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Resonance Auger and autoionization processes in solid gadolinium and europium following 4d → 4f resonant excitations with synchrotron radiation

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Abstract. Decay processes in solid gadolinium and europium after 4d → 4f resonance excitations have been studied by means of Auger and photoelectron spectroscopy. Several photon energies covering the whole resonance region were used. Excitations corresponding to the narrow absorption peaks at the low-energy side of the main resonance were found to decay mostly via autoionization involving 5p or 5s orbitals. However, the $N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger processes were also found to play a significant role. After excitations corresponding to the main 4d — 4f giant resonance the autoionization leading to a $4f^{-1}$ one-hole state proved to be the strongest decay channel although the $N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}N_{6,7}N_{6,7}$ normal Auger transitions were also observed.

1. Introduction

In rare-earth elements the strong interaction between discrete core-excited 4d → 4f states and the 4d ionization continua leads to a large enhancement of photoabsorption cross-section close to the 4d ionization threshold. In this energy region the absorption spectra contain some narrow peaks and a broad strong maximum which can extend several eV above the 4d ionization limit [1–8]. Because of the complicated nature of this giant resonance the Auger and photoelectron spectra of rare-earths undergo large changes when the excitation energy varies through this resonance region [9–10].

The 4d → 4f resonance excitation in rare-earths can decay through three principal channels:

(i) the excited electron tunnels through the potential barrier leading to an excited ionic state $4d^{-1}$ [11] which predominantly decays via a normal Auger process;

(ii) the excited electron takes part in the decay process via autoionization (direct recombination) leading to electron emission from one of the 5s, 5p, 4f core levels, or valence band;

(iii) the excited electron remains as a spectator during the recombination process which is then called a spectator resonance Auger process or, in short, a resonance Auger process.

The autoionization processes appear in the photoelectron spectrum as the enhanced intensity of the corresponding photopeaks. In resonance Auger decay the

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spectator electron affects the outgoing Auger electron and this leads to an energy shift relative to the normal Auger energies [12, 13].

Excitation to the partly filled subshell causes some difficulties in separating autoionization processes from the corresponding resonance Auger processes. The strongest Auger processes in rare-earths are $N_{4,5}O_{2,3}O_{2,3}$, $N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}N_{6,7}N_{6,7}$. In the $N_{4,5}O_{2,3}O_{2,3}$ resonance Auger process there are two holes in the 5p orbital and one extra electron in the 4f orbital in the final state, so it can be clearly distinguished from the different autoionization processes. The separation is not so straightforward with the $N_{4,5}O_{2,3}N_{6,7}$ and the $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger decays. In the NON resonance Auger process one of the 4f electrons takes part in the decay leading to a $5p^{-1}$ one-hole final state so the process is phenomenologically similar to the 5p autoionization process. In the NNN resonance Auger decay two 4f electrons take part in the recombination leading to a $4f^{-1}$ final state, the process thus being phenomenologically similar to the 4f autoionization. The question is whether the 4f electron that takes part in the decay process is the excited electron (autoionization) or not (resonance Auger).

The two processes mentioned above can, however, be distinguished in some cases. According to the Hund rule electrons fill the 4f subshell so that they all have parallel spins until the subshell is half filled. After that the states involving opposite spin start to get filled. Thus if the excited 4f electron has an opposite spin as compared with the electron(s) taking part in the decay process, the 4f subshell is left in an excited state. This will lead to a lower kinetic energy for the emitted electron compared with the autoionization (or direct photoionization) process and can be resolved in the electron spectrum. Gerken *et al* [14] have discussed this phenomenon in the case of gadolinium $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger process. We would like to generalize this picture to distinguish a resonance Auger decay involving a 4f electron from the corresponding autoionization decay. In the resonance Auger process the 4f subshell is left in an excited state, whereas in the corresponding autoionization decay the

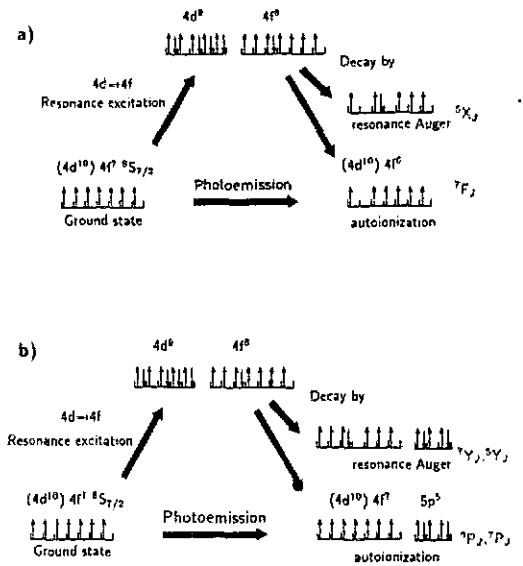

Figure 1. Illustration of the differences between (*a*) NNN resonance Auger and 4f-autoionization (reference [14]); (*b*) NON resonance Auger and 5p-autoionization.

4f subshell is left in the ground state as in the direct photoemission process. This difference is illustrated in figure 1.

The purpose of this study is to determine the decay channels of the 4d→ 4f giant resonance excitations in solid gadolinium and europium. Especially, we want to look at the importance of the resonance Auger process which has been found to be a significant decay channel, e.g. in rare gases [15–18] and some molecules [12, 13, 19, 20]. Gadolinium and europium are interesting elements because they have a half-filled 4f subshell and therefore the excited electron will have an opposite spin compared to the other 4f electrons. This work is an extension to our earlier study for solid lanthanum [21].

2. Experiment

The measurements were carried out at the MAX synchrotron radiation laboratory in Lund, Sweden, using the 4.7 m toroidal grating monochromator with a 1200 l mm^{-1} laminar grating. The bandwidth of the monochromatized light was less than 0.5 eV. The spectra were recorded with a commercial double-pass cylindrical mirror analyser applying a constant 20 eV pass energy, giving a spectrometer resolution of about 0.3 eV.

The sample foils were evaporated on a tantalum substrate *in situ* from a tungsten wire. The background pressure during the measurements was 4–8 × 10^{-10} mbar and the purity of the sample was controlled regularly by recording the valence band photoelectron spectrum. No noticeable contamination was detected.

In order to study the decay channels of the giant resonance excitations we measured the electron spectra of solid Eu and Gd using photon energies below, at, and above the giant resonance of each element. The important background estimation and subtraction procedure is discussed elsewhere [18]. The energy calibration was based on the binding energies taken from the study of Riviere *et al* [22]. To determine the 4d → 4f resonant energies we also recorded the electron yield spectra with the constant-final-state method, i.e. by scanning the photon energy through the range of the giant resonance and by measuring the intensity of (in this case) 10 eV secondary electrons. The electron yield spectrum has been shown to be analogous to the photoabsorption spectrum [23] so it also reveals the sharp absorption fine structure below the main resonance.

3. Results and discussion

In order to visualize the changes in the intensities of different decay channels the pure photoelectron spectrum measured with photon energy well below any resonance energies was compared to the resonance spectra. Intensities were normalized relative to the line which has the lowest relative intensity compared to the non-resonant spectrum. This means that the 'difference' spectra do not display the absolute increase in intensity, only the relative portion of different decay channels. Immediately below the giant resonance, when the comparison is done relative to the 4f photoline, one has to bear in mind that the cross-section of this line is not exactly constant there but undergoes an intensity minimum because of the asymmetric Fano-type behaviour.

3.1. Gadolinium

As mentioned, the $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger process in solid state gadolinium has earlier been discussed by Gerken *et al* [14]. Spin-polarized Auger electron spectroscopy has also been used successfully by Taborelli *et al* [24] to study the final states of different recombination processes. Recently, Richter *et al* [25] have discussed the decay channels in atomic gadolinium.

The electron yield spectrum from metallic Gd is displayed in figure 2. The main giant resonance maximum is seen around 149 eV photon energy and smaller maxima at 138.5 eV, 140 eV and 142 eV photon energies. All the smaller maxima are below the first 4d-ionization energy 142.7 eV [22].

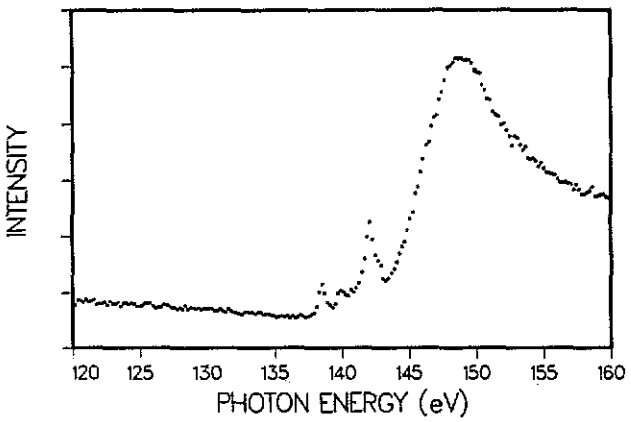

Figure 2. The electron yield spectrum of Gd.

The background-subtracted electron spectra of Gd measured with photon energies 137 eV, 138.5 eV, 140 eV, 142 eV, 143.5 eV, 145 eV, 149 eV and 155 eV are shown in figure 3. The spectra are normalized to the spectrum measured with 130 eV, which is—as the electron yield spectrum shows—clearly below any resonance excitations. In the pure photoelectron spectrum we can see a 5s photoemission structure around 45 eV binding energy, a 5p photoemission structure around 30–20 eV binding energies, a 4f photoline around 8 eV binding energy, and valence photoemission structure on the right-hand side of the 4f line. The interaction with the partly filled 4f subshell splits the $5s^{-1}$ and $5p^{-1}$ emission lines into several components. Direct photoemission from the half-filled 4f orbital leads to final states ^7F_J ($J = 1, \ldots, 6$) that cannot be resolved and are thus seen as one intense peak.

From figure 3 we can see that with low excitation energies the intensities of 5s and 5p photolines as well as valence emission increase relative to the 4f photoline, implying autoionization effects even though the enhancement is probably partly due to a decrease in the cross-section of the 4f photoline. The development of the relative changes in intensities have the same direction in all of these cases: at first the intensity begins to increase, being strongest at 143.5 eV photon energy, and then it decreases so that at the photon energy of 149 eV—which corresponds to the main giant resonance—it is the 4f photoline that has increased relative to the others. The only exception is the spectrum measured with 142 eV photons where the relative intensities of 5s, 5p and valence emission are suddenly lower than in the previous spectra.

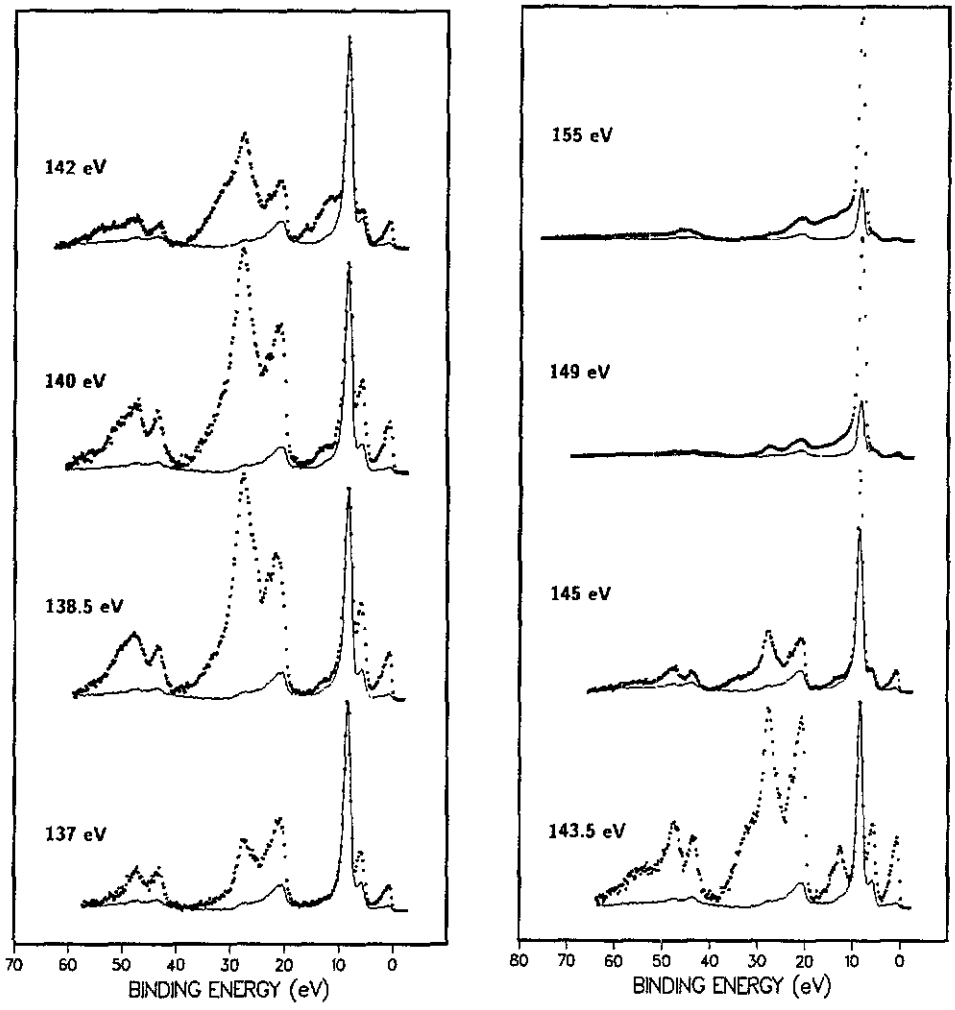

Figure 3. The electron spectra of Gd measured with 137 eV, 138.5 eV, 140 eV, 142 eV, 143.5 eV, 145 eV, 149 eV and 155 eV photons. The full curve corresponds to the reference spectrum measured with 130 eV photons.

Let us next look at the different resonance Auger processes in Gd. The normal Auger spectrum taken with 180 eV photon energy is presented in figure 4. Three different Auger structures can be resolved in the spectrum: $N_{4,5}O_{2,3}O_{2,3}$ structure around 89 eV, $N_{4,5}O_{2,3}N_{6,7}$ structure around 110 eV, and $N_{4,5}N_{6,7}N_{6,7}$ super Coster–Kronig structure around 125 eV kinetic energies [22, 26]. The doublet structure around 132–137 eV originates from direct 5s photoemission.

Already in the spectrum measured with 140 eV photons (figure 3) an intensity increment can be seen on the left-hand side of the 4f photoline. The increment relative to the intensity increment of the other structures is strongest with 142 eV photons, but it is still clearly seen in the spectrum taken with 143.5 eV photons. This structure is caused by $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger processes, i.e. when the 4f subshell is left in an excited state including five electrons with parallel spins and one electron with an opposite spin. We obtain an energy shift of 5.5 ± 1.0 eV relative to

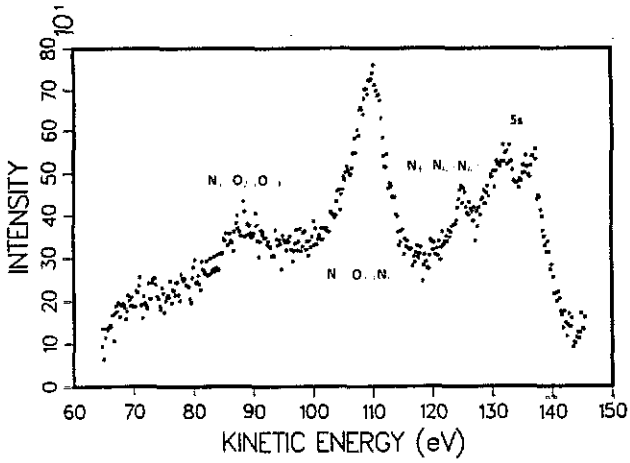

Figure 4. The normal Auger spectrum of Gd measured with 180 eV photons.

the normal NNN Auger energies. To reach an NNN resonance Auger final state a spin-flip has to take place either during the excitation or during the decay process. The intensity of NNN resonance Auger transitions obviously does not follow the shape of the main giant resonance absorption but is more correlated to the excitation energies near the third smaller maximum (at 142 eV) in the electron yield spectrum. This is in good agreement with the results of Gerken *et al* [14].

In order to study the $N_{4,5}O_{2,3}N_{6,7}$ resonance Auger phenomenon we have subtracted the reference spectrum (130 eV) from the resonance spectra normalized relative to the $5p_{3/2}$ photoline. The 'difference' spectra at 140 eV, 142 eV, 143.5 eV and 145 eV photon energies are shown in figure 5. Throughout the series the dominating structure in the spectrum is a strong peak around 28 eV binding energy. It is mainly caused by autoionization decay through the $5p_{1/2}$ orbital. It is noticeable that in the 5p autoionization process the decay through $5p_{1/2}$ is much stronger than through $5p_{3/2}$. However, there is a broad shoulder on the left-hand side of the autoionization peak in the spectrum measured with 142 eV photons. A similar shoulder is also seen in the following spectra although it gets lower and broader. This shoulder is caused by NON resonance Auger decay processes. Our estimate for the kinetic energy shift is 2.0 ± 0.5 eV which is much smaller than in the case of the NNN resonance process. The reason for this may be found in the decay mechanism. Likewise in the 5p autoionization process the NON resonance Auger process decays predominantly through the $5p_{1/2}$ spin–orbit component. This means that in the resonance structure the $N_{4,5}O_2N_{6,7}$ component dominates which gives rise to an apparent energy shift towards lower kinetic energies and therefore closer to the normal Auger energies. In the excitation with 143.5 eV and 145 eV photons 4d ionization becomes possible and some of the excited electrons can escape through the potential barrier causing the giant resonance. This leads to a normal Auger decay and is responsible for the broadening of the resonance structure.

The only resonance Auger process that does not involve the 4f subshell, $N_{4,5}O_{2,3}O_{2,3}$, can also be distinguished in the resonance spectra (figure 3). It is seen as a shoulder on the left-hand side of the 5s photopeaks. The structure is, however, so weak and broad that any energy shift relative to the corresponding normal Auger is very difficult to determine.

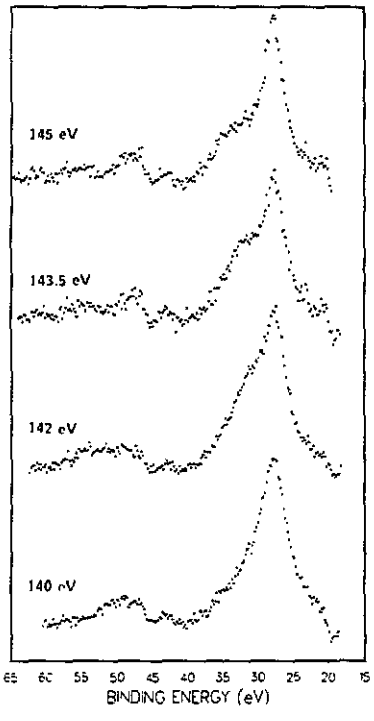

Figure 5. The 'difference' spectra of Gd measured with 140 eV, 142 eV, 143.5 eV and 145 eV photons when the reference spectrum is normalized relative to the $5p_{3/2}$ photoline.

3.2. Europium

A comprehensive electron-spectroscopic study of europium using electron impact excitation has been recently presented by Hocking and Matthew [27]. Atomic Eu has been discussed earlier both experimentally [10, 25, 28] and theoretically [29–32].

The electron yield spectrum from solid Eu is shown in figure 6. It looks very similar to the electron yield spectrum of Gd, having the main maximum around 140 eV and the smaller maxima at 131.5 eV, 132.9 eV and 134.7 eV photon energies.

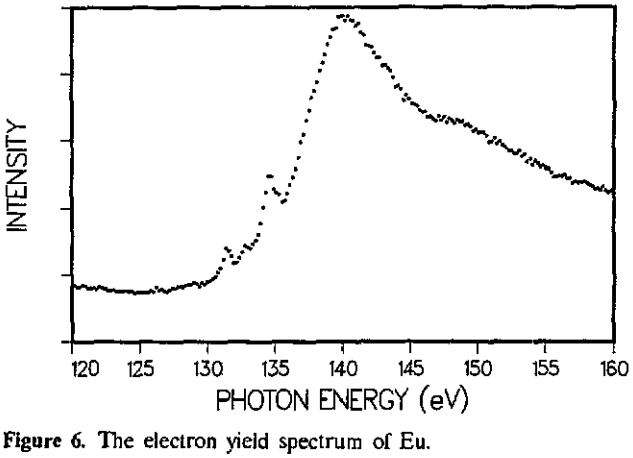

Figure 6. The electron yield spectrum of Eu.

Unlike gadolinium, all the smaller maxima are now above the first 4d ionization energy 129.2 eV [22].

The background-subtracted electron spectra of Eu measured with photon energies 128 eV, 131.5 eV, 133 eV, 134.7 eV, 137 eV and 140 eV are shown in figure 7. The spectra are normalized to the photoelectron spectrum measured with 120 eV photons (displayed as a full curve). 5s, 5p, and 4f photoemission structures can be seen at 45–37 eV, 25–19 eV and 2 eV binding energies, respectively. The 4f peak is accompanied by a satellite structure on the left-hand side and by valence emission structure on the right-hand side. Direct photoemission from the 4f orbital leads, like in gadolinium, to final states ^7F_J $(J = 1, \ldots, 6)$ which cannot be resolved. The sharp peak at 49 eV binding energy which is seen in some spectra does not originate from europium, but probably from MgO impurity attached to the sample during preparation.

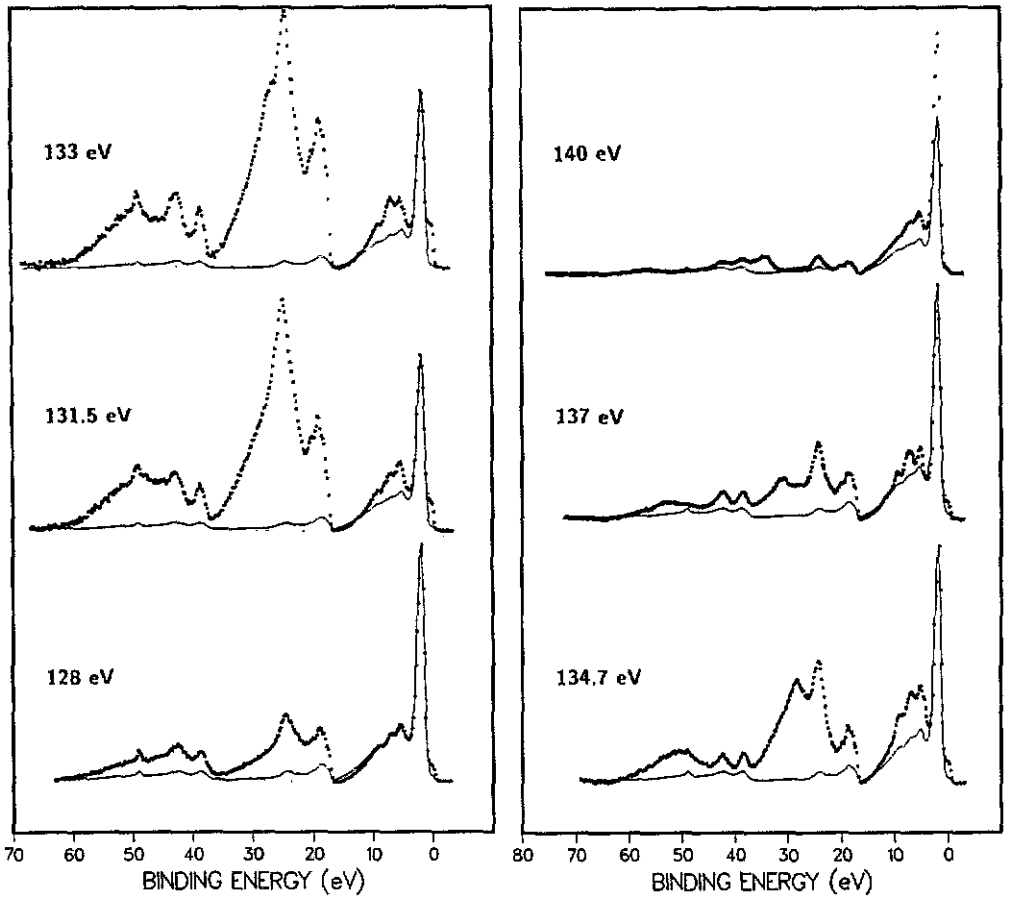

Figure 7. The electron spectra of Eu measured with 128 eV, 131.5 eV, 133 eV, 134.7 eV, 137 eV and 140 eV photons. The full curve corresponds to the reference spectrum measured with 120 eV photons.

From figure 7 we can see again that with low excitation energies 5s, 5p and valence autoionization processes are stronger than autoionization through the 4f orbital. The difference is biggest in the 133 eV spectrum. With higher excitation energies 4f

autoionization becomes stronger, being the strongest autoionization channel at 140 eV photon energy which corresponds to the main giant resonance excitation.

The normal Auger spectrum of Eu measured with 160 eV photons is presented in figure 8. The three different Auger structures can be identified as $N_{4,5}O_{2,3}O_{2,3}$ processes around 83 eV, $N_{4,5}O_{2,3}N_{6,7}$ processes around 105.3 eV, and $N_{4,5}N_{6,7}N_{6,7}$ processes around 125 eV kinetic energies. The sharp peak at 121 eV is the 5s photoline (~ 39 eV binding energy).

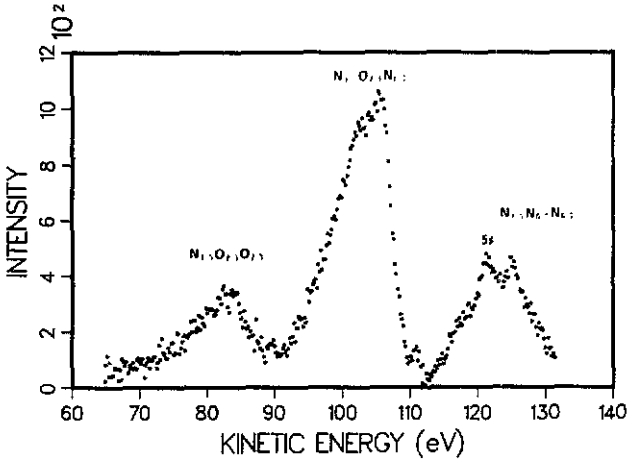

Figure 8. The normal Auger spectrum of Eu measured with 160 eV photons.

In figure 7, in the spectra from 131.5 eV to 137 eV, we can see clear intensity increment on the left-hand side of the 4f photoline. Even though the excitation energy is above the 4d ionization threshold, the enhancement can be determined as the $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger processes (instead of the corresponding normal Auger processes) because of an energy shift of about 1 eV relative to the normal NNN super Coster–Kronig energies. The excited electron thus remains in a quasi-bound state during the recombination process affecting the outgoing Auger electron. The enhancement is at its strongest at the excitation energy corresponding to the third smaller maximum (134.7 eV) in the electron yield spectrum (figure 6). The energy shift is not so large as in gadolinium which indicates that the excited state has more continuum-like character in Eu than in Gd.

Some 'difference spectra' of Eu when normalization is achieved relative to the $5p_{3/2}$ photopeak are diplayed in figure 9. As in gadolinium the $5p_{1/2}$ photopeak (~ 24.5 eV binding energy) is strong, showing the strength of $5p_{1/2}$ component in the 5p autoionization process. With 133 eV photon energy a peak can be distinguished at 26.8 eV binding energy corresponding to 106.2 eV kinetic energy. The peak originates from $N_{4,5}O_{2,3}N_{6,7}$ resonance Auger processes, the energy shift again being about 1 eV. The resonance Auger process is the most intensive decay channel at 134.7 eV excitation energy and is also clearly seen with 137 eV photons. The resonance Auger structure is much sharper in Eu than in Gd.

The $N_{4,5}O_{2,3}O_{2,3}$ Auger process is also very clearly seen in the resonance spectra (figure 7) on the left-hand side of the 5s photopeaks. It seems that this stucture has also a slight energy shift relative to the normal NOO Auger process (figure 8), but

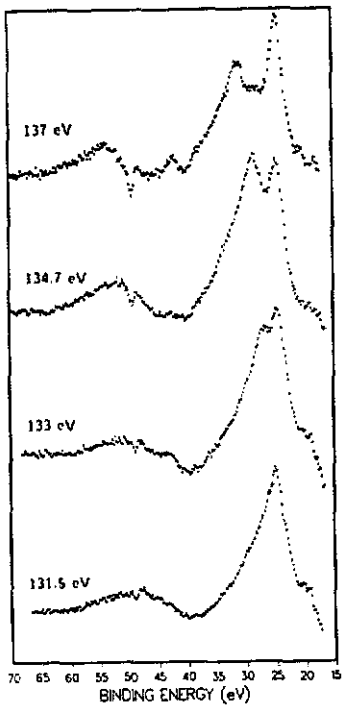

Figure 9. The 'difference' spectra of Eu measured with 131.5 eV, 133 eV, 134.7 eV and 137 eV photons when the reference spectrum is normalized relative to the $5p_{3/2}$ photoline.

the broadness of the structure makes any estimations inaccurate. The NOO Auger transitions are much more intense in Eu than in Gd. Because the excitation energy is above the 4d ionization threshold, the excited electron can escape from the influence of the Eu atom and the state decays more easily through a process in which the 4f orbital takes no part.

4. Conclusions

In this work we have studied the decay channels of solid gadolinium and europium after excitation with different photon energies corresponding to the 4d $\rightarrow$ 4f giant resonance area. On the low-energy side of the resonance region, autoionization channels $4d^94f^85s^25p^6 \rightarrow 4d^{10}4f^75s5p^6$ and $4d^94f^85s^25p^6 \rightarrow 4d^{10}4f^75s^25p^5$ are strong but the $N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}N_{6,7}N_{6,7}$ resonance Auger processes also give a significant contribution to the spectra. The energy shift relative to normal Auger energies in gadolinium was estimated to be 5.5 eV for NNN processes and 2 eV for NON processes. In europium the energy shift was smaller, only about 1 eV for both.

With excitation energies closer to the main giant resonance the decay channels mentioned above lose their strength and the 4f autoionization process $4d^94f^85s^25p^6 \rightarrow 4d^{10}4f^65s^25p^6$ becomes more significant, being the strongest decay channel at the top of the main giant resonance. The strength of different autoionization and resonance Auger channels implies that the 4d $\rightarrow$ 4f resonance is discrete in character even though the excitation energy is above the 4d ionization threshold.

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References

[1] Zimkina T M, Formichev V A, Gribovskii S A and Zhukova I I 1967 *Sov. Phys.–Solid State* **9** 1128
[2] Formichev V A, Zimkina T M, Gribovskii S A and Zhukova I I 1967 *Sov. Phys.–Solid State* **9** 1163
[3] Haensel R, Rabe P and Sonntag B 1970 *Solid State Commun.* **8** 1845
[4] Connerade J P 1987 *Giant Resonances in Atoms, Molecules, and Solids* ed J P Connerade, J M Esteva and R C Karnatak (New York: Plenum) p 3
[5] Dehmer J L, Starace A F, Fano U, Sugar J and Cooper J P 1971 *Phys. Rev. Lett.* **26** 1521
[6] Starace A F 1972 *Phys. Rev.* B **5** 1773
[7] Mansfield M W D and Connerade J P 1976 *Proc. R. Soc.* A **352** 125
[8] Wendin G and Starace A F 1978 *J. Phys. B: At. Mol. Phys.* **11** 4119
[9] Becker U 1987 *Giant Resonances in Atoms, Molecules, and Solids* ed J P Connerade, J M Esteva and R C Karnatak (New York: Plenum) p 473
[10] Gerken F, Barth J and Kunz C 1982 *Proc. Int. Conf. on X-ray and Inner-Shell Physics* ed B Crasemann (AIP Conf. Proc. No 94) pp 602
[11] Egelhoff W F, Tibbetts G G, Hecht M H and Lindau I 1981 *Phys. Rev. Lett.* **46** 1071
[12] Aksela S, Sairanen O-P, Aksela H, Bancroft G M and Tan K H 1988 *Phys. Rev.* A **37** 2934
[13] Bancroft G M, Tan K H, Sairanen O-P, Aksela S and Aksela H 1990 *Phys. Rev.* A **41** 3717
[14] Gerken F, Barth J and Kunz C 1981 *Phys. Rev. Lett.* **47** 993
[15] Aksela H, Aksela S, Bancroft G M, Tan K H and Pulkkinen H 1986 *Phys. Rev.* A **33** 3867
[16] Aksela H, Aksela S, Pulkkinen H, Bancroft G M and Tan K H 1986 *Phys. Rev.* A **33** 3876
[17] Aksela H, Aksela S, Pulkkinen H, Bancroft G M and Tan K H 1988 *Phys. Rev.* A **37** 1798
[18] Aksela H, Aksela S, Tulkki J, Åberg T, Bancroft G M and Tan K H 1989 *Phys. Rev.* A **39** 3401
[19] Aksela H, Aksela S, Ala-Korpela M, Sairanen O-P, Hotokka M, Bancroft G M, Tan K H and Tulkki J 1990 *Phys. Rev.* A **41** 6000
[20] Aksela S, Tan K H, Aksela H and Bancroft G M 1986 *Phys. Rev.* A **33** 258
[21] Sairanen O-P, Aksela S and Kivimäki A 1991 *J. Phys.: Condens. Matter* **3** 8707
[22] Riviere J C, Netzer F P, Rosina G, Strasser G and Matthew J A D 1985 *J. Electron Spectrosc. Relat. Phenom.* **36** 331
[23] Gudat W and Kunz C 1972 *Phys. Rev. Lett.* **29** 169
[24] Taborelli M, Allenspach R and Landolt M 1986 *Phys. Rev.* B **34** 6112
[25] Richter M, Meyer M, Pahler M, Prescher Th, von Raven E, Sonntag B and Wetzel H E 1989 *Phys. Rev.* A **40** 7007
[26] Richter M, Prescher Th, Meyer M, von Raven E, Sonntag B and Aksela S 1988 *Phys. Rev.* B **38** 1763
[27] Hocking W H and Matthew J A D 1990 *J. Phys.: Condens. Matter* **2** 3643
[28] Becker U, Kerkhoff H G, Lindle D W, Kobrin P H, Ferrett T A, Heimann P A, Truesdale C M and Shirley D A 1986 *Phys. Rev.* A **34** 2858
[29] Amusia M Ya, Sheftel S I and Chernysheva 1981 *Zh. Tech. Fiz.* **51** 2441 (Engl. Transl. 1981 *Sov. Phys.–Tech. Phys.* **26** 1441)
[30] Amusia M Ya, Ivanov V K and Kupchenko V A 1989 *Z. Phys.* D **14** 219
[31] Pan C, Carter S L and Kelly H P 1987 *J. Phys. B: At. Mol. Phys.* **20** L335
[32] Pan C, Carter S L and Kelly H P 1991 *Phys. Rev.* A **43** 1290