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$N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}O_{2,3}O_{2,3}$ resonance Auger processes in solid samarium

O-P Sairanen and S Aksela
Department of Physics, University of Oulu, SF-90570 Oulu, Finland

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Abstract. Resonance Auger processes (AP) in solid samarium after 4d→4f excitations have been studied using electron spectroscopy with synchrotron radiation. The $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}N_{6,7}$ resonance AP were found to play a significant role in excitations corresponding to the low-energy side of the resonance region. Kinetic energy shifts relative to the normal $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}N_{6,7}$ AP were estimated to be 1.0 eV and 1.5 eV, respectively. In excitations corresponding to the main giant resonance the normal AP were found to be stronger than in the case of heavier rare earths indicating stronger continuum-like character for the main resonance in samarium.

1. Introduction

The availability of tunable synchrotron radiation has made it possible to excite inner shell electrons selectively into unoccupied bound states below the ionization threshold. This has led to a growing interest in studying decay processes of these excited states during last decade. In general, a resonant photoexcitation can decay in two principal ways: either the excited electron takes part directly in the recombination process leading to an emission of an outer shell electron, or it remains as a spectator leading to a two-hole final state with one electron excited [1–3]. In the former case, which is called a participator Auger or autoionization process, the final state is the same as in direct photoionization of the outer shell involved and it is seen in the photoelectron spectrum as increased intensity of the corresponding photopeak. In the latter case, known as a resonance AP, the spectator electron will affect the outgoing Auger electron which is seen in the electron spectrum as an Auger electron having slightly different kinetic energy. In the resonance Auger process the spectator electron can also shake up/down or even shake off during the recombination process. In gas phase studies (rare gases [4–10] and some molecules [2, 3, 11–14]) it has been found that the resonance AP (with different shake phenomena associated) plays a more important role than the autoionization process. Recently [15, 16] it has been noticed that the resonance Auger process can be a significant decay channel after resonant excitation in solids as well.

In this paper we shall study the resonance AP in solid samarium after 4d → 4f giant resonance excitations. As is well known, the absorption spectra of rare earth elements near the 4d ionization threshold are characterized by some narrow peaks and a strong broad maximum, which may extend several eV above the ionization threshold [17–19]. The large enhancement of photoabsorption cross section has been interpreted as due to the strong interaction between discrete core excited 4d → 4f states and the 4d

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ionization continua [20–24]. An excellent review of this giant resonance phenomenon has been edited by Connerade *et al* [25].

Decay channels and photoionization cross sections near the 4d ionization threshold have been extensively studied for both atomic [26–31] and solid [32–45] rare earths. However, especially for solid rare earths, the role of possible resonance Auger effects has not gained much attention, until now. This paper is an extension to our recent studies for solid La, Eu, Gd, Tb and Dy [46–48].

2. Experimental details

The experimental work was done at MAX synchrotron radiation laboratory in Lund, Sweden. The measurements were carried out on BL22 which uses a modified SX-700-type monochromator [49] and a high-resolution hemispherical analyser. The experimental set-up is described in more detail in [50]. Due to a high counting rate only a 20 μm exit slit in the monochromator and (in most cases) 75 eV constant pass energy in the analyser were used, leading to an overall energy resolution less than 0.3 eV.

The sample films were evaporated *in situ* from a tungsten wire. A copper plate was used as a substrate. The pressure in the preparation chamber was $1–3 \times 10^{-8}$ mbar during evaporation, but decreased immediately after evaporation below 10^{-9} mbar. During the measurements the background pressure was less than 10^{-10} mbar. The purity of the sample was controlled regularly by recording a photoelectron spectrum over the O 1s and C 1s range with 750 eV photons. No visible change in the control spectra was observed.

In order to determine the $4d \rightarrow 4f$ resonant energies we first recorded the total electron yield spectrum of Sm near the 4d ionization threshold. The photoelectron and Auger electron spectra were then recorded using excitation energies below, at and above the giant resonance.

3. Results and discussion

The electron yield spectrum of solid Sm is shown in figure 1. It is consistent with earlier measurements and similar to the bulk photoabsorption spectrum [33,38]. In the spectrum some fine structure is visible between 126 eV and 133 eV photon energies, along with the main broad maximum around 140 eV, preceded by two shoulders at 135.5 eV and 137 eV, and followed by another broad maximum around 149 eV photon energy. The first ionization energy is reported to be 128.3 eV [51]structure lies on both sides of the threshold, whereas both broader maxima are well above the threshold.

Figure 2 displays the electron spectra of samarium measured with 120 eV, 126.5 eV, 129 eV, 132.2 eV, 135.5 eV, 137 eV, 140 eV, 145 eV and 148.8 eV photon energies. A 'continuous' background, discussed in more detail in [46], has been subtracted from the original spectra. Energy calibration is based on the binding energies taken from the study of Riviere *et al* [51].

The pure photoelectron spectrum, taken with 120 eV photons and therefore below any resonance energies, shows three different line groups: valence and 4f photoemission lines from 0 eV to 10 eV binding energies, the 5p photoemission line group between 16 eV and 26 eV binding energies, and 5s photoemission structure from 36 eV to 45 eV binding energies. Samarium has two different valence configurations in the solid state, namely $4f^5(5d6s)^3$ for bulk atoms and $4f^6(5d6s)^2$ for surface atoms [52]. Thus the 4f

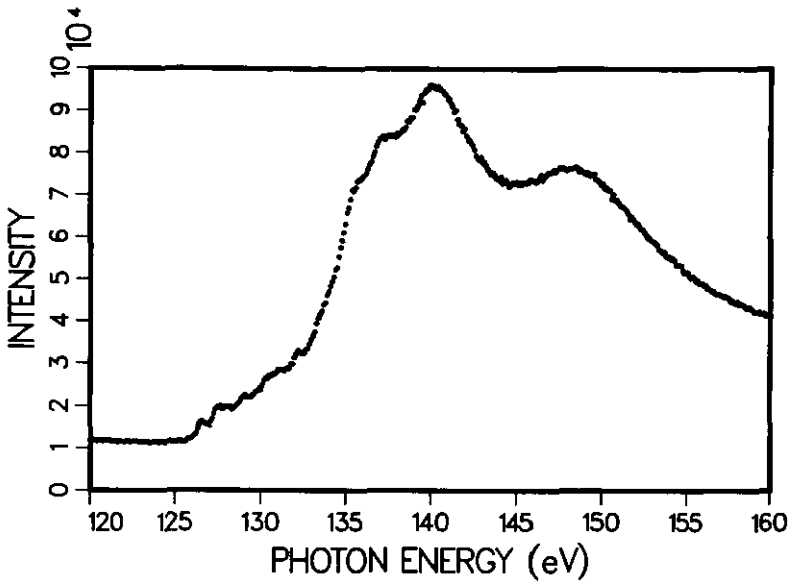

Figure 1. The electron yield spectrum of solid samarium.

emission structure can be divided into two groups: the $4f^5 \rightarrow 4f^4$ (bulk) photoemission lines from 4.5 eV to 10 eV corresponding mainly to final states ^5I, ^5F, ^5G and ^5D, and the $4f^6 \rightarrow 4f^5$ (surface) emission lines on the low binding energy side corresponding to final states ^6H, ^6F and ^6P [53]. The $5p^{-1}$ and $5s^{-1}$ photoemission lines are split into several components due to interaction with the partly filled 4f subshell. The strong sharp peak at 49 eV binding energy does not originate from samarium but most probably from MgO impurity attached to the sample during preparation. However, this small impurity does not disturb the effects studied here; on the contrary, it gives us a good intensity reference.

The resonance spectra in figure 2 undergo large changes with increasing excitation energy. To illustrate these changes we have subtracted the pure photoelectron spectrum (120 eV) from the resonance spectra. We used the impurity peak as an intensity reference because it should not resonate in this energy region. The difference spectra are presented in figure 3. We can see that at first the 5p and 5s photoemission structures grow, whereas the 4f emission structure undergoes an intensity minimum (intensity in the first resonance spectra is lower than in the reference spectrum). When the excitation energy increases the 4f emission structure begins to dominate. This reveals strong autoionization processes at first through 5p and 5s orbitals and later also through a 4f orbital. The minimum in the 4f emission intensity can be explained by the overlap of 4d and 4f wavefunctions which leads to an asymmetric Fano-type behaviour in the 4f cross section. The results are consistent with the cross section studies for atomic samarium [26, 29] and are therefore expected in solid samarium, too. The intensity variation between the different 4f components also agrees well with earlier studies [38]. However, the shape of the structure near 5p and 5s photolines also changes showing some structure to remain nearly constant in kinetic energy therefore indicating some Auger or resonance Auger effects. This structure is especially strong at photon energies below or near the 4d ionization limit. In order to study those effects more closely we normalized the reference spectrum (120 eV) relative to the $5p_{3/2}$ photoline and subtracted it from the resonance

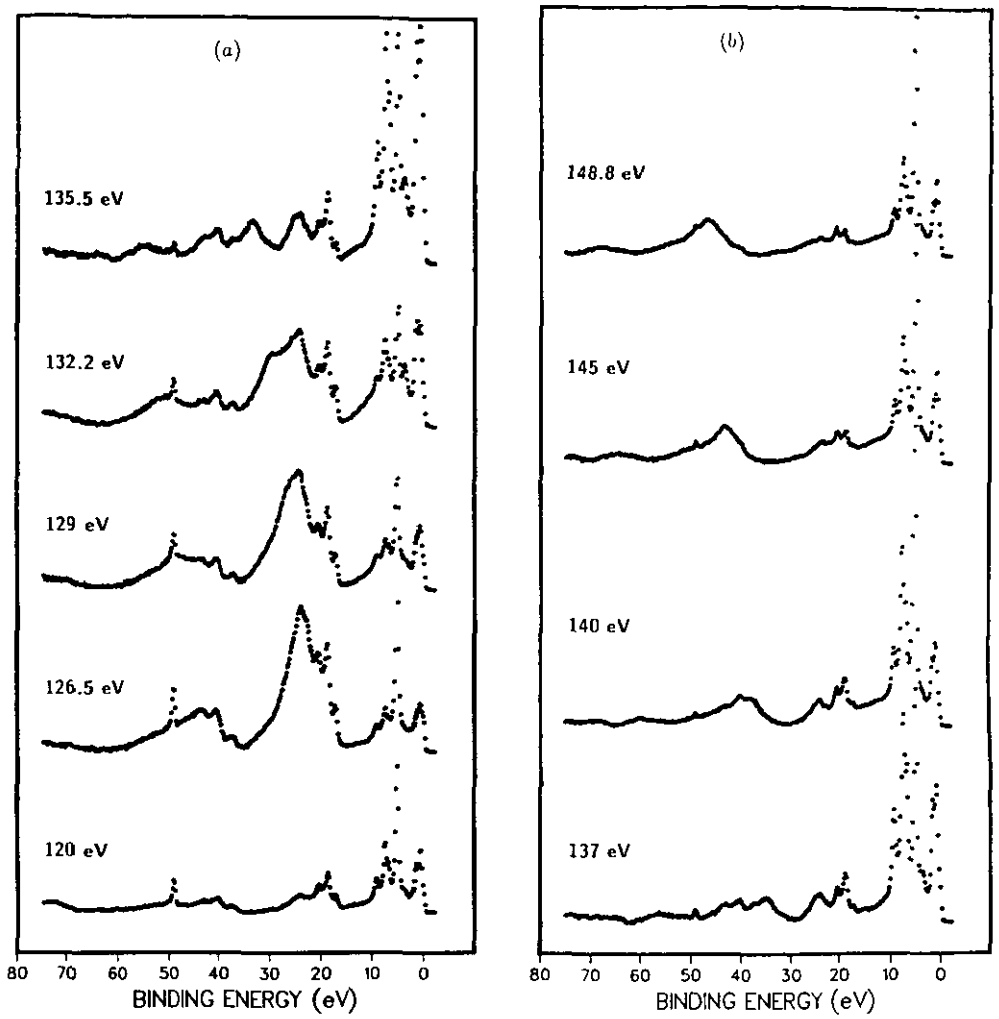

Figure 2. The electron spectra of solid samarium measured with photon energies (*a*) 120 eV, 126.5 eV, 129 eV, 132.2 eV, 135.5 eV and (*b*) 137 eV, 140 eV 145 eV and 148.8 eV.

spectra. These difference spectra are shown in figure 4.

Before going on it might be useful to discuss briefly the definition of a resonance AP because excitation to a partly filled subshell causes some difficulties in separating a resonance AP from the corresponding autoionization process when that subshell is involved in the decay process. In samarium this concerns the $N_{4,5}O_{2,3}N_{6,7}$ resonance AP. There, one of the 4f electrons takes part in the decay process leading to a $5p^{-1}$ one-hole final state, the process being phenomenologically similar to the 5p autoionization process. The question is whether the 4f electron that takes part in the recombination process is the excited one (autoionization) or not (resonance Auger). We shall distinguish these processes by the spin of the participating 4f electron. All the 4f electrons in samarium have, according to the Hund rule, parallel spins. If the 4f electron participating in the decay and the excited electron have opposite spins, the decay process is a resonance AP, but if spins are parallel we are dealing with an autoionization process.

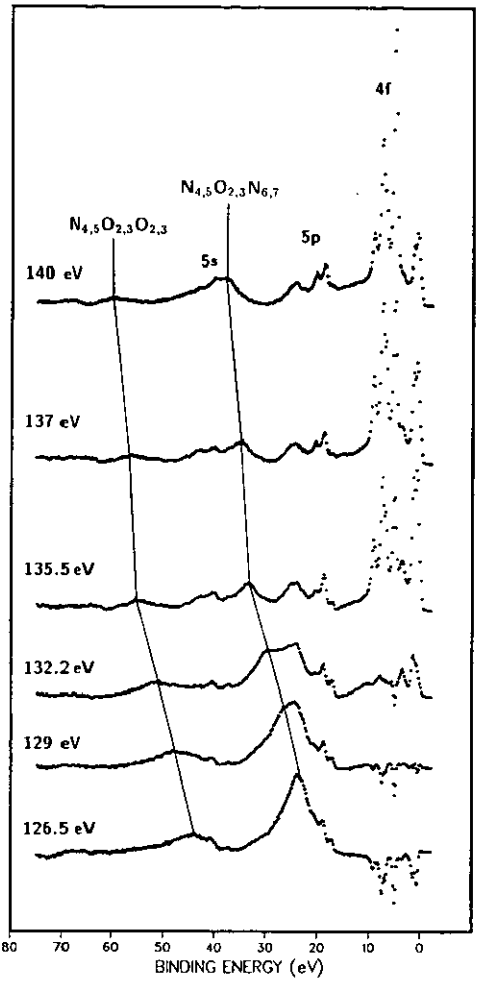

Figure 3. The difference spectra of solid samarium at 126.5 eV, 129 eV, 132.2 eV, 135.5 and 137 eV photons. Intensity normalization is done relative to the impurity peak.

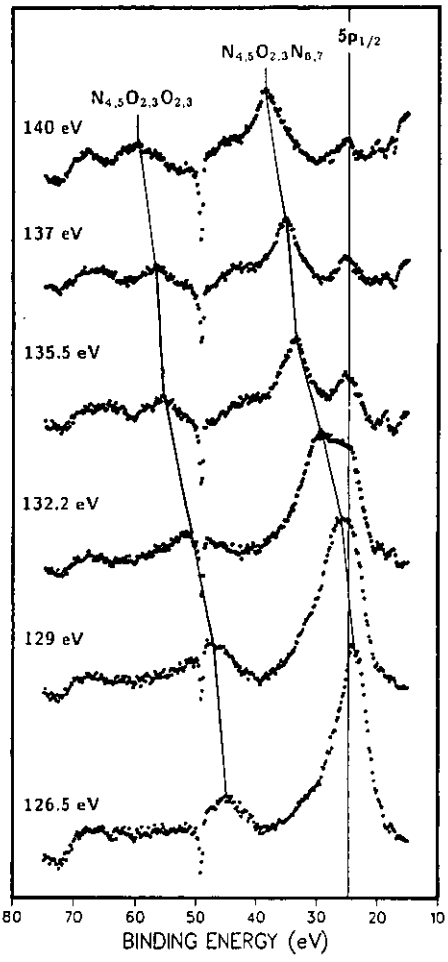

Figure 4. The difference spectra of solid samarium at 126.5 eV, 129 eV, 132.2 eV, 135.5 eV, 137 eV, 140 eV, 145 eV and 148.8 eV photons. Intensity normalization is done relative to the $5p_{3/2}$ photoline. The dip is due to the impurity peak.

Thus after a resonance AP the 4f orbital is left in an excited state leading to a lower kinetic energy for the emitted electron as compared to the corresponding autoionization process. This definition has been discussed more closely in our study of resonance Auger effects in solid Gd and Eu [48].

In the spectra in figure 4 two structures can be seen to remain almost constant with *kinetic energy* and one structure to remain constant with *binding energy*. This indicates that the first two stuctures are related to Auger-like processes whereas the third structure is caused by an autoionization process. The binding energy of the autoionization peak is 24.5 eV which agrees well with the reported binding energy of $5p_{1/2}$ subshell (24.3 eV [51]). Since the reference spectrum is normalized relative to the $5p_{3/2}$ peak, this structure reveals that the $5p_{1/2}$ component is more strongly involved in

the 5p autoionization process than the $5p_{3/2}$ component. The same effect has also been found for other solid rare earths [47, 48]. The two other structures which in the first spectra have kinetic energies 103.0 eV and 81.5 eV, but are shifted in later spectra slightly towards lower kinetic energies, can be identified as due to $N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}O_{2,3}O_{2,3}$ resonance AP, respectively. Figure 5 shows the normal Auger spectrum of solid samarium measured with 180 eV photons, which is clearly above the resonance energies. The $N_{4,5}O_{2,3}N_{6,7}$ Auger structure can be seen at 101.5 eV and the $N_{4,5}O_{2,3}O_{2,3}$ Auger structure at 80.5 eV kinetic energy [43, 51]. The broad structure above 110 eV is mainly caused by $N_{4,5}N_{6,7}N_{6,7}$ Auger transitions, the sharp peak being due to the MgO impurity. By comparing figures 4 and 5 we can estimate that with low excitation energies (126.5 eV, 129 eV and 132.2 eV) the energy shift of the resonance Auger structure relative to the corresponding normal Auger structure is 1.5±0.5 eV for the $N_{4,5}O_{2,3}N_{6,7}$ resonance Auger and 1.0±0.5 eV for the $N_{4,5}O_{2,3}O_{2,3}$ resonance Auger. The overlap with the $5p_{1/2}$ autoionization structure disturbs the energy estimation for the NON resonance AP. Also, when studying the NOO resonance structure we have to bear in mind that the spectra have been normalized relative to the $5p_{3/2}$ photoline. Thus some of the structure might be caused by 5s autoionization because there is no reason to believe that 5s and $5p_{3/2}$ autoionization channels would have exactly equal relative strengths.

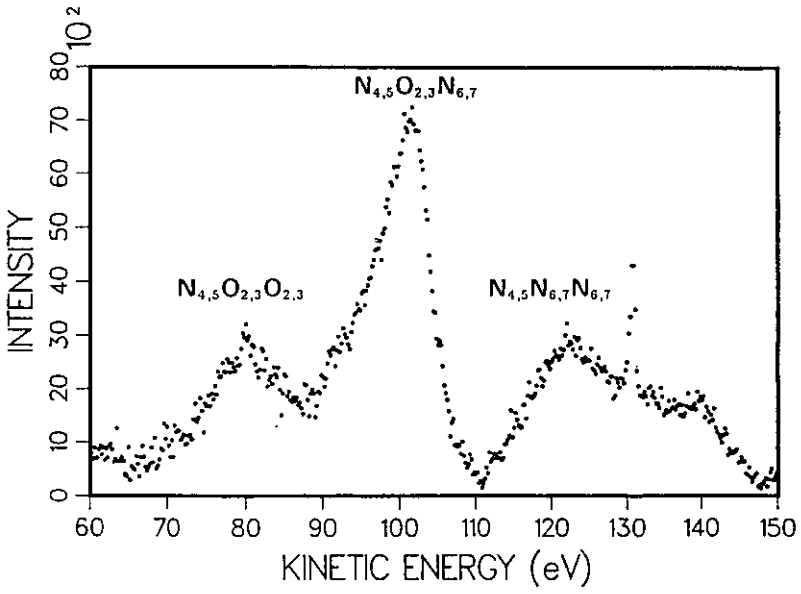

Figure 5. The normal Auger spectrum of solid samarium measured with 180 eV photons.

When the excitation energy increases the kinetic energy shift decreases for both Auger-like processes. At 135.5 eV and 137 eV excitation energies there can still be found some shift (~0.5 eV) for the $N_{4,5}O_{2,3}N_{6,7}$ structure. This structure might therefore be a mixture of normal and resonance AP. At the main giant resonance excitation both structures have the same kinetic energy as in the Auger spectrum (figure 5) and therefore they can be regarded as pure normal AP.

Our results show that the excited electron remains as a spectator near the first 4d ionization edge, at photon energies corresponding to the fine structure in the electron

yield spectrum. But when the excitation energy approaches the main giant resonance the excited electron can escape into the continuum leading to normal Auger decay processes. It is also interesting to notice that the strength of the $5p_{1/2}$ autoionization decay clearly decreases when resonance Auger processes begin to change into normal AP.

As compared to our earlier studies for Eu, Gd, Tb and Dy the biggest differences can be found in excitations corresponding to the main broad resonance. In all of these cases autoionization through the 4f subshell is the main decay channel, but in samarium direct ionization followed by normal Auger processes is much stronger than in those heavier rare-earth metals. This indicates that the $4d \rightarrow 4f$ giant resonance is more of continuum character in light rare earths than in heavy rare earths.

4. Conclusions

In this paper we have studied the decay processes in solid samarium after resonant $4d \rightarrow 4f$ excitations. Especially we have looked for possible resonance Auger effects. The $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}N_{6,7}$ resonance Auger decays were found to be significant decay channels in excitations corresponding to the low-energy-side fine structure of the resonance region. Kinetic energy shifts relative to the corresponding normal AP were estimated from the experimental spectra to be 1.0 eV for the $N_{4,5}O_{2,3}O_{2,3}$ process and 1.5 eV for the $N_{4,5}O_{2,3}N_{6,7}$ process. In the excitations corresponding to the main giant resonance the kinetic energy of the Auger electrons were the same as in the pure Auger spectrum indicating that the excited electron can escape to the continuum before the decay process. The intensity of the AP relative to the dominant 4f autoionization decay was found to be stronger than what has earlier been found for Eu, Gd, Tb and Dy. This suggests that the $4d \rightarrow 4f$ giant resonance has more continuum character in samarium than in heavier rare-earth metals.

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