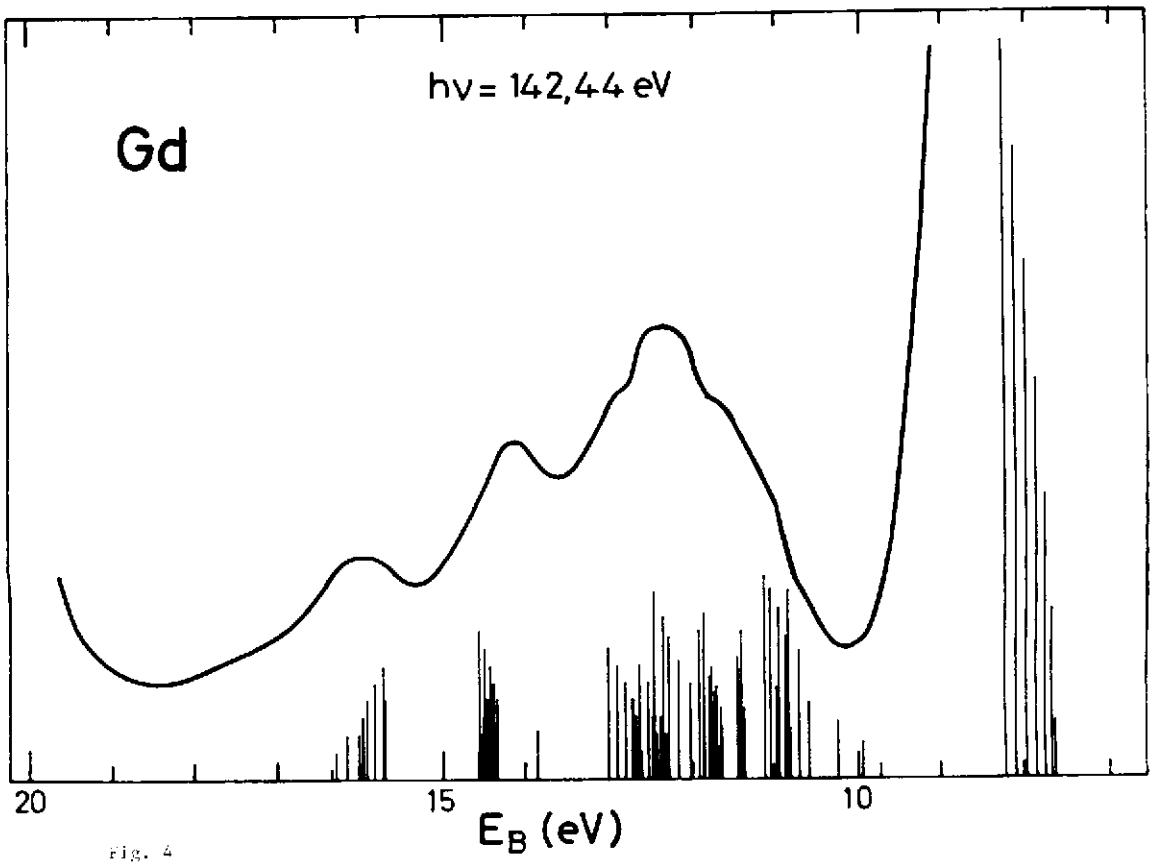
hν = 142,44 eV
Gd
20
15
10
E_B (eV)

Fig. 4

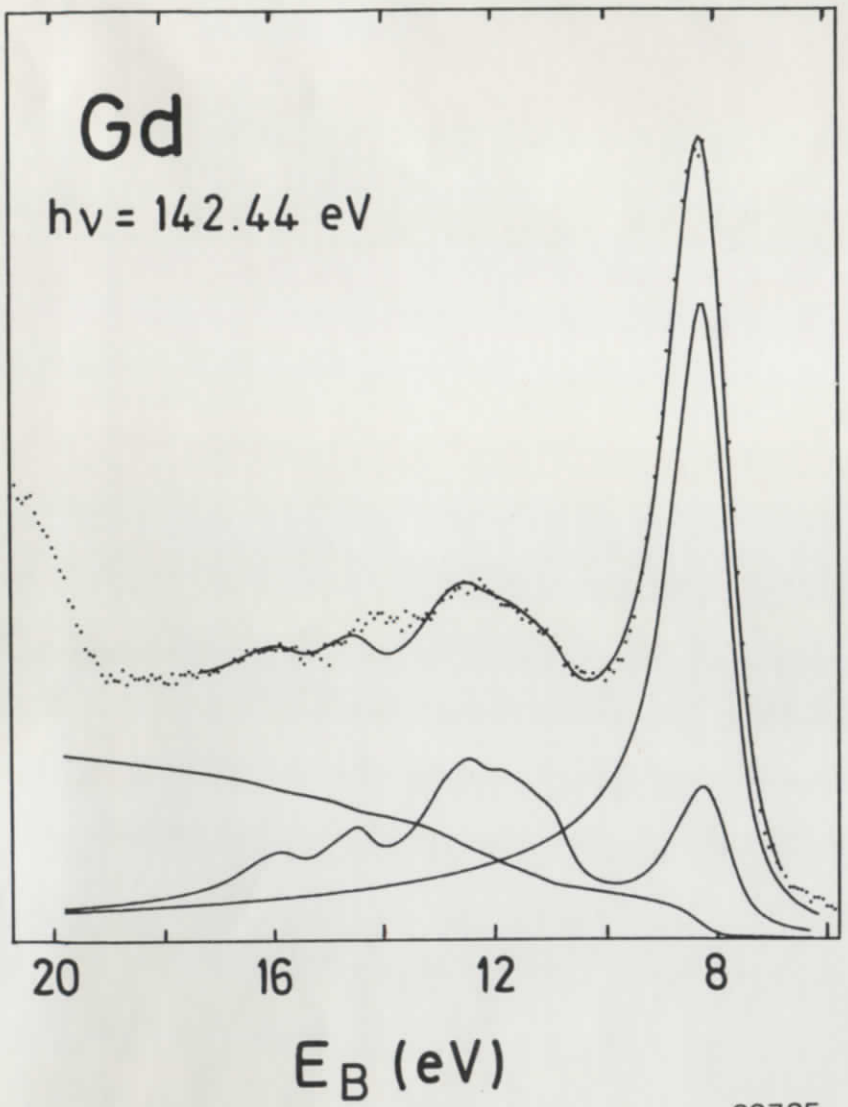

Fig. 5