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X-Ray Spectra, L-Subshell Fluorescence and Coster-Kronig Yields in Bismuth and Neptunium*

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The Bi L x-ray spectrum from the decay of Pb^{210} and the Np L x-ray spectrum from the decay of Am^{241} were measured at high resolution with a Si(Li) spectrometer. From these data values for the L-subshell fluorescence, Coster-Kronig and Auger yields in Bi and Np were derived.

Os espectros de raios-X L do Bi e do Np foram obtidos a partir da desintegração β do Pb^{210} e α do Am^{241}, respectivamente. A análise desses espectros, com um detetor Si(Li) de alta resolução (180 eV), permitiu a determinação de rendimentos de fluorescência e probabilidades de transição Auger e Coster-Kronig nas subcamadas L do Bi e do Np.

1. Introduction and Experimental Procedure

When an atom is ionized in one of its inner shells, the electrons rearrange themselves to fill the vacancy, with the transition energy either released as a photon or transferred to an electron. Thus, the fluorescence yield or the probability of x-ray emission is in competition with two non-radiative processes: 1) Auger transitions in which the vacancy in one shell is filled by an electron from another shell, with the transition energy being delivered to an electron in another shell, ejecting it from the atom; and 2) Coster-Kronig transitions in which the vacancy is filled by an electron of a different subshell of the same major shell with the transition energy being delivered, in a similar way, to an electron of a higher shell.

This paper reports the determination of some L-subshell fluorescence and nonradiative yields in bismuth and neptunium atoms.

The following notation is used. Let ω_i represent the fluorescence yield of a subshell, or the probability that the filling of the vacancy in a subshell

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be accompanied by the emission of an L x-ray. Let a_i represent the Auger yield and f_{ij} the Coster-Kronig (CK) yield. The subscripts i, j (= 1, 2, 3), with i < j, indicate in this work the L-subshells (L_I, L_{II} and L_{III}, respectively).

In the experiments described in this paper, all primary L-vacancies are assumed to be produced by the internal conversion process. The six independent unknown quantities for the radiative and non-radiative yields can be calculated from the intensities of the unconverted gamma rays, the intensities of the L x-ray lines, the L-subshell internal conversion coefficients (ICC), and additional available information on the filling of the L-subshell vacancies as described in the text.

The singles L x-ray spectra were studied with an ORTEC Si(Li) spectrometer (model 7416-04180) with a resolution of 180 eV full width at half maximum for 6.4 keV Fe K, x-rays from Co^{57}. The detector with a sensitive depth of 3 mm and an active diameter of 4 mm is enclosed in a housing with a 0.025 mm Be window and a 200 Å gold contact. The photopeak relative efficiency curve of the detector was obtained in the usual way with standard radioactive sources with well known low energy transitions (y, *K* and L x-rays). The efficiency curve covers a region from 3 to 140 keV, and it was observed that the detector had almost flat response for photopeak detection in the energy range of interest, namely, 8-22 keV, and so was ideally suited for measurements of relative L x-ray intensities.

Most of the individual L,, L_β and L, lines were not fully resolved, and hence a peak fitting procedure had to be used to extract accurate values for the intensities of the various x-ray lines. The energies adopted for the L x-rays of Np and Bi are given in Tables I and IV, respectively. A graphical peeling method was used and full-energy-peak profiles were determined experimentally for the different portions of the spectra. The FWHM was observed to vary linearly with the energy and was determined by interpolation for each value of the energy. The low energy tail of the profiles was carefully determined for each interval of 3 keV.

Carrier free radioactive sources of Am^{241} and Pb^{210} were used in our two experiments. With these sources we were free of the difficulties caused by sources-thickness effects. Absorption in air was observed to be negligible in the considered energy interval.

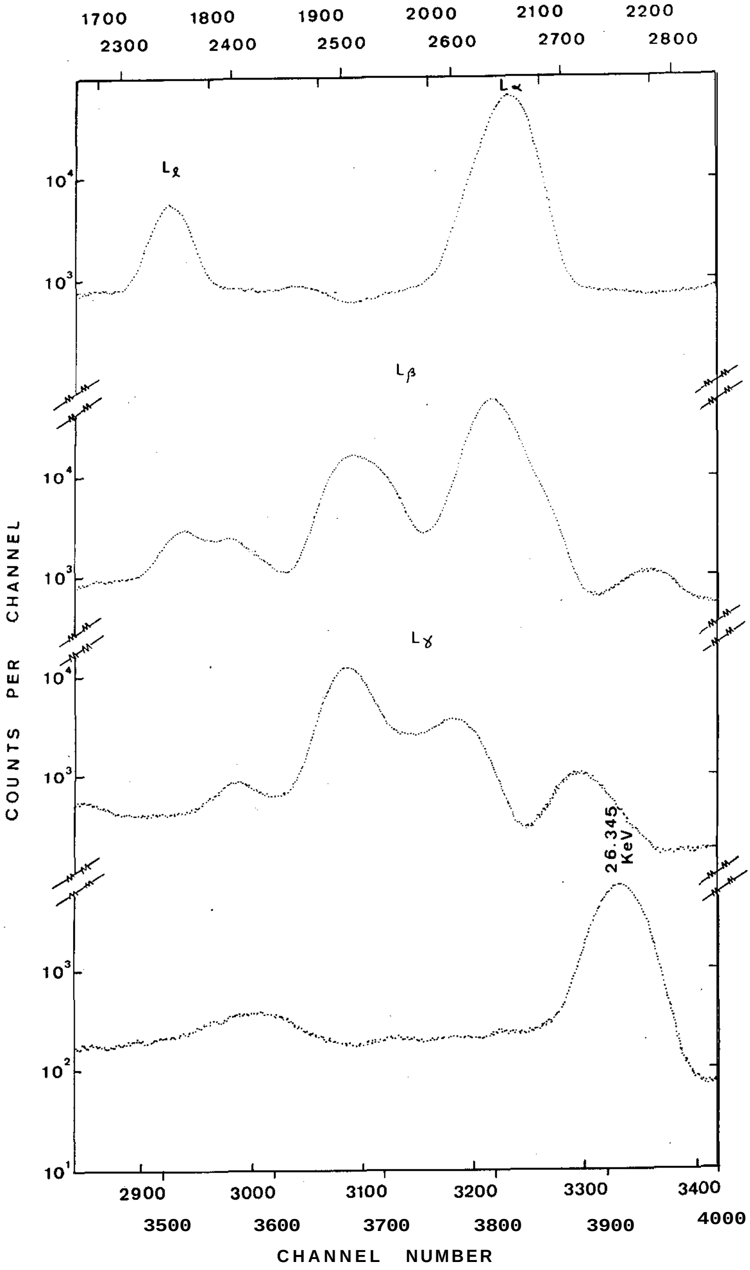

Fig. 1 - Neptunium L x-ray spectrum associated with the a-decay of Am^{241}.

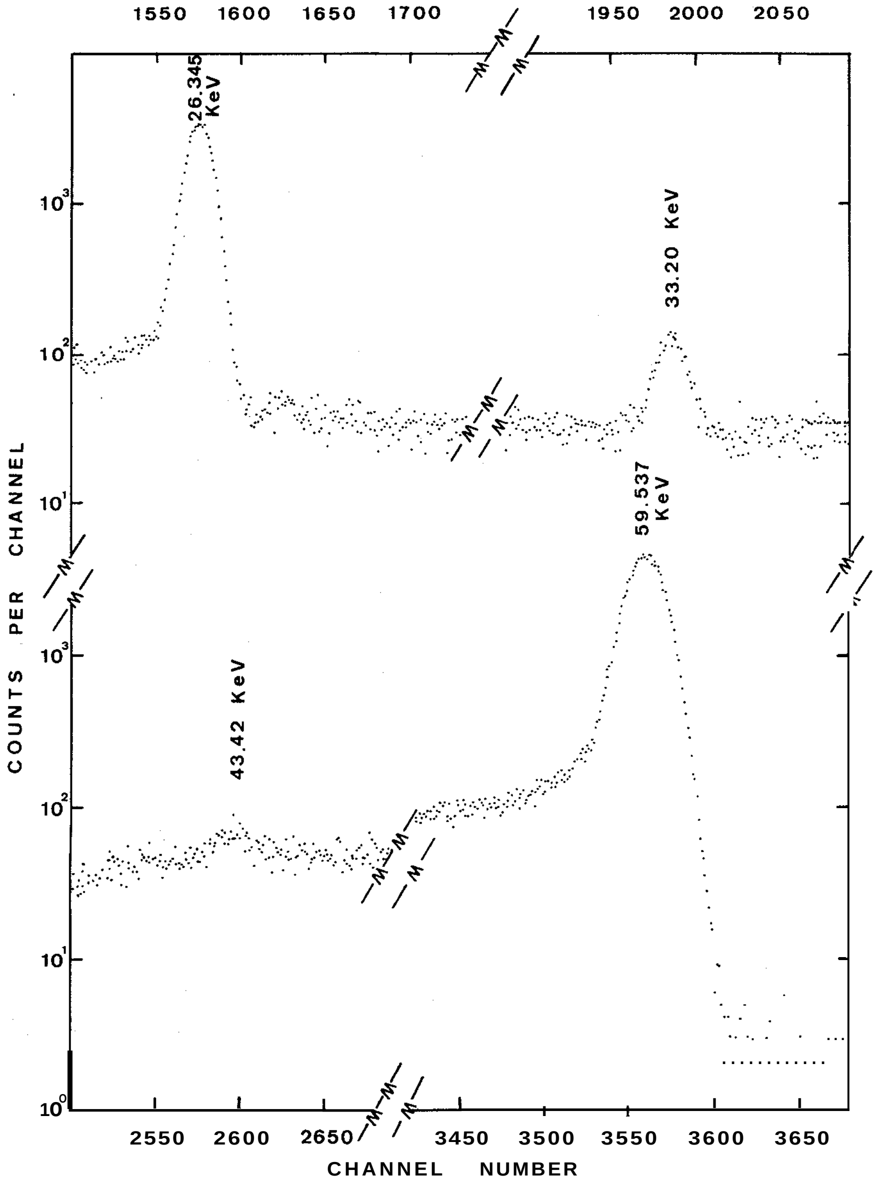

Fig. 2 - The four gamma-rays arising from the α-decay of Am^{241} considered in this work.

2. Results: Neptunium

The L x-rays of Np^{237}, following the decay of Am^{241}, were first analysed by Jeffe *et al.*[1] and by Day[2] with bent crystal spectrometers. From relative intensities of the most relevant lines they found for the ratios $N(XL_I)/N(XL_{II})/N(XL_{III})$ the values 1/3.2/1.9 and 1/4.5/4.3, respectively. A more recent study of these L x-rays was reported by Watson and Li[3] giving, for these same ratios, the values 1/4.30/4.47.

We have reinvestigated the L x-ray spectrum with an average resolution of 195 to 200 eV. The measured relative intensities are presented in Tables I and II, where they are compared with the results of Watson and Li[3]. Table III gives the intensities of the 1, a, β and γ groups of L x-rays as well the intensities of the relevant low energy gamma-rays. These results are compared with those of Gehrke and Lokken[4].

The number of primary vacancies in the L subshells was calculated in the following way. All nuclear transitions with intensities less than 3% of the most intense transition (59.5 keV) were neglected, i.e., we only considered the 26.35, 33.20, 43.42 and 59.54 keV transitions. As a consequence no creation of vacancies in the K shell is considered, although some K vacancies might be shifted to the L-subshells by the Auger process. The L-vacancies produced by the 55.5 keV M1 + E2 transition are likewise neglected. These restrictions introduce an uncertainty of less than 2% in the number of vacancies in the L-subshells.

The total number of vacancies produced in the subshell L_i by the internal conversion of the above mentioned four gamma rays is thus simply given by

$$N_i = \sum_{j=1}^{4} N(\gamma_j)\alpha_j(L_i),$$

in a self-explaining notation. The photon intensities $N(\gamma)$ were determined by us and the ICC's were taken from the literature.

For the 59.543 keV electric dipole transition, Yamazaki and Hollander[5] give for the L-subshells: $\alpha(L_I) = 0.240 \pm 0.029$, $\alpha(L_{II}) = 0.468 \pm 0.047$ and $\alpha(L_{III}) = 0.131 \pm 0.013$, and for the M-subshells: $\alpha(M_I) = 0.061 \pm 0.010$, $\alpha(M_{II}) = 0.121 \pm 0.016$ and $\alpha(M_{III}) = 0.032 \pm 0.006$. It can be seen that the $M_I : M_{II} : M_{III}$ ratios follow closely the L ratios and are correspondingly anomalous, as was first noted by Rasmussen *et al.*[6]. The N ratios, as measured by Wolfson and Park[7], are also equal to the

TABLE I

Line	Energy (keV)	Relative		Intensities	
		Present Work		Watson and Li[3]	
$L_{I}L_{III}$	4.817	0.94 ± 0.20			
$L_{III}M_{I}$	11.887	2.20 ± 0.08		2.35 ± 0.07	
$L_{III}M_{IV}$	13.760	3.65 ± 0.17	37.61 ± 0.95	4.05 ± 0.30	36.55 ± 1.34
$L_{III}M_{V}$	13.944	33.95 ± 1.05		32.50 ± 2.35	
$L_{II}M_{I}$	15.877	0.87 ± 0.11	1.50 ± 0.13	0.97	1.61 ± 0.20
$L_{III}N_{I}$	16.109	0.63 ± 0.07			
$L_{III}N_{IV-V}$	16.835	8.14 ± 0.78	12.88 ± 0.33	8.38 ± 1.01	13.20 ± 0.34
$L_{I}M_{II}$	17.061	4.73 ± 0.45		4.69 ± 0.67	
$L_{II}M_{III}$	17.165	0.40 ± 0.08			
$L_{III}N_{VI-VII}$	17.200				
$L_{III}O_{I}$	17.272				
$L_{III}O_{IV-V}$	17.500	1.18 ± 0.13			
$L_{II}M_{IV}$	17.750	33.50 ± 1.05		33.5	
$L_{I}M_{III}$	17.992	3.65 ± 0.30		3.79 ± 0.54	
$L_{I}M_{IV}$	18.577	0.54 ± 0.06			
$L_{I}M_{V}$	18.761				
$L_{II}N_{I}$	20.099	0.30 ± 0.05		0.37 ± 0.07	
$L_{II}N_{IV}$	20.784	8.37 ± 0.28		8.71 ± 0.23	
$L_{I}N_{II}$	21.099	1.34 ± 0.16		1.57 ± 0.27	
$L_{II}N_{VI}$	21.185	0.13 ± 0.03			
$L_{II}O_{I}$	21.262				
$L_{I}N_{III}$	21.340	1.31 ± 0.16			
$L_{II}O_{IV}$	21.491	1.80 ± 0.20		2.58 ± 0.54	
$L_{I}N_{IV-V}$	21.640	0.13 ± 0.02			
$L_{I}O_{II}$	22.144	0.36 ± 0.05	0.71 ± 0.06	0.67 ± 0.07	
$L_{I}O_{III}$	22.221	0.35 ± 0.05			
γ_1	26.347	6.45 ± 0.20		6.47 ± 0.30	

Table I - Relative intensities of Np L x-rays arising from the a-decay of Am^{241}. The intensities of Ref. 3 were multiplied by a constant factor (33.5) to make coincident the intensities of the $L_{II}M_{IV}(L_{\beta 1})$ transitions as determined in the present work and in Ref. 3.

Photon Energy (keV)	Relative Intensities		
	Present Work	Gerke and Lokken[4]	Day[2]
11.887 (L_ℓ x-rays)	2.20 ± 0.08	2.25 ± 0.20	1.32
13.90 (L_α x-rays)[a]	37.61 ± 0.95	35.1 ± 2.5	27.5
17.75 (L_β x-rays)[a]	53.63 ± 1.83	53.2 ± 3.8	49.5
20.08 (L_γ x-rays)[a]	14.21 ± 0.70	13.3 ± 1.0	12.8
26.347 (γ_1)	6.45 ± 0.20	6.2 ± 0.5	7.5
33.208 (γ_2)	0.30 ± 0.02	0.29 ± 0.03	0.40
43.467 (γ_3)	0.18 ± 0.02	0.16 ± 0.05	0.26
59.537 (γ_4)	100.	100.	100.

a. X-ray energies are averages of the measured components.

Table II - Relative intensities of the major L x-ray groups and of the most prominent gamma rays following the α-decay of Am^{241}.

Subshell	Relative Intensity	
	Present Work	Watson and Li[3]
L_I x-rays	13.34 ± 0.95	10.72 ± 1.01
L_{II} x-rays	45.28 ± 1.80	46.13 ± 0.60
L_{III} x-rays	49.97 ± 1.05	47.91 ± 0.27
Total L x-rays	108.59 ± 2.08	104.76

Table III - Total L-subshell relative intensities. The normalization is the same as described in Table 1.

M and L ratios within the experimental errors. We adopted the experimental values of $\alpha(L_i)$ for this transition from Ref. 5.

The 26.35 keV transition is known also to be of the E1 type from its position in the level scheme and from its measured[5] value of $\alpha(L_{III}) = 1.48 \pm$ $\pm$ 0.19, in close agreement with the theoretical result. From the measured values of the ratios for the M (Ref.5) and N (Refs. 5, 7) shells and by analogy with the 59.54 keV transition, this transition is also expected to be anomalously converted in the L_I and L_{II} subshells. If the assumption is made that the L ratios are the same as the M and N ratios, as found for the 59.54 keV transition, it is possible to estimate $\alpha(L_I)$ and $\alpha(L_{II})$ from the knowledge of $\alpha(L_{III})$. This procedure for estimating the $\alpha(L)$ ICC's is essentially the same as adopted by Asaro et *al.*[8].

The heavily converted 33.2 and 43.4 keV transitions are M1 + E2 mixtures. The L ratios, as determined by Samailov *et al.*[9], Kondratev *et al.*[10], Wolfson and Park[7] and Yamazaki and Hollander[S], are consistent and point to the same degree of electric quadrupole-magnetic dipole admixture. We adopted $\delta = 0.014$ for the first transition and $\delta = 0.163$ for the second one and the theoretical ICC of Hager and Seltzer[11] in order to estimate the $\alpha(L_i)$ values.

A summary of the relevant ICC in the L-subshells is given in Table IV.

Transition Energy (keV)	Internal Conversion Coefficient			
	α (L_I)	α (L_{II})	α (L_{III})	α (L)
26.34	1.67	3.30	1.48	6.45
33.20	89.6	26.9	17.9	134.4
43.42	37.0	49.0	39.5	125.5
59.54	0.240	0.468	0.131	0.839

Table IV - Adopted internal conversion coefficients of the transitions contributing to the production of L-subshell vacanciec, after the r-decay of Am^{241}

The resulting number of vacancies normalized to $\Sigma n_i = 1$ and the fraction of L x-rays per total number of vacancies X_i, are given in Table V.

From these results we find $\omega_1 = 0.196 \pm 0.020$ and the total fluorescence field $\bar{\omega}_L = 0.576 \pm 0.040$. The relatively large errors in the present determination of $\bar{\omega}_L$ are mainly due to uncertainties in the values of internal conversion coefficients. The quantity $\bar{\omega}_L$ depends on the primary ionization process. However, our result is in close agreement with those reported by Burne *et al.*[12] and Lazzaro and Missoni[13] in Uranium as well as with the value reported by Akalaev *et al.* in neptunium but it strongly disagrees with the value determined by Gil et *al.*[15] in uranium.

Our set of experimental data is not complete enough to allow an independent determination of the other fluorescence yields. Values of $\omega_3 =$

Neptunium Subshell	n_i	X_i
L_I	0.362	0.071
L_{II}	0.451	0.240
L_{III}	0.187	0.265
	$\Sigma n_i = 1.$	$\Sigma X_i = 0.576$

Table V - Number of primary vacancies (n_i) and fraction of L x-rays per total number of vacancies (X_i) in the decay of Am^{241}

$= 0.480 \pm 0.20$ and v, $= 0.600 \pm 0.025$ were adopted by interpolating between experimental points corresponding to the values reported in Table II of Ref. 16 plus the recent measurements of Mc George and Fink[17] in $Z = 96$. Theoretical predictions of Chen *et al.*[16] and of Mc Guire[18] can also be used as a guide. The values of ω_3 and v, $= \omega_2 + f_{23}\omega_3$ can be accurately determined by measuring the L x-ray spectra in coincidence with the $K\alpha_1$ and $K\alpha_2$ lines, respectively.

We chose also the value $f_{12} = 0.10 \pm 0.020$. This choice is relatively unimportant for the determination of the other radiative and non-radiative yields.

Finally, we get: $\omega_2 = 0.493 \pm 0.042$, $f_{23} = 0.223 \pm 0.020$, $f_{13} = 0.707 \pm$ $\pm$ 0.065 and the Auger yields $a_1 \simeq 0.00$ and $a_2 = 0.28 \pm 0.03$..
For the L, subshell our results can only be compared with the result of Chu et al.[19] in $Z = 96$. Experimental information for the transition probabilities to 4 subshell in high Z atoms is rather scarce but our results confirm the great importance of the $L_I - L_{III}$ X CK transitions which result in a shift of vacancies from L_I to L_{III} subshells. Our value of ω_1 does not disagree with extrapolated results derived from the theoretical calculations of Crasemann et *al.*[20] and Mc Guire[18].

A process equivalent to Coster-Kronig electron transitions is the radiative transition of electrons between subshells of a major shell. This is the case of the $L_I L_{III}$ transition observed in the high energy tail of the M x-ray group. We localized this transition in the Np x-ray spectra on the basis of its energy (4.817 keV). Its measured intensity was 0.94 ± 0.20 corresponding to the branching ratio $\& L_{III}/(L_I N_{II} + \& N_{III} + \& O_1)$ $=$ $= 0.28 \pm 0.07$. This ratio is compatible with the extrapolated theoretical branching ratio of Scofield[30], 0.254. This gives for the radiative component ω_{13} of the Coster-Kronig transition a value of 0.014 ± 0.003 which corresponds to a correction of about 2% in the value of f_{13}.

For the L_{II} subshell our value of ω_2 is in good agreement with the results of Burne *et al.*[12] in $Z = 92$ ($\omega_2 = 0.497 \pm 0.035$) and in $Z = 94$ ($\omega_2 =$ $= 0.466 \pm 0.023$). The results of Ref. 12 were revised by Mc George and Fink[17], becoming 0.529 ± 0.035 and 0.523 ± 0.023, respectively. These last authors found $\omega_2 = 0.552 \pm 0.032$ in $Z = 96$. The theoretical[16] prediction for neptunium is $\omega_2 = 0.460$.

Our value of f_{23} is in quite good agreement with the values of Salgueiro *et al.*[20] and of Byrne *et al.*[21], both in $Z = 94$, the nuclide parent being the Cm^{242}. It also agrees with the revised values of Ref. 12 presented in Ref. 17 and with the theoretical[16] calculation $f_{23} = 0.209$.

Since the $L_{II} - L_{III} M_{IV,V}$ CK transitions become energetically possible only for $Z > 91$, a sharp break in the L_{II} subshell fluorescence yield, as well as an abrupt increase in the value of f_{23}, should be expected above $Z = 91$. The recent values of ω_2 and f_{23} reported in Refs. 3 and 19 as weil the present results do not seem to confirm any dramatic discontinuity in the ω_2 (f_{23}) vs. Z curve but only a decrease (increase) in the slope of the curve.

3. Results: Bismuth

There were two main reasons to reinvestigate the L-subshell fiuorescence yields and CK transition probabilities in bismuth. On the one hand, there is much more experimental information available in the neighborhood of $Z = 83$ than in the actinide region. Thus, the measurement of the ω_i's and f_{ij}'s could be an excelent test for the reliability of our experimental methods. On the other hand, a recent determination[21] of **o,** in bismuth itself gave a value much lower than indicated by the systematic trend in this region.

A radioactive source of Pb^{210} of about 0.60 μCi was used. Primary vacancies in Bi were created by the internal conversion of the 46.5 keV magnetic dipole transition in Pb^{210} decay. We adopted for the ICC the following values[22,23]: $\alpha(L) = 14.4 \pm 0.5$ and $\alpha(L_I)/\alpha(L_{II})/(L_{III}) = 100/10.34/0.87$. The X_L/γ ratio was measured by us and was found to be 5.24 ± 0.25 in good agreement with the result of Gehrke and Lokken[4]. From this we get $\bar{\omega}_L = 0.364 \pm 0.020$. A recent determination of $\bar{\omega}_L$ by Freund and Fink[21] gave 0.330 ± 0.016. These authors have recalculated a previous result of Fink[24] who used a proportional counter, obtaining $\bar{\omega}_L = 0.344 \pm 0.020$.

The measured intensities of the L x-ray lines are presented in Table VI and compared with the results of Freund and Fink[21] who used a method analogous to ours, and Goldberg[25] who employed bent crystal spectrometry. The normalization used was the same as described in Ref. 21.

Line	Energy (keV)	Relative Intensities				
		Present Work		Freund and Fink[21]	Goldberg[25]	
$L_{III}M_I$	9.420	1.70 ± 0.09		2.27	1.6	
$L_{III}M_{IV}$	10.731	4.0 ± 0.5	42.07 ± 1.40	45.5	4.3	42.5
$L_{III}M_V$	10.839	38.0 ± 1.5			38.2	
$L_{II}M_I$	11.712	0.40 ± 0.05		0.8	0.3	
$L_{III}N_I$	12.480	0.60 ± 0.06			0.7	
$L_I M_{II}$	12.691	9.03 ± 0.50		11.4	8.2	
$L_{III}N_{IV-V}$	12.975	8.71 ± 0.65		11.6	9.2	
$L_{II}M_{IV}$	13.024	13.80 ± 0.72		11.6	13.4	
L_IM_{III}	13.211	10.96 ± 0.43		6.5	8.6	
$L_{III}O_{IV-V}$	13.393	1.19 ± 0.07			1.5	
L_IM_{IV-V}	13.76	0.92 ± 0.09		0.9	1.6	
$L_{II}N_I$	14.777	0.12 ± 0.03				
$L_{II}N_{IV}$	15.248	3.03 ± 0.25		3.28	3.8	
L_IN_{II}	15.582	2.62 ± 0.22	6.80 ± 0.33	5.55	2.6	6.5
$L_{II}O_{IV}$	15.685	0.40 ± 0.10			0.5	
L_IN_{III}	15.709	3.78 ± 0.32			3.4	
L_IN_{IV-V}	15.941	0.16 ± 0.04				
L_IO_{II}	16.270	0.55 ± 0.07	1.19 ± 0.06	1.19	1.2	
L_IO_{III}	16.295	0.65 ± 0.08				

Table VI - Relative intensities of B,L x-rays arising from the β-decay of Pb^{210}. The normalization is as described in Table II of Ref. 21. We have made the total number of counts corresponding to L x-rays equal to 100 in our spectra.

The $L_l/L_\alpha/L_\eta + L_\beta/L_\gamma$ relative intensities were found to be 1.7 ± 0.1/43.0 ± ± 1.4/47.1 ± 1.5/8.2 ± 0.6. The resulting number of vacancies and the fraction of L x-rays per total number of vacancies are given in Table VII. A simple inspection of the L x-ray spectrum points to the importance of the L, – L_{III}X CK transitions, as measured by the f_{13} yield, since a pure M1 transition, as in this case, is almost entirely converted in the L_I-subshell. The intensity of the L, + L, group vouches for a considerable participation of the L_{III}-subshell which can only be explained in terms of an internal shift of vacancies.

Bismuth Subshell	n_i	X_i
L_I	0.900	0.106
L_{II}	0.0922	0.064
L_{III}	0.0078	0.194
	$\Sigma n_i = 1$	$\Sigma X_i = 0.364$

Table VII - Number of primary vacancies and fraction of L x-rays per total number of vacancies in the decay of Pb^{210}.

From the ratio X_1/n_1, we get o, = 0.118 ± 0.011, a result slightly greater than that of Ref. 21.

For calculating the other fluorescence and CK yields we have adopted the following experimental results: v, = 0.417 ± 0.015 and f_{23} = 0.164 ± ± 0.016. These values were determined by Rao *et al.*[26] from Bi^{207} decay. These results are extracted from L x-rays in coincidence with the $K_{\alpha 2}$ line of Pb^{207}. The total spectrum gives v„ and the L, + L, fraction of the spectrum allows the determination of f_{23}.

In the Bi x-ray spectra the $L_I L_{III}$ transition (2.96 keV) was not clearly observed due to bad statistics and poor resolution. On the basis of our results in Np, we supposed that the L,$L_{III}/(L_I N_{II} + L_I N_{III}$ + L,Q) branching ratio is not different from the theoretical[30] ratio, namely 0.145. This assumption gives an intensity estimate of 1.1 for the $L_I L_{III}$ transition. Accordingly, an increase of about 2% was made in f_{23} to account for the radiative component of the Coster-Kronig transition. This results in the adoption of the value 0.61 ± 0.03 for f_{13} in order to incorporate both radiation and radiationless transitions. This choice is otherwise relatively irrelevant for the determination of the other unknown quantities.

Finally, we get: $f_{12} = 0.093 \pm 0.009$, o, $= 0.364 \pm 0.027$, o, $= 0.320 \pm$ ± 0.018 and the Auger yields $a_i = 0.18 \pm 0.02$, a, $= 0.472 \pm 0.038$ and $a, = 0.680 \pm 0.020$.

Our value of o, is very different from that of Ref. 21 and in much better agreement with the systematic trend in this region of the periodic table. The value of f_{12} given in Ref. 21 is almost twice as large as ours, and consequently a, is also very different. Let us examine the possible reasons for such important discrepancies. First of all we note that the results of Ref. 21 based on f,, data from Ref. 26 imply v, $= 0.29$, although this value is in complete disaccord with that given in Ref. 26. This value of v, is also much lower than any experimental determination ever reported in the range $76 < Z \leq 96$. Since f_{23} is obtained from a section of the same spectrum that furnishes the value of v„ it is obvious that there is a serious internal inconsistency in the results of Freund and Fink.

The experimental approach of Freund and Fink is somewhat different from ours. They adopted the value of f_{23} given by Rao *et* al. and the three Auger electron intensities of Bashilov and Chervinskaya[27]. These intensities differ substantially from those of Haynes ***et*** *al.*[28] who have measured the L-Auger electron spectrum at 0.18% resolution in Pb^{210}, as can be seen in Table IV of Ref. 21. The difference is mainly in the intensities of the transitions to the L_{II} subshell. The fact that this intensity is lower by a factor of two in the set of values given by Haynes et al. than in the set of Bashilov *et* al. would give a much large result for the fluorescence yield o, if it were preferred by Freund and Fink. In Table VIII, the original results of Ref. 21 are given as well as the revised values obtained by using the electron intensities of Ref. 28. The recalculated value of ω_2 is now about 0.3, a little lower than neighboring values in Tl($\omega_2 = 0.319 \pm 0.010$) (Ref. 29) and Pb($\omega_2 = 0.363 \pm 0.015$) (Ref. 26). But the new value of v, $= 0.347$ is still very different from the experimental value that is compatible with the chosen value of f_{23}.

This residual disagreement comes from the X_2 intensities. Freund and Fink assumed for the most intense transition responsible for the filling of an L„ vacancy the intensity L,, M„ $= 0.5$ (L,,M_{IV} + L„, N„, $_{V}$) since these lines were not resolved by their spectrometer. In fact, the energy difference between the $L_{II}M_{IV}$ line and the doublet $L_{III}N_{IV,V}$ is only 49 eV.

	Present Work				Freund and Fink	
Assumptions / Yields	ν_2= 0.417 ± 0.015 f_{23}= 0.164 ± 0.016 f_{13}= 0.61 ± 0.03		A_i from ref. 28 f_{23}= 0.164 t 0.016		A. from ref. 28 f_{23}= 0.164 ± 0.016	A_i from ref. 27 f_{23}= 0.164 t 0.016
ω_1	0.118 I 0.011	(0.118)	0.118	(0.118)	0.095	0.095 ± 0.005
ω_2	0.364 ± 0.027	(0.366)	0.350	(0.353)	0.296	0.23 ± 0.02
ω_3	0.320 ± 0.018	(0.327)	0.319	(0.319)	0.310	0.345 ± 0.018
f_{12}	'0.093 ± 0.009	(0,092)	0.101	(0.099)	0.089	0.18 ± 0.02
f_{13}			0.635	(0.636)	0.662	0.58 ± 0.02
a_1	0.18 ± 0.02	(0.18)	0.147	(0.147)	0.115	0.133 ± 0.009
a_2	0.472 ± 0.038	(0.478)	0.486	(0.491)	0.540	0.61 ± 0.02
a_3	0.680 ± 0.020	(0.673)	0.681	(0.681)	0.690	0.655 ± 0.018
ν_2	-		0.402	(0.403)	0.347	0.29 ± 0.03
$\bar{\omega}_L$	0.364 ± 0.020		0.364		0.330	0.330 ± 0.016

Table VIII - Radiative and nonradiative yieids in Bismuth. The different assumptions are discussed in the text. Numbers in parenthesis correspond to take $f_{23} = 0.156$, a more recent value recommended by Rao et *al.*[33] for Z = 82.

They are also unresolved in our spectra. However, a better estimate of the intensities of the relevant $L_{\beta 1}$ line was possible.

It happens that the L, t L, group is due to transitions of electrons to the *L*„„ subshell. On the other hand, energetics of the L x-rays in Z = 83 allows an almost complete splitting of the L, group into three subgroups (see Figure 3). In the first subgroup, by order energy, there is essentially only one line, arising from electron jumps from N_{IV} to $L_{II}(\gamma_1)$. The second subgroup is mainly composed of transitions arising from the filling of vacancies in L, by electrons from the N subshells. The most conspicuous exception is the $L_{II}O_{IV}(\gamma_6)$ line. In the third subgroup we find essentially the $L_I O_{II,III}$ doublet (γ_4). These subgroups can be easily separated and the measured γ_1/γ_4 ratio divided by same ratio given in the theoretical paper of Scofield[30] gives a coefficient c,. If the theoretical branching ratios were correct this coefficient would be a constant for any pair of transitions of the type $L_{II}X/L_I Y$. We multiplied the theoretical relative intensity of the γ_6 line by c, and we were able to reproduce the intermediate subgroup (γ_2 t $\gamma_6 + \gamma_3$) after small adjustments. An analogous coefiicient

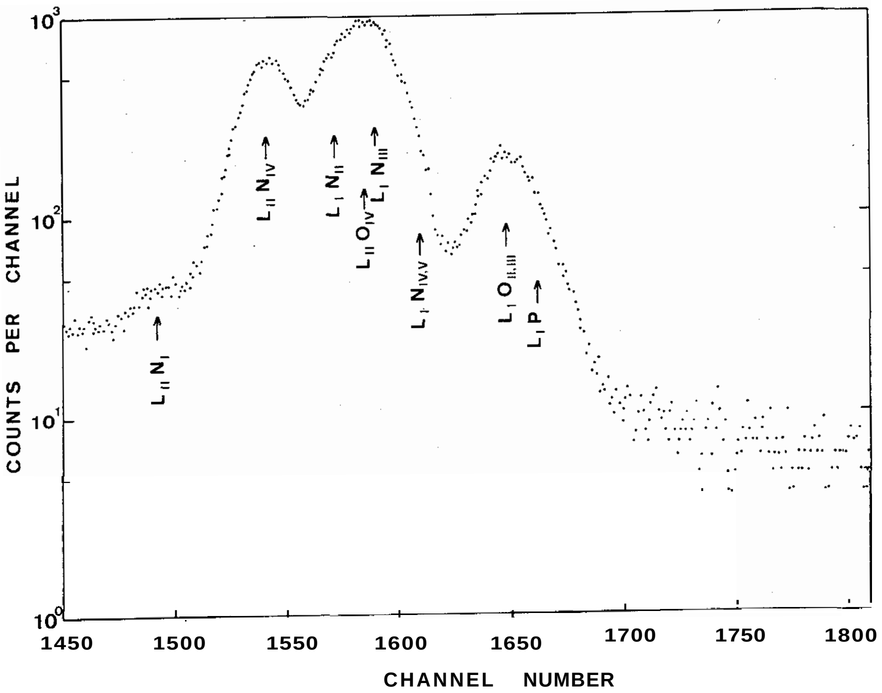

Fig. 3 - Fraction of the Bismuth L_γx-ray spectrum associated with the β-decay of Pb^{210} showing the Ly group.

c, was determined by comparing the ratio of the (L, + L,) groups to γ_4 with the correspondent theoretical ratio. The coefficients, c, (from the fitting of the L, group), c, and Scofield's branching ratios, were used as a zeroth order approximation to reproduce the very complex L_β group.

This procedure is a much more reasonable way of determining the $\beta_{2,15}/\beta_1$ ratio. We found 1.58 for this ratio, a value substantially different from unity, the value adopted by Freund and Fink. This difference is reflected in the value of X_2 which in Ref. 21 is 22% below our value.

As a test of consistency we recalculated our results using the f_{23} value of Ref. 26 and the Auger intensities of Ref. 28. After renormalizing these intensities to give a mean L-fluorescente yield of $\bar{\omega}_L = 0.364$, we got: A, = 0.132, A, = 0.089 and *A*, = 0.415. The A_i are quantities analogous to the $X_i's$ and $\Sigma(A_i + X_i) = 1$. The new set of values is equivalent to the previous one as shown in Table VIII, and, in particular, the experimental value of ν_2 is very well reproduced. This result seems to corroborate the electron intensities of Haynes *et al.*[28]. It is to be noted that the f_{12} yield is much nearer to the theoretical[20] values than some previous results in $Z = 82$ (Refs. 26, 29) and $Z = 83$ (Refs. 21, 31).

4. Conclusions

Table IX summarizes the most probable values for the radiative and nonradiative yields in Bi and Np. Numbers inside the parenthesis are estimated relative errors given in terms of percentage. All these values are consistent with the general experimental and theoretical trends obtained at $Z > 70$ with a few notable exceptions besides those discussed in the text.

Yields	Z = 93		Z = 83		Z = 83 (Theoretical)
ω_1	0.19	(10)	0.12	(10)	0.120
f_{12}	0.10	(20)	0.10	(10)	0.069
f_{13}	0.70	(10)	0.63	(5)	0.656
a_1	0.01	(100)	0.15	(15)	0.155
ω_2	0.49	(8)	0.37	(5)	0.417
f_{23}	0.22	(10)	0.15	(10)	0.101
a_2	0.29	(10)	0.48	(10)	0.482
ω_3	0.48	(5)	0.32	(5)	0.389
a_3	0.52	(5)	0.68	(5)	0.611
ν_2	0.60	(5)	-	-	0.456

Table IX - Most probable values for the radiative and nonradiative yields in Neptunium and Bismuth. Theoretical values of Mc Guire[18] are given for comparison.

The interpolated L_I-level theoretical values of Crasemann et *al.*[20] at $Z = 83$, namely $\omega_1 = 0.12$, $f_{12} = 0.09$, f_{1}, = 0.61 and a, = 0.18, do not differ significantly from Mc Guire's[18] results. The relative minimum around

Z = 79,80 suggested in both theoretical papers in the ω_1 vs. Z curve is strongly supported by our data but the need for more experimental work is obvious. On the other hand, we observe a marked decrease in the value of the Auger relative transition probability for very high values of the atomic number. The extrapolation of the theoretical results is very hazardous, notwithstanding that a value a, $\simeq$ 0.0 at $Z = 96$ does not seem to be indicated by the theoretical calculations of Mc Guire. The reason for this disagreement comes from the experimental determination of f_{13} since a, was obtained from the difference $1-\omega_1-f_{12}-f_{13}$. In both Refs. 18 and 20, the CK yield f_{13} increases by a factor of two between $Z = 74$ and $Z = 79$. However, Mc Guire's results suggest a decrease of f_{13} at $Z = 90$ not confirmed by our experimental result at $Z = 93$ which seems to incidcate a continuous rise in the value of f_{13}.

As a complementary result, we report in Table X some L subshell x-ray branching ratios and compare our values with the theoretical ratios of Scofield. Within the relatively large experimental errors, a generally good agreement is found. Some systematic[32] deviations are, however, confirmed; for instance, the L_l/L_α ratio is lower than the theoretical ratio, and the $L_{\beta 4}/L_{\beta 3}$ ratio lower in Z =83 and greater in Z =93 when compared with Scofield's results. Special care was taken in the determination of

Branching Ratios		Z = 83		Z = 93	
		Experimental	Theoretical[30]	Experimental	Theoretical[30]
L_I	$L_{\beta 4}/L_{\beta 3}$	0.824 ± 0.055	0.934	1.30 ± 0.17	1.186
	$L_{\gamma 4}/L_{\beta 3}$	0.109 ± 0.007	0.105	0.195± 0.025	0.157
L_{II}	$L_\eta/L_{\gamma 1}$	0.132 ± 0.017	0.132	0.104± 0.012	0.126
	$L_{\beta 1}/L_{\gamma 1}$	-	4.85	4.00 ± 0.17	4.38
	$L_{\gamma 5}/L_{\gamma 1}$	-	0.034	0.037± 0.004	0.034
	$L_{\gamma 6}/L_{\gamma 1}$	0.13 ± 0.03	0.131	0.215± 0.022	0.196
L_{III}	$L_\ell/L_{\alpha 1+\alpha 2}$	0.040 ± 0.002	0.054	0.058± 0.0025	0.063
	$L_{\beta 6}/L_\alpha$	0.014 ± 0.0015	0.013	0.017± 0.0018	0.016
	$L_{\beta 2,15}/L_\alpha$	-	0.195	0.216± 0.020	0.211
	$L_{\beta 5}/L_\alpha$	0.028 ± 0.002	0.025	0.031± 0.003	0.040

Table X - L-subshell branching ratios as compared with the theoretical values derived from the work of Scofield[30].

	Z = 83		Z = 93	
Branching Ratios	Experimental	Theoretical[30]	Experimental	Theoretical[30]
s_1	0.364	0.320	0.391	0.351
s_2	0.254	0.237	0.314	0.276
s_3	0.240	0.225	0.255	0.250

Table XI - The radiative decay branching ratios s_i : comparison of experimental and theoretical values for Z = 83 and 93.

the L_l/L_α ratio due to possible interference of the K-escape peak of the L, group with the L, peak. To reduce limitations due to resolution that introduce large errors in the branching ratios we calculated (Table XI) the radiative decay branching ratios s_i, as defined by Rao *et al.*[32]. They correspond for each subshell L,, to the ratio of the intensities of all x-rays originating from electron transitions from $N + O + \ldots$ subshells to intensities of all x-rays originating from electron transitions from M-subshells. For Z = 83, we confirm the suggestion presented in Ref. 32 that transitions involving outer-shell (N, O...) electrons compared to inner-shell (M) electrons are underestimated in the relativistic Hartree-Fock-Slater calculations of Scofield. For $Z = 93$, this discrepancy is apparent except in the s_3 ratio.

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