DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-79/30
November 1979

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Observation of Resonance Recombination Lines in Electron Excited Auger Spectra of Gd

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Abstract

Combined measurements of electron excited $N_{4,5}$ Auger spectra and photoelectron emission on clean and oxidized Gd lead to a distinction between Auger lines originating from 4d → continuum and 4d → 4f resonance excitations. Several Auger structures are identified as due to the direct recombination of $4d^9 4f^8$ states with the 4f and valence electrons. The shape of the most prominent Auger line for oxidized Gd agrees perfectly with the Fano profile of the 4f photoemission intensity.

Recent photoemission measurements on rare earth (RE) materials with photon energies in the region of the 4d → 4f "giant absorption resonance" [1,2] have revealed new insight into the decay processes of these excited states[3-7]. It was shown that the 4f subshell cross section is dramatically enhanced when the photon energy scans the giant resonance of the 4d absorption thus indicating that the excitation of the 4d → 4f transitions interferes with the 4f continuum excitation via direct recombination. In some cases Fano type line profiles[8] could be fitted to the experimental data of the 4f cross section[3,4,7] while a more complicated behaviour was also reported[5,6].

In this letter, we report on the first combined measurements of resonance photoemission and electron excited Auger spectroscopy on a RE metal. The combination of these technique enables us to identify several pronounced structures in the Auger spectrum as being due to the same direct recombination decay that we find in photoemission spectroscopy. They are clearly distinguished from the Auger decay of the 4d continuum excitations. For the investigations we chose Gadolinium with its half filled 4f shell because the multiplett splitting of the excited $4f^6$ configuration is not very large leading to a single 4f peak in the valence band spectrum at 8.5 eV binding energy well separated from other structures[9] (see table 1). The results are of great importance for the interpretation of Auger spectra from materials where excitations to bound or quasibound states play a dominant role.

Gd films were evaporated under UHV conditions (base pressure of the system $1 \cdot 10^{-10}$ Torr, pressure during evaporation $2 \cdot 10^{-9}$ Torr). Initial ionizations were created by 3 keV primary electrons for the

Auger measurements and by synchrotron radiation of the storage ring DORIS monochromatized by the Flipper monochromator[10] for the photoemission measurements respectively. For analyzing the emitted electrons we used a commercial double pass cylindrical mirror analyzer. The total instrumental resolution was set to 0.8 eV.

Fig. 1 shows the Auger spectrum of Gd up to 150 eV kinetic energy obtained in 1^{st} and 2^{nd} derivative mode by use of modulation technique. The spectrum exhibits a variety of sharp structures between 80 eV and 150 eV where Auger electrons from the decay of a 4d excitation are to be expected. We also took an energy distribution curve (EDC) at 190 eV photon energy. While the Auger spectrum of Fig. 1 clearly shows two dominant lines at 105 eV and 135 eV, both comparable in intensity, the EDC only reflects one structure at 105 eV but no structure at 135 eV is resolved. This shows the principal difference between photon and electron induced excitation. Since the 3 keV primary electrons may lose an arbitrary amount of their energy when scattered inelastically, the 4d electrons can be excited to either bound or continuum states which is equivalent to excitation with white light in the energy region where $\mathrm{Im}\ \varepsilon^{-1} \propto \varepsilon_2$ ("optical approximation")[11]. Contrary, an EDC taken with monochromatic photons of an energy above the absorption maximum (150 eV[1]) of the 4d → 4f transitions can only contain Auger structures related to 4d → εl excitations.

From these facts it follows that the Auger peak at 105 eV originates from 4d → εl transitions. Its energy positions fit reasonably well with a $N_{4,5}\ O_{2,3}\ N_{6,7}$ transition (see table 1). For the strong Auger peak at 135 eV, however, we assume that a decay process of the $4d^9\ 4f^8$ resonance excitation ("direct recombination") is responsible. Such a process

provides the full excitation energy for the emitted electron rather than the 4d one electron binding energy.

For the investigation of the decay of $4d^9\ 4f^8$ states the use of a tunable light source is essential. The photoemission measurements of the energy range under consideration revealed a resonance enhancement of both the valence band and the 4f peak. The intensity of the valence band emission is about 30 times weaker than that of the 4f - peak in the maximum of the giant resonance and the intensity gain at resonance is of the same order of magnitude in both cases. The variation of the 4f intensity obtained over a large photon energy range is displayed in Fig. 2 together with a fit of a Fano type line profile. The excellent agreement between the fit and the data points indicates that the theoretical description based on a single discrete excitation line interacting with an underlying continuum[8] is a reasonable approach. We want to point out, however, that two absorption peaks at 139 eV and 143 eV[1] preceeding the giant resonance also lead to weak maxima in the 4f photoemission intensity.

For a comparison of the 4f resonance behaviour with the Auger structures the sum of 4f binding energy and analyzer work function has to be subtracted from the photon energy scale of Fig. 2. As the result, the bottom part of Fig. 3 shows the absorption fine structure taken from Ref. 1 for

which an interaction with the 4f excitation was also observed. The arrow indicates the maximum position of both the absorption and the Fano profile from Fig. 2. The middle curve shows the high energy part of the Auger spectrum from Fig. 1. From this comparison it is obvious that all maxima of the 4f resonance correspond to structures in the Auger spectrum. We note that for the 2nd derivative curve a peak height strongly depends on the width of the original structure and the maximum position depends on its asymmetry. The resonance of the valence band can account for the high energy Auger maximum at 142 eV kinetic energy. Nevertheless, the situation is complicated because further structures from the valence band resonance overlap with the 4f resonance and in addition a small contribution from $N_{4,5}$ VV transitions may also show up in this energy region.

In order to avoid these complications similar measurements on oxidized Gd films were carried out. Since oxidation removes the valence electrons from the Gd atoms, valence band photoemission was found to be negligible after exposure of $\lesssim$10 L oxygen while the 4f peak is chemically shifted by 1.0 eV to higher binding energy and broadened to 2.8 eV FWHM. The absorption structures, however, remained unchanged as we could prove by use of yield spectroscopy. Consequently, for the Auger spectrum of oxidized Gd (upper curve of Fig. 3) we only have to deal with transitions involving the 4f states. The low energy absorption maxima must be corrected for the chemical shift of the 4f peak (arrows in Fig. 3). Again they correspond to structures in the Auger spectrum. The Fano type resonance of the 4f photoemission intensity can now be the only origin for the dominant maximum that is also shifted by 1 eV to lower kinetic energy. As a final proof, the 2nd derivative of the

Fano type profile obtained in Fig. 2 has been evaluated (Fig. 4a) and folded with the shape of the 4f peak experimentally obtained from photoemission EDC's. This mathematical procedure accounts for the principal difference between the two applied techniques: the photoemission process labels the 4f intensity versus photon energy while the Auger process does versus kinetic energy. As the result, Fig. 4b shows an excellent agreement between the line profile evaluated from the photoemission measurements and the shape of the Auger structure. The agreement has been optimized by shifting the energy scale of the photoemission curve to lower energy by $\sim$ 0.5 eV. This shift is in the order of the accuracy of the measurements.

We have demonstrated that not only a number of peaks in the Auger spectrum must be attributed to the direct recombination of $4d^9\ 4f^8$ states but also the shape of the most prominent structure for oxidized samples perfectly agrees with the line shape of the 4f resonance excitation obtained in photoemission measurements. For the investigations Gd was chosen as an ideal material for several reasons. The strong 4d - 4f intershell interaction gives a considerable fraction of the 4d oscillator strength to the 4d $\rightarrow$ 4f excitations. The resonance enhancement of the 4f photoemission intensity could be well fitted by a Fano profile which allowed a rather simple comparison with the line shape of the related Auger structure. The particular results presented in this letter lead us to the general conclusion that beyond this example Auger spectra of many other materials will contain related structures especially if excitations to bound or quasibound states occur.

Acknowledgment

We wish to thank E.E. Koch for a critical reading of the manuscript.

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Table 1: Binding energies of Gd and work function of the analyzer in eV.

VB maximum	4f	$5p_{3/2}$	$5p_{1/2}$	5s (Ref.9)	4d (Ref.12)	analyzer work function
0,75	8,5	21,4	27,7	43	~143	5

Figure captions

Fig. 1 $N_{4,5}$ Auger spectrum of Gd in 1st and negative 2nd derivative (E_p = 3 keV).

Fig. 2 Fano profile with parameters given.
The crosses indicate the heights of the 4f photoemission peak for different photon energies taken from EDC's after subtraction of linear background.

Fig. 3 Auger spectra of clean and oxidized Gd compared with the absorption structures. The photon energy scale is shifted by the sum of 4f binding energy and analyzer work function relative to the kinetic energy scale. The maximum position of the giant resonance is indicated by the large arrow. For oxidized Gd the expected positions of the corresponding structures are shifted by the 4f chemical shift of 1 eV (small arrows).

Fig. 4 a) Fano profile I (E) from Fig. 2 and its negative 2nd derivative.

b) The negative 2nd derivative of the Fano profile I (E) folded with the line shape F (E) of the 4f peak of oxidized Gd taken from a photoemission EDC is compared with the related structure of the Auger spectrum.

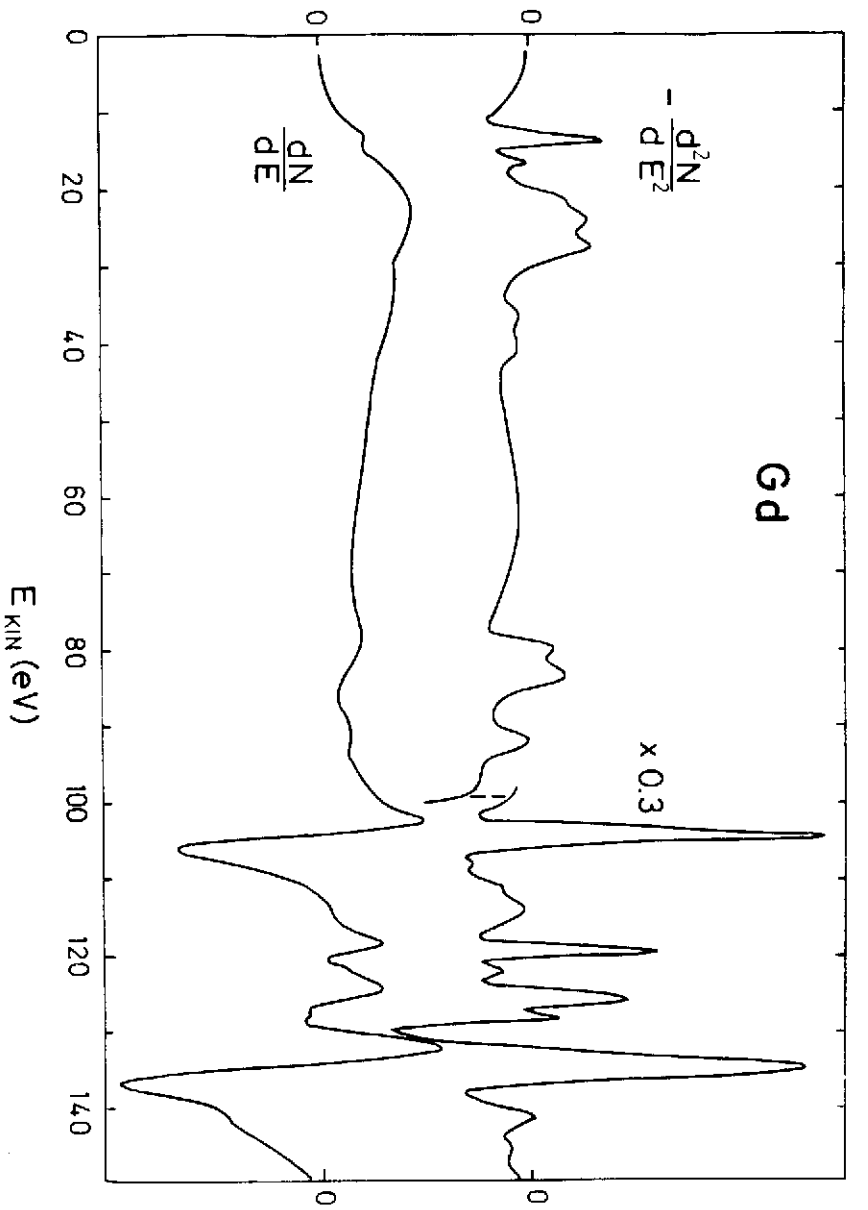

Fig. 1

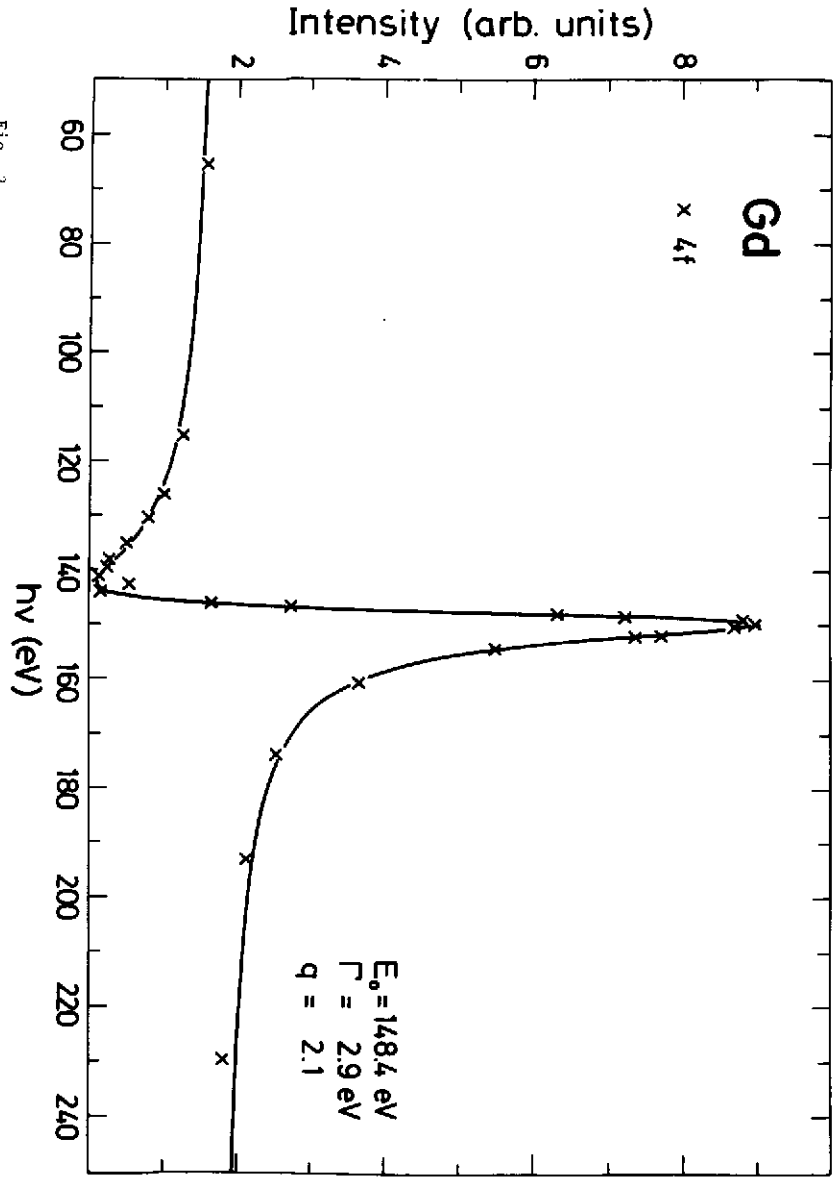
Intensity (arb. units)
2
4
6
8
Gd
× 4f
hν (eV)
60
80
100
120
140
160
180
200
220
240
E₀=148.4 eV
Γ = 2.9 eV
q = 2.1

Fig. 2

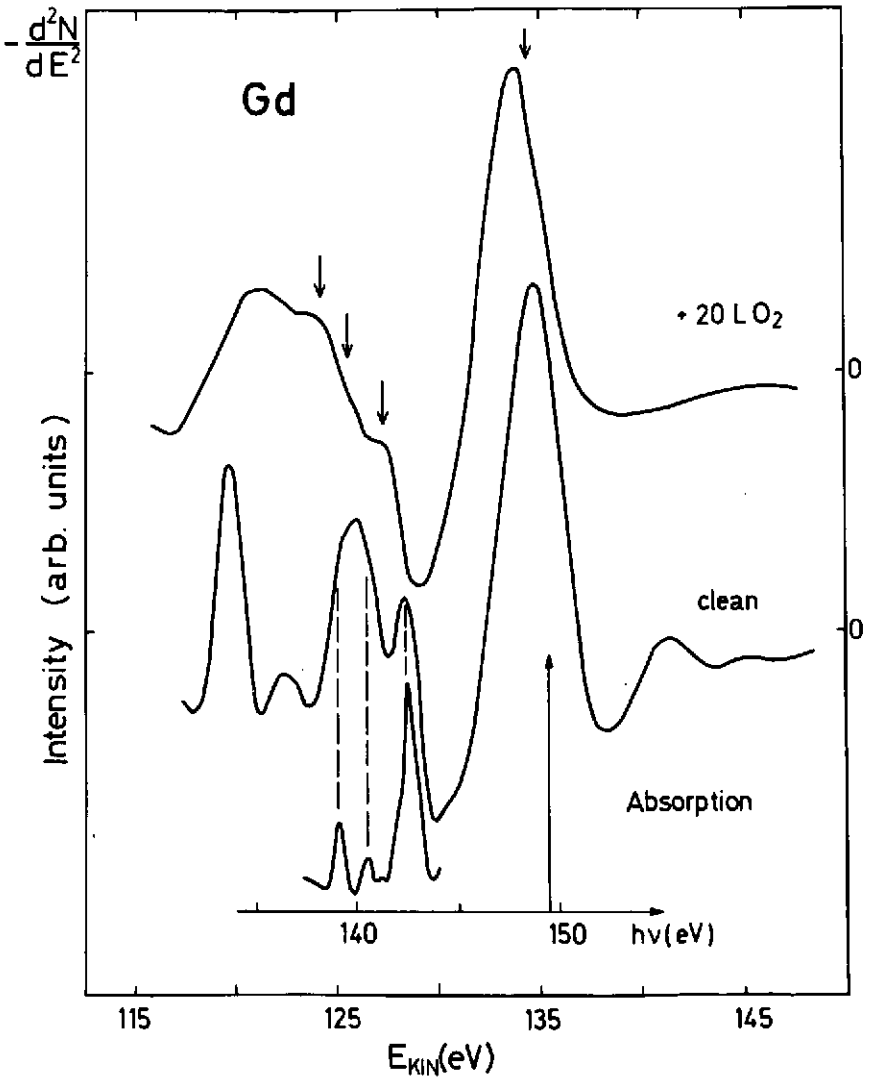
-d²N/dE²
Gd
+ 20 L O₂
clean
Absorption
Intensity (arb. units)
140
150
hν(eV)
115
125
135
145
E_KIN(eV)

Fig. 3

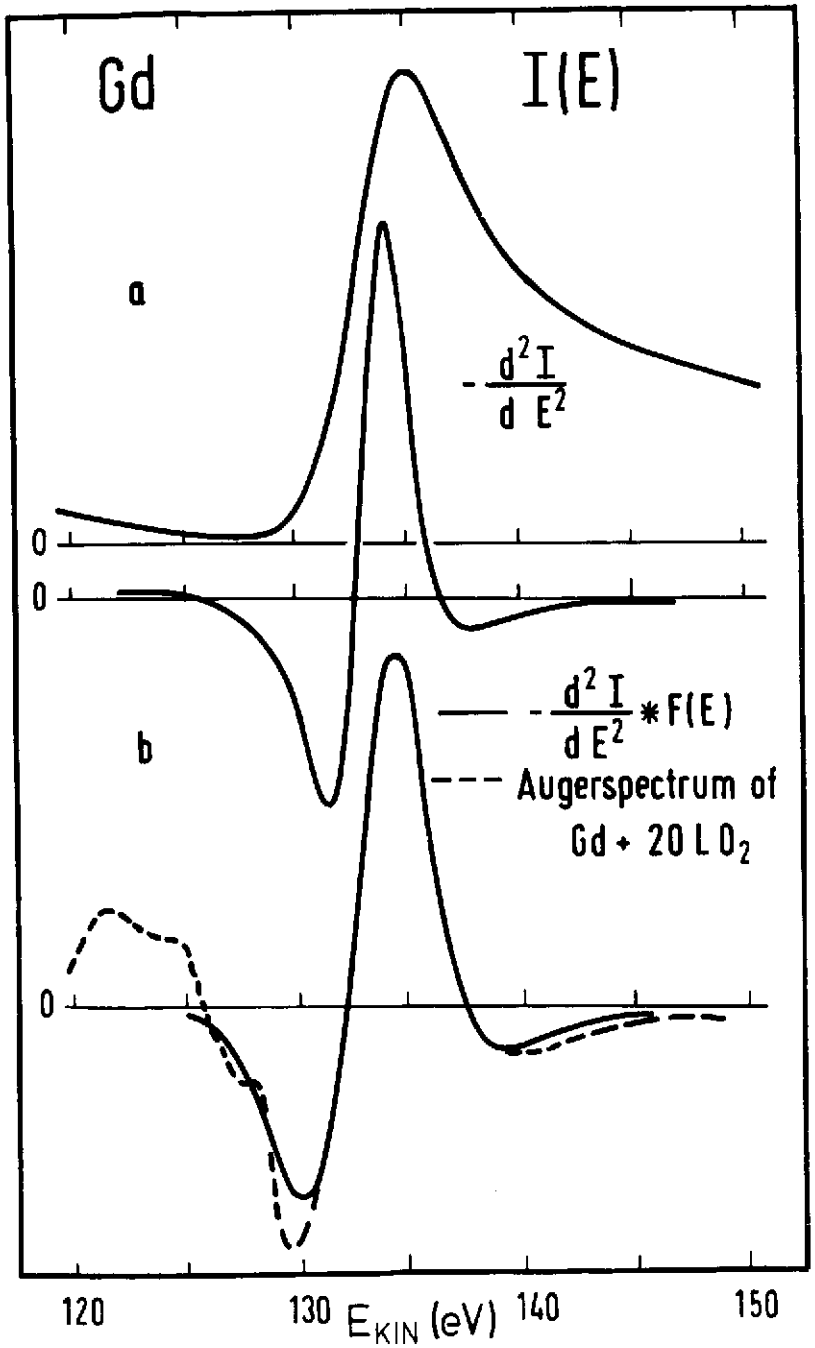
Gd
I(E)
a
$-\frac{d^2I}{dE^2}$
0
0
b
$-\frac{d^2I}{dE^2} * F(E)$
Augerspectrum of
Gd + 20 L O_2
0
120
130
E_{KIN} (eV)
140
150

Fig. 4