K-shell autoionization accompanying the beta decays of ^{99}Tc, ^{147}Pm, ^{151}Sm, and ^{204}Tl

C. E. Laird, Parl C. Hummel,* and Hsing-Chung Liu†
Department of Physics, Eastern Kentucky University, Richmond, Kentucky 40475
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The K-shell autoionization probabilities of ^{99}Tc, ^{147}Pm, ^{151}Sm, and ^{204}Tl have been determined to be $(3.52 \pm 0.20) \times 10^{-4}$, $(0.936 \pm 0.063) \times 10^{-4}$, $(0.024 \pm 0.003) \times 10^{-4}$, and $(1.22 \pm 0.16) \times 10^{-4}$, per decay, respectively. The first excited state branching ratios for ^{147}Pm and ^{151}Sm are $(6.48 \pm 0.56) \times 10^{-5}$ and $(0.94 \pm 0.06) \times 10^{-2}$, respectively. The K-shell electron capture to beta decay ratio for ^{204}Tl is $(1.22 \pm 0.06) \times 10^{-2}$. The autoionization probabilities are compared to the theory of Law and Campbell as modified by Isozumi, Shimizu, and Mukoyama.

[RADIOACTIVITY ^{99}Tc, ^{147}Pm, ^{151}Sm, ^{204}Ti, measured P_K, beta and K-shell branching ratios, Si(Li), Ge(Li) detectors.]

I. INTRODUCTION

The processes in which an atom becomes ionized or excited during the process of negatron decay of its nucleus have been the subject of considerable theoretical and experimental study. This process called autonionization has been theorized as coming from three mechanisms[1]: shake-off (SO) in which the orbital electron is ejected from the atom by the rapid change in its coupling to the residual core, simultaneously with the beta particle; shake-up (SU) where the orbital electron is excited to higher vacant orbitals by the same sudden change; and direct collision (DC) in which the emitted beta particle interacts with the (ejected or excited) orbital electron through the Coulomb interaction. The combined probability for these mechanisms may be studied by determining the number of primary vacancies created in the nth shell per beta particle emitted, P_n. Several recent theoretical studies[2-7] have yielded values for P_K. The latest and most accurate is the Law and Campbell (LC) theory[4] as corrected by Isozumi, Shimizu, and Mukoyama (ISM).[7]

Three experimental methods using high-resolution semiconductor detectors that have been used in studying K autoionization include independent absolute beta and x-ray disintegration rate measurements,[8,9] x-ray to gamma-ray relative intensity measurements on the same photon detector using known gamma branching ratios[10,11] to determine the beta decay rate, and x-ray-beta coincidence measurements.[12-16]

Most experimental investigations of autoionization have used the x-ray to gamma-ray relative intensity technique and previously published beta branching ratios in their determination of autoionization probabilities. In this paper we shall report the results of experiments using independent absolute beta, x-ray, and gamma-ray counting to determine the K shake-off probability and the beta branching ratio of several isotopes.

II. EXPERIMENTAL PROCEDURE

A. Absolute calibration of radioactive sources

Solutions of the radioisotopes ^{99}Tc, ^{147}Pm, ^{151}Sm, and ^{204}Tl having approximate volumetric activities of 100 μC/ml were purchased commercially from ICN corporation. In order to determine accurately the volumetric activity, the beta decay rate was measured using a Beckman LS-100 liquid scintillation counter. This instrument is essentially a 4π beta counter incorporating a system of reflectors and two photomultiplier tubes operating in the coincidence mode. The beta efficiency for this instrument is 0.97 ± 0.01 for ^{14}C ($E_{max} = 157$ keV) and 0.61 ± 0.01 for ^{3}H ($E_{max} = 18$ keV) as determined with solutions of these two isotopes which had been previously calibrated by Beckman against identical NBS (National Bureau of Standards) solutions. These results correspond to the calculations of Horrocks[17] indicating that an average energy of 1.5 keV is expended in the scintillator per electron emitted from the photocathode and indicate that the beta efficiency for decays for which $E_{max} > 200$ keV is essentially 100%.

The procedure used in measuring the volumetric activity consisted of placing 10 microliters or less of the radioactive solution dissolved in 10 milliliters of "scintillation cocktail" into a cylindrical polyethylene vial having an inner diameter of 2.2 cm and a length of 5.8 cm. The cocktail consisted of one liter toluene, 5 ml of Bio Solv,[18] and 4 grams of Omnifluor.[19] These solutions were then counted in the liquid scintillation (LS) count-

er.

Since these vials and the cocktail used in these measurements differed from those containing the calibration standard solutions supplied by the manufacturer, a test of the calibration procedure was made using ^{3}H, ^{60}Co (E_{max} = 314 keV), and ^{137}Cs (E_{max,β_1} = 1176 keV, 6%, and $E_{max\beta_2}$ = 514 keV, 94%). The volumetric activities of the ^{60}Co and ^{137}Cs were determined as outlined above, and also by evaporating 10 μl of each solution onto a metallized Mylar disk and gamma counting with a Ge(Li) detector which was calibrated with an NBS source containing both isotopes. After correction for the delayed internal conversion component in ^{137}Cs, both comparisons showed that the activities as measured by the LS method were 3% higher although the uncertainties in the gamma counting was also 3%. An estimate of the excess contribution to the LS counter rate caused by delayed gammas, x rays, and Auger electrons using efficiencies given by Horrocks[17] and Gibson and Gale[20] accounts for this possible 3% discrepancy. Therefore, we assume that the efficiency for counting beta decays having $E_{max} > 200$ keV is 100%.

The determination of the efficiency for beta decays with maximum energies less than 200 keV was more difficult. To estimate the low energy efficiency, a sample of ^{3}H was prepared from a solution of known activity supplied by the National Bureau of Standards. The efficiency obtained from this sample was 0.44 ± 0.02. Extrapolating the calculations of Horrocks[17] to this measured tritium efficiency gives an average energy deposited per photoelectron of 2.25 keV and leads to a detection efficiency of 0.78 ± 0.04 for ^{151}Sm (E_{max} = 76 keV) with the efficiency approaching unity (± 0.03) at E_{max} = 200 keV.

B. Gamma and x-ray spectroscopy

A Ge(Li) detector was used to measure the gamma rays emitted from ^{60}Co, ^{137}Cs, and ^{147}Pm as well as the Hg K x-rays emitted following the K electron capture decay branch of ^{204}Tl. At 1332 keV the detector has a resolution of 2.1 keV and an efficiency of 6.15% relative to a 7.5 cm × 7.5 cm NaI detector. The efficiency was measured using an NBS calibrated mixed gamma-ray source at energies of 88, 122, 166, 392, 662, 1173, 1332, and 1836 keV. The efficiency ϵ from 392 to 1836 keV was found to fit (to $\pm 3\%$) the following polynomial in energy (E) with adjustable coefficients A :

$$\ln\epsilon = A_1 \ln E + A_2(\ln E)^2 + A_3(\ln E)^3 + A_4 . \quad (1)$$

The low energy efficiency was determined by normalizing the relative efficiency for the low energy photons in the decays of ^{133}Ba and ^{207}Bi to the efficiencies of high energy photons in these decays determined using Eq. (1). This fit was consistent with the low energy efficiency points determined with the NBS source. The error of the efficiency fit below 400 keV was determined to be 5%.

A 3 mm thick Si(Li) detector was used to study the low energy photons emitted by the radioisotopes studied. The efficiency of this detector was measured in three different source locations using the aforementioned NBS calibration source and commercially purchased sources of ^{57}Co, ^{54}Mn, ^{133}Ba, ^{207}Bi, and ^{241}Am.[21,22] The attenuation of source covers were carefully measured experimentally and the efficiency was corrected for this attenuation.

The detector manufacturer specified the detector to be located 0.25 inches from the Be window. This was confirmed by carefully measuring the activity of several sources placed at known distances from the detector and by calculating the unknown distance using the solid angle equation. The 80 mm^2 area of the detector was consistent with the absolute determination of the efficiency as specified by the manufacturer. These measurements and the measured efficiency points were consistent with the following analytical expression:

$$\epsilon = \Omega(1 - e^{-\alpha E^{-\beta}}) , \quad (2)$$

where Ω is the solid angle and the α and β parameters, 35 000 keV$^{+3.16}$ and 3.16, respectively, are consistent with values usually found for 3 mm Si(Li) detectors. In addition, location and depth of the detector was independently determined by moving a collimated gamma source (^{57}Co) along the outside of the cryostat container and observing the change in count rate as a function of position. The estimated error in the efficiency curve is 3% from 5 to 25 keV and 5% from 25 to 122 keV.

Both gamma and x-ray spectra were taken with sources made by drop evaporation onto 3.6 mg/cm^2 aluminized Mylar disks attached to annular plexiglass mounts. Depending on the end point energy, the betas were absorbed either by the Mylar disks, by two small plastic absorbers, or by a thicker plexiglass absorber. The attenuation of the photons was measured in the low energy regions and fitted to the equation $I = I_0 e^{-\eta E^{-5}}$. This attenuation equation was then used to correct the measured photon intensities. The thickness of each source was negligible (<0.5 mg/cm^2), so the self-absorption was neglected.

III. RESULTS

^{147}Pm

The beta decay of ^{147}Pm proceeds either to the ground state or to the 121.8 keV first excited

TABLE I. Experimental data used in analysis.

Parameter [a]	^{99}Tc	^{147}Pm	^{151}Sm	^{204}Tl
$K\alpha/K_T$	0.8326 [b]	0.8 [b]	0.7987 [c]	0.7819 [b]
ω_K	0.793 ± 0.031 [b]	0.928 ± 0.023 [d]	0.925 ± 0.023 [c]	0.968 ± 0.013 [d]
f	(1.2 ± 0.4) × 10^{-5} [f]	(6.48 ± 0.56) × 10^{-5} [g]	(0.94 ± 0.06) × 10^{-2} [g]	
α	1.5 [f]	1.05 ± 0.01 [e]	28.1 ± 0.5 [h]	
α_K	1.21 [i]	0.826 ± 0.003 [e]		

[a] (See text for definitions.)
[b] Reference 29.
[c] Reference 30.
[d] Reference 31.
[e] Reference 11.
[f] Reference 24.
[g] Table III.
[h] Reference 25.
[i] Reference 23.

state of ^{147}Pm.[23] Using the measurement of the intensity of the 121.8 keV gamma with the Ge(Li) detector, its internal conversion coefficient (Table I), and the measured beta activities, the branching ratio to the 121.8 keV level is calculated to be $(6.48 \pm 0.56) \times 10^{-5}$. This is consistent with the most recent value of $(5.7 \pm 0.7) \times 10^{-5}$ reported by Schupp *et al.*[16]

The $K\alpha$ x-ray intensity measured with the Si(Li) detector comes from two sources—the autoionization process and internal conversion of the 121.8 keV transition. The total K vacancies are calculated by using the well known $K\alpha/K_{\text{total}}$ x-ray intensity ratio, and the K-shell fluorescence yield ω_K. Using the K internal conversion coefficient α_K, the branching ratio found above, and Eq. (3), the total K vacancies caused by autoionization was determined.

$$P_K = \frac{I_{K\alpha}}{I_\beta \epsilon \omega_K (K_\alpha/K_t)} - f_\gamma \alpha_K . \tag{3}$$

In Eq. (3) I_β is the absolute beta activity, $I_{K\alpha}$ the $K\alpha$ x-ray intensity, ϵ the x-ray detector efficiency, ω_K the K-shell fluorescent yield, and $K\alpha/K_t$ the ratio of the $K\alpha$ x-ray intensity to the total K x-ray intensity. ω_K and $K\alpha/K_t$ are listed in Table I. The K-shell autonionization probability is listed in Table II along with some previous determinations. $f_\gamma = f/(1+\alpha)$; where α is the total conversion coefficient.

^{99}Tc

The decay of ^{99}Tc is similar to ^{147}Pm in that there is a first excited state to which beta decay branching does occur. The branching ratio has been measured by Legrand and Morel[24] who quote the value given in Table I. The measured $K\alpha$ x-ray intensity was then used to determine the K-shell autoionization probability using Eq. (3), where the factors in these equations are listed in Table I. The result and P_K value is listed in Table II.

TABLE II. Autoionization probabilities per β decay ($\times 10^4$).

Z	SO + SU [a]	SO + SU + DC [a]	ISM [b]	Previous exp. [a]	Present work
^{99}Tc	1.65 [c]	1.76 [c]	2.29	3.9 ± 0.2	3.52 ± 0.20
	1.87 [c]	2.00 [c]			
^{147}Pm	0.416	0.490	0.451	0.90 ± 0.09	0.936 ± 0.063
^{151}Sm	0.0145	0.0201	0.011	0.023 ± 0.003	0.024 ± 0.003
^{204}Tl	0.60	0.662	0.663	1.10 ± 0.08	1.22 ± 0.16

[a] Reference 6.
[b] Reference 7.
[c] The upper values are calculated using an approximate correction factor for the known forbidden beta spectrum shape. The lower value ignores this factor; i.e., assumes an allowed shape.

^{151}Sm

Again, the decay of ^{151}Sm is similar to the previous two radioisotopes in that there is a 21.54 keV first excited state.[23] However, since the K-shell binding energy of Eu is 48.5 keV, no K-shell internal conversion of the 21.54 keV transition can occur. Therefore, all K vacancies created arise from the autoionization process. The K-shell autoionization probability was determined using Eq. (3), the data listed in Table I, and the measured K x-ray activities.

In addition, the intensity of the 21.54 keV gamma transition was measured. With the internal conversion coefficient given by Antman *et al.*,[25] this gamma intensity led to a branching ratio of $(0.94 \pm 0.06) \times 10^{-2}$. This is in agreement with the value of $(0.88 \pm 0.06) \times 10^{-2}$ obtained by Freedman and Beery.[15]

^{204}Tl

No excited state transitions occur in the beta decay nor in the electron capture of ^{204}Tl. Therefore, the measurement of the K x-ray intensity of ^{204}Pb led directly to the value of the K autoionization probability found in Table II. This value of $(1.22 \pm 0.16) \times 10^{-4}$ is in agreement with the results obtained by previous authors.[9,26,27] The intensity of the Hg K x-rays from the electron capture to the ^{204}Hg ground state was used to determine the fractional branching through K electron capture. The K x-rays from Hg were measured with the Si(Li) detector and with the Ge(Li) detector. The resulting ratio of K electron capture to beta decay is $(1.17 \pm 0.07) \times 10^{-2}$ for the Si(Li) detector and $(1.35 \pm 0.11) \times 10^{-2}$ for the Ge(Li) detector. A weighted average gives $(1.22 \pm 0.06) \times 10^{-2}$ for the K capture to beta ratio. Assuming the K capture to total electron capture ratio to be 0.592,[28] we obtain an electron-capture-to-beta branching ratio of $(2.05 \pm 0.13) \times 10^{-2}$ or an electron capture per decay branch of $(2.01 \pm 0.13) \times 10^{-2}$. As can be seen in Table III, this result is systematically lower than previous results, although there is an overlap with the most recent measurement. Analysis of the beta spectrum taken with the liquid scintillation counter and of the x-ray and gamma-ray spectra over the range of 5 keV to 1 MeV showed no evidence of source contamination. No explanation can be given for the disagreement between our electron capture per decay branch and previous measurements.

IV. CONCLUSIONS

Table II contains the values of the K-shell autoionization probabilities obtained in the present work, the comparable values from the theoretical calculations, and the experimental values compiled by Law and Campbell.[6] The overall results of this work are slightly but not significantly higher than the complied experimental values. The theoretical results of Law and Campbell[6] as presented here include SO, SU, and DC components after correcting SO by a factor $\frac{1}{2}$ as proved necessary by Isozumi, Shimizu, and Mukoyama.[7] Thus, the theoretical K-shell autoionization probabilities are calculated with the equation

$$P_K = \tfrac{1}{2} P_K(\mathrm{SO}) + P_K(\mathrm{SU}) + P_K(\mathrm{DC}),$$

using the individual values of P_K(SO), P_K(SU), and P_K(DC) found in Ref. 6. The results of ISM (which do not include the small DC contribution) are also listed for comparison.

As previously mentioned, the present values of the branching ratios to the first excited states in ^{147}Pm and ^{151}Sm (Table III) are in good agreement with the recent values found by Freedman and co-workers.[15,16] The values obtained for P_K (Table II) are also in good agreement with previous experimental results; although all experimental

TABLE III. Experimental branching ratios.

	Present values	Previous results
^{147}Pm-decay to 1st excited state	$(6.48 \pm 0.56) \times 10^{-5}$	$(5.7 \pm 0.7) \times 10^{-5}$ [a]
^{151}Sm-decay to 1st excited state	$(0.94 \pm 0.06) \times 10^{-2}$	$(0.88 \pm 0.06) \times 10^{-2}$ [b]
^{204}Tl-K-shell electron capture	$(1.22 \pm 0.06) \times 10^{-2}$	$1.53 \pm 0.05 \times 10^{-2}$ [c] 1.57 ± 0.20 [d] 1.59 ± 0.04 [d] 1.48 ± 0.15 [d]

[a] Reference 16.
[b] Reference 15.
[c] References 26 and 28.
[d] Reference 28.

results are not in agreement with the present revised LC theory, either with or without DC. Since the values for P_K found in this work and those found in the previous experiments of many other authors have been determined with a variety of experimental techniques, the probability of a systematic error having caused the aforementioned disagreement with theory is virtually nonexistent.

The current theoretical treatment of the shake-off process is obviously inadequate to describe autoionization during β-decay. Whether the use of improved atomic wave functions, such as relativistic Hartree-Fock wave functions, the inclusion of multielectron effects,[32] an improved treatment of beta-electron correlations (direct-collision) or some other theoretical modification will bring theory into agreement with experiment remains for future investigation. Barring unexpected success in this process, perhaps newer untried interactions may need to be investigated to determine their contribution to autoionization.

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*Present address: McDonald-Douglas, St. Charles, Missouri 63301.

†Present address: Dept. of Physics, Kent State University, Kent, Ohio 44242.

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