Unexpectedly small intrashell L_1 - L_3 vacancy transition rate in ${}_{62}\text{Sm}$

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The individual decay channels of samarium L -subshell vacancy states were experimentally investigated by the synchrotron photoionization method. For the Coster-Kronig yield f_{13} , i.e., the relative contribution of the nonradiative L_1 - L_3 channel to the total decay of L_1 -vacancy states, the value $f_{13} = 0.19 \pm 0.03$ was obtained. This is a surprisingly small value regarding both prediction from theory (e.g., $f_{13} = 0.32$ according to Chen, Craseman, and Mark [Phys. Rev. A **24**, 177 (1981)]) and extrapolation from neighboring elements ($f_{13} \approx 0.32$ for the elements with $Z = 72$ – 74 according to our previous work [U. Werner and W. Jitschin, Phys. Rev. A **38**, 4009 (1988)]).

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Inner shells of atoms bear the fascination of conceptual simplicity due to the hydrogenic nature of inner-shell vacancies. Energy levels of K and L shells are predicted by *ab initio* relativistic calculations with uncertainties below 0.1% [1–3] and radiative transition rates with uncertainties below 10%. However, the nonradiative decay deserves special attention: although this two-electron process was discovered already in 1922 [4] and has been the subject of considerable theoretical effort [5–7], severe deviations between calculated transition rates and experimental results have been observed in a number of cases [8,9]. The situation becomes particularly bad when the excess energy of the nonradiative decay is small. In such a case the slowly outgoing electron interacts with the residual atomic electrons. As a consequence, the two-electron model fails and the decay of a vacancy state becomes a multielectron process [10]. The L_1 subshell provides a particular interesting testing case for the nonradiative transitions since the radiative decay plays only a minor role (the radiative yield remains below 20% for all stable elements [11]) and since the various nonradiative decay channels (Auger, L_1 - L_3 Coster-Kronig, L_1 - L_2 Coster-Kronig) with substantially different excess energies compete with each other. For elements with $Z \geq 80$ or $Z \leq 47$ the L_1 - L_3 Coster-Kronig transition is the dominant decay channel; however, for elements with intermediate Z this channel is blocked for energy reasons [12]. Accordingly, the L_1 - L_3 Coster-Kronig yield f_{13} changes strongly in the regime of these Z numbers (Fig. 1).

Experimental data on the various nonradiative yields (Auger, Coster-Kronig) are scarce and for lighter elements practically nonexistent [8,11,13,14]. The recently introduced method of photoionization of consecutive

subshells by tunable synchrotron radiation is capable of providing reliable results for all L -subshell yields [15]. By this method comprehensive f_{13} data for elements $Z = 72$ – 82 and also data for lighter elements have been obtained [16,17]. The experimental values for f_{13} are in reasonable agreement with theoretical calculations. This result is remarkable in particular for $Z \approx 80$ where the excess energy of the dominating L_1 - L_3 Auger transition is rather small (about 100 eV [12] compared to the L_1 binding energy (about 15 keV) and thus a breakdown of the two-electron model would not be surprising. In our previous work for $Z = 72$ – 74 we got for the L_1 - L_3 Coster-Kronig yield $f_{13} \approx 0.32$, in nice agreement with

FIG. 1. Coster-Kronig yield f_{13} for the different elements. The solid line is a semiempirical function [11]. Squares represent calculated values [27,28]. Solid circles are experimental values obtained by the synchrotron photoionization method [9,16–18]; the value for $Z = 62$ is the result of the present work.

theory [9]. For an element with somewhat smaller Z , say 62, we do expect a very similar situation and thus almost the same f_{13} . This expected trend is supported by a semiempirical tabulation, which gives the value $f_{13}=0.30\pm 10\%$ [11] which is presumably strongly based on theory due to lack of any experimental data available at that time.

The present measurement on the L_1 yields of ^{62}Sm was performed at the RÖMO II (Röntgenmonochromator II) station at HASYLAB (Hamburger Synchrotronlabor). During the measurements the storage ring DORIS II (Doppelringspeicher II) was operated at an electron energy of 5 GeV and a ring current of 25–40 mA. The photon flux at the monochromator output was of the order of 10^{11} s^{-1} for a horizontal width of about 1 cm. By a set of slits the photon beam was collimated in order to match it to the smaller size of the samples and to reduce the flux on the samples since otherwise the induced fluorescence would be too strong for the x-ray detector. A detailed description of the apparatus has been given previously [9]. Specific details of the present experiment are the following: The monochromated photon beam goes through a Sm foil, immediately followed by a Ti foil; both foils are sufficiently thin ($\leq 0.1\text{ }\mu\text{m}$) to keep the absorption of the photon beam below a few percent. The foils and the photon paths are in vacuum in order to avoid two disturbing effects, i.e., intensity loss due to absorption and scattering of the primary photons into the detector. The energy of the primary photons was scanned in the range of the Sm L edges from 6.5–8.5 keV in 0.1-keV steps, and at each energy the induced Sm L fluorescence was recorded for about 15 min by a Si(Li) detector. Ti has no absorption edges in the scanned energy range and hence the simultaneously recorded Ti K fluorescence allows an elegant way for an intensity normalization of the Sm L radiation. The fluorescence spectra were evaluated as usual by fitting Gaussian peaks and applying minor corrections for x-ray absorption in the foils.

Figure 2 shows the intensity of the Sm $L\alpha$ line (which originates from the L_3 subshell) normalized to the Ti $K\alpha$ line at various primary photon energies. Abrupt intensity jumps occur at the Sm L_2 - and L_1 -absorption edges which originate from the onset of Coster-Kronig cascades leading to an indirect creation of L_3 vacancies. In more detail, the intensity $I(L\alpha)$ of the Sm $L\alpha$ line at different photon energies is proportional to, below the Sm L_2 edge,

$$I(L\alpha) \sim \sigma_{L_3}; \quad (1)$$

between the Sm L_2 and L_1 edges,

$$I(L\alpha) \sim \sigma_{L_3} + f_{23}\sigma_{L_2}; \quad (2)$$

above the L_1 edge,

$$I(L\alpha) \sim \sigma_{L_3} + f_{23}\sigma_{L_2} + (f_{13} + f_{12}f_{23})\sigma_{L_1}, \quad (3)$$

where the symbol σ denotes the photonization cross section of the indicated samarium L subshell. These subshell cross sections can be taken from theoretical calculations [19] which are estimated to be accurate within about at least a few percent as judged from the agreement

FIG. 2. Sm $L\alpha$ intensity normalized to the Ti $K\alpha$ intensity for various energies of the primary photons. For comparison, the analogous data for $I(\text{Hf } L\alpha)/I(\text{Mn } K\alpha)$ and $I(\text{Au } L\alpha)/I(\text{Cu } K\alpha)$ are also shown. The height of the hatched area is a measure for the f_{13} Coster-Kronig yield.

of the predicted total photoelectric cross section with the experimental data on an absolute scale [20]. A quantitative analysis of our data is hindered by the curvature of the $L\alpha$ -intensity curve with resonancelike diminutions towards the absorption edges (Fig. 2) which is caused by electron correlation effects in the photoionization process [21]. Unfortunately, no detailed information of this structure is available for Sm. Our previous investigations of the correlation effects for heavier elements gave a poor quantitative description above the L_1 edge [21]. For these reasons we decided to draw simple horizontal lines through our data points. For comparison, in Fig. 2 the analogous curves of the $L\alpha$ intensities for the elements ^{72}Hf and ^{79}Au are also shown. For all three elements the photoionization cross sections σ of corresponding subshells show a similar behavior so that differences in the data directly reflect differences in the intrashell vacancy transfer.

The sizes of the jumps are a direct measure for the sizes of the corresponding Coster-Kronig yields. The relative increase of the $L\alpha$ intensity at the L_1 edge (i.e., the height of the hatched area in Fig. 2) can be calculated from Eqs. (2) and (3):

$$\frac{(f_{13} + f_{12}f_{23})\sigma_{L_1}/\sigma_{L_3}}{1 + f_{23}\sigma_{L_2}/\sigma_{L_3}}. \quad (4)$$

Our data give a relative increase of 0.068 ± 0.011 ; the uncertainty stems from the scatter of the data points and from the problem of fitting the curvature by a straight line. In order to extract f_{13} from Eq. (4), for the ionization cross sections at the L_1 edge we take the calculated values [19] $\sigma_{L_1}/\sigma_{L_3}=0.333$, $\sigma_{L_2}/\sigma_{L_3}=0.581$. In Eq. (4) the numerator term $f_{12}f_{23}$ and the denominator term f_{23} play only a minor role and their exact values are less important; we adopt the values $f_{12}f_{23}=0.03$ and $f_{23}=0.14$ of a preliminary evaluation of our residual data which are in agreement with an empirical tabulation [11]. Thus we obtain the final result

$$f_{13}=0.19\pm 0.03. \quad (5)$$

TABLE I. Calculated partial L_1 -level widths and deduced f_{13} Coster-Kronig (CK) yield of ^{62}Sm .

Ref.	Radiative (eV)	L_1 Auger (eV)	L_1 - L_2 CK (eV)	L_1 - L_3 CK (eV)	Total (eV)	f_{13}
[26]	0.339	2.114	0.834	1.603	4.89	0.328
[22]	0.332	1.993	1.03	1.55	4.91	0.316
[27,28]	0.339	1.718	0.961	1.504	4.52	0.333

Another, more crude approach of data evaluation is the comparison of the present data with the previously obtained data of neighboring elements: Previous work gave $f_{13}=0.58\pm0.01$ for ^{79}Au and $f_{13}=0.31\pm0.01$ for ^{72}Hf [9]. Comparing the heights of the hatched areas in Fig. 2 for the three elements Sm, Hf, and Au, almost the same value $f_{13}\approx0.20$ for Sm as above is obtained.

The experimental result can be compared to various calculations of radiative and nonradiative decay rates.

Radiative decay rates have been calculated with nonrelativistic screened hydrogenic wave functions by McGuire [22]; the radiative width of the ^{62}Sm L_1 subshell is $\Gamma=0.332$ eV. Various relativistic calculations have been carried out by Scofield. Values obtained are $\Gamma=0.333$ eV (Hartree-Slater potential [23]); $\Gamma=0.341$ eV (separate Hartree-Fock solutions for initial and final states [24]); $\Gamma=0.334$ eV (additionally nuclear charge distribution of finite extent used [25]). All calculated values agree reasonably with each other.

The *nonradiative decay* has been treated by McGuire in nonrelativistic calculations [22], and by Crasemann and co-workers both in nonrelativistic [26] and in relativistic [27,28] calculations. The results are compiled in Table I. The agreement of the results obtained by the three different treatments seems quite reasonable. Apparently the inclusion of relativistic effects reduces the rates to a certain extent whereby the reduction is rather the same for the various channels. Remarkably, the f_{13} values predicted by the various calculations are almost identical, i.e., $f_{13}\approx0.32$.

There is a significant deviation between our experimental result [Eq. (5)] and the just mentioned prediction of existing theories [22,26–28]. The calculated numbers are sensitive to the matrix elements; these involve the overlap of three bound-state wave functions with a long-wavelength continuum function. One might even suspect that electron correlations may cause a breakdown of the

commonly employed two-electron model for treating the nonradiative transitions. The various decay channels of Sm L_1 -vacancy states differ substantially in their excess energies: about 6 keV for the Auger transition, between 43 and 419 eV for the L_1 - L_2 Coster-Kronig transition, and between 638 and 1014 eV for the L_1 - L_3 Coster-Kronig transition [12]. Accordingly, one would expect the strongest deviation between theory and experiment for the L_1 - L_2 Coster-Kronig transition and a smaller deviation for the L_1 - L_3 transition. However, our f_{12} value is rather close to the predicted value. Thus the data provide no confirmation of the suspicion. Calculated rates may be unreliable when the limits of blocking particular decay channels are approached since in such cases minor energy shifts (e.g. due to exchange or relaxation effects or due to the chemical environment) may open or close a particular channel resulting in drastic changes of decay rates [28,10,18]. This is not the case here for the L_1 - L_3 Coster-Kronig decay in Sm: The otherwise strong L_1 - L_3 M transition is energetically forbidden by a rather large amount of at least 127 eV [12]. Also, any possible coupling between radiative and nonradiative transitions should not significantly affect the interesting strong nonradiative rates due to the small size of the radiative rates. Apparently further work seems necessary to resolve the observed deviation [29].

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