K AND L SHELL FLUORESCENCE AND AUGER YIELDS AND AUGER ELECTRON SPECTROSCOPY

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K AND *L* SHELL FLUORESCENCE AND AUGER YIELDS AND AUGER ELECTRON SPECTROSCOPY (*)

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Résumé. — Nous passons en revue nos calculations récentes de la fluorescence des couches *K* et *L*, ainsi que des débits de Coster-Kronig. Les rapports théoriques de l'intensité d'électrons *KLL* sont comparés avec les dépouillements expérimentaux. Enfin, nous comparons les spectres de l'intensité électronique pour des transitions d'Auger et Coster-Kronig, provenant de la couche *L*, avec les mesures faites sur Ar et U.

Abstract. — Our recent calculations of *K* and *L* shell fluorescence and Coster-Kronig yields are reviewed. The computed *KLL* electron intensity ratios are compared with experiment. The *L*-shell Auger and Coster-Kronig electron intensity spectra are compared with measurements on Ar and U.

I. **Introduction.** — The approach we use in calculating Auger, Coster-Kronig and radiative transition rates is discussed elsewhere [1] but we will briefly review it here. First, we approximate the quantity $(-rV(r))$ of a Herman and Skillman [2] ion by a series of straight lines. This leads to an exactly solvable one-electron Schrdöinger equation with a piecewise continuous potential. This exactly solvable equation leads to an eigenvalue equation for bound orbitals. Thus we have two sets of eigenvalues, those of Herman and Skillman and those of our approximation. These two can be brought in reasonable agreement by varying the number and location of the straight lines in the approximation. In addition one has the ESCA [3] tabulation of ionization thresholds. Thus three sets of values. A comparison of the three for Th ($Z = 90$) is shown in Table I. It is clear that the departure of the model eigenvalues from those of Herman and Skillman is far smaller than the departure of both sets of one-electron eigenvalues from the experimental thresholds. How will this affect the calculations ? For the Auger and radiative yields we use the model orbitals and eigenvalues to compute the transition rates. We then plot the computed Auger transition rates and radiative oscillator strengths against a significant energy difference, generally the energy difference of the strongest radiative transition. We then use the experimental value [4] of the energy for the strongest radiative transition to determine Auger transition rates and oscillator strengths with which we then do the yield calculations. The energy of the Auger electron E_c is given (in a one-electron picture) by

$$E_c = -E^z_{nl} + E^z_{n'l'} + E^{z+1}_{n''l''}$$

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TABLE I

Eigenvalues of Herman and Skillman, model and ESCA ionization thresholds

Level	$-E_{HS}$ (Ry)	$-E_{model}$ (Ry)	$-E_{ESCA}$
1 s	7.104	7 233	8 063
2 s	1 243	1 205	1 505
2 p	1 206	1 188	1 403 — 1 167
3 s	316	318	381
3 p	297	302	355-298
3 d	261	252	257-245
4 s	81.1	84.2	97.8
4 p	72.2	75.4	85.9-71.2
4 d	55.5	54.9	52.5-49.8
4 f	31.9	33.7	25.3-24.6
5 s	19.1	20.4	21.3
5 p	15.6	16.7	16.8-13.4
5 d	9.5	9.6	7.0-6.5
6 s	3.86	4.00	4.41
6 p	2.79	2.90	3.60-3.16
6 d	1.18	1.20	0.15
7 s	0.823	0.717	

where one starts with an nl hole and ends with $n'\ l'$ and $n''\ l''$ holes. However, in Coster-Kronig transitions $n' = n$ and whether a particular transition is allowed depends significantly on the energy values used to determine E_c. For this reason in computing Coster-Kronig transition rates we used the ESCA ionization thresholds in place of the model eigenvalues. We did no calculations for $E_c > 1\,500$ Ry. as relativistic effects become important.

II. **The Fluorescence and Coster-Kronig Yields.** — In figure 1 we show our calculated *K*-shell fluorescence yields for $18 \leqslant Z \leqslant 54$, some recent measurements, and some older ones [5]. In no case does the best recent measurement differ from the calculation by more than

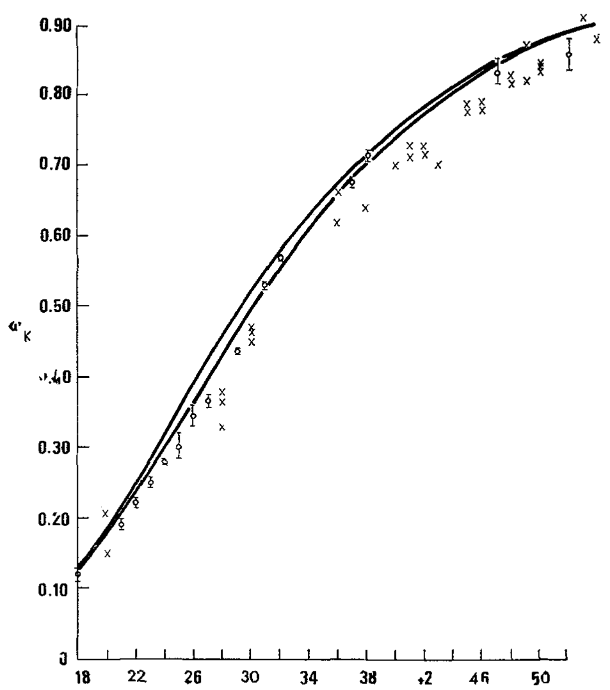

FIG. 1. — ω_K vs Z. The higher solid curve is our calculation without correction to experimental energies; the lower solid curve includes the correction. The points with error bars are recent measurements while the crosses are from Ref. 5.

8 %. Characteristically the computed ω_K values are higher than experiment. In figure 2 we compare the computed L-shell ω_3 value with measured ω_3 values for $Z > 66$ and ω_{KL} values for $Z < 66$. Agreement between the two sets of ω_3 values is reasonable. However, there appears to be a significant disagreement between experimental values, dependent on how the L_3 hole is made. That is, ω_3 obtained following nuclear beta decay is generally lower than ω_3 following X-ray ionization of the L-shell. At $Z = 80$, Rao and Crasemann [6] measure $\omega_3 = 0.40 \pm 0.02$ following X-ray ionization; Palms, Wood, Rao, and Kostroun [7] measure $\omega_3 = 0.30 \pm 0.01$ following beta decay. The two groups overlap in personnel but their measurements do not overlap. In figure 3 we compare the calculated ω_1 and ν_1 values with some experimental values, and in figure 4 we compare the calculated f_{12} and f_{13} values with experiment. The data is scanty but agreement is reasonable.

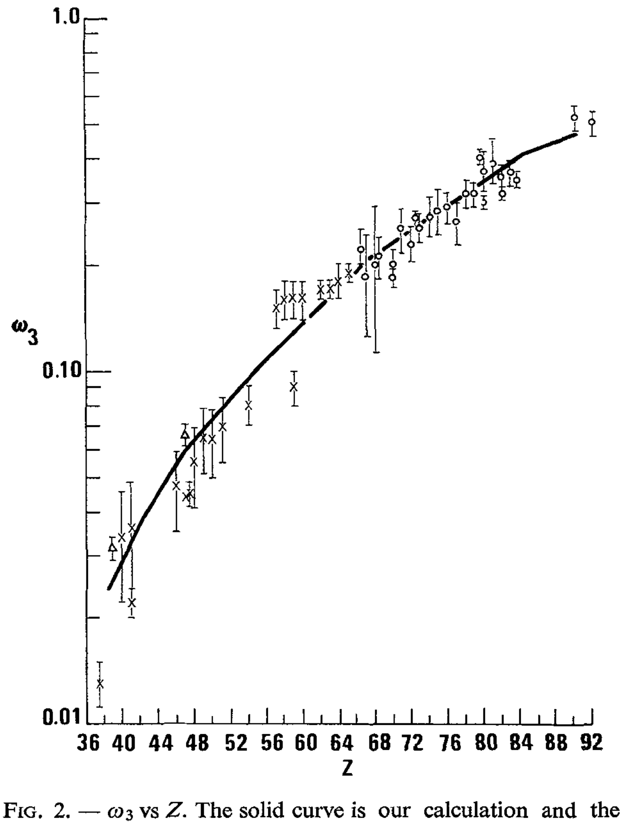

FIG. 2. — ω_3 vs Z. The solid curve is our calculation and the points are measured values of ω_3 and ω_{KL}.

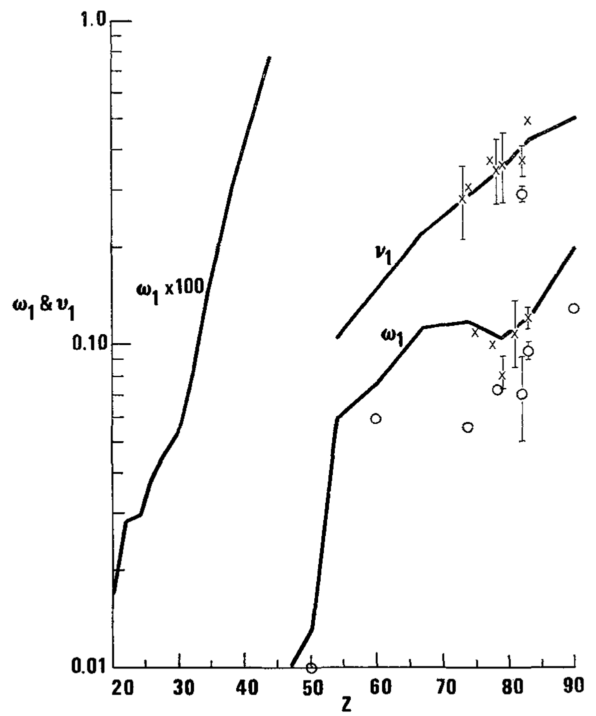

FIG. 3. — ω_1 and ν_1 vs Z. The experimental points are from Ref. 5.

III. **Auger and Coster-Kronig electron spectroscopy.** — In figure 5 we plot the ratio of intensities for $KL_1 L_1/\Sigma$, $KL_1 L_{2,3}/\Sigma$ and KL_{23} L_{23}/Σ where Σ is the total KLL transition rate. The curves A, B and C are our calculations, A′, B′ and C′ are Callen's [8] hydrogenic calculations, the open symbols are measurements, and the solid symbols are other calculations. Agreement between our calculations and experiment is good for $18 \leqslant Z \leqslant 54$. Above $Z = 54$ relativistic effects are important. For $9 \leqslant Z \leqslant 12$ there is a significant difference, but so long as the measurements are of relative intensities only one cannot tell whether the calculated KL_{23} L_{23} intensity is too low or the KL_1 L_{23} is too high.

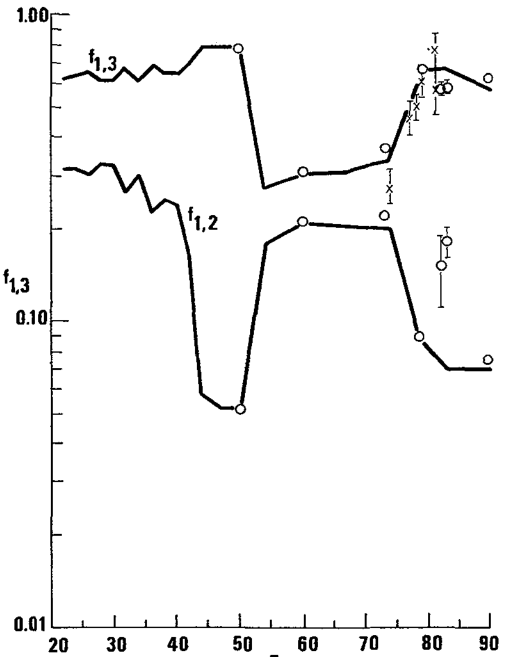

FIG. 4. — The L-shell Coster-Kronig yields $f_{1,2}$ and $f_{1,3}$ vs Z. The experimental points are from Ref. 5.

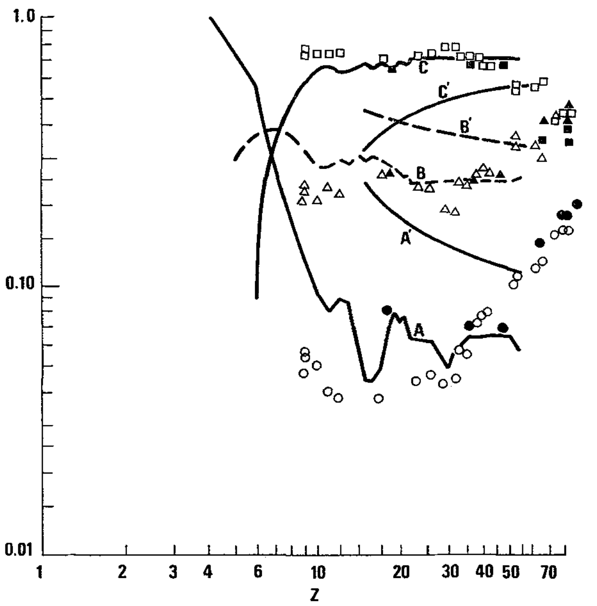

FIG. 5. — The ratio of $KL_1 L_1$ (A and A'), $KL_1\ L_{23}$ (B and B') and $KL_{23} L_{23}$ (C and C') transition rates to the total transition rate. A, B and C are our calculations, A', B' and C' are from Ref. 8, the open points are experimental measurements and the solid points are other calculations.

There are far fewer measurements of electron intensities following decay of an L-shell hole. In Table II we compare relative intensities computed for Th with those measured by Zender, Pou, and Albridge [9] for U. The first column contains L_1 and L_2 Coster-Kronig transition intensity ratios and L_3 Auger intensity ratios. The computed total intensity for each group has been normalized to the total experimental intensity for each group. Agreement is not

TABLE II

Electron intensities for L-shell decay in uranium. See text for normalization

Term	Meas.	Comp.	Group.	Meas.	Comp
$L_1 L_3 M_4$	73.	66.	1	3.6	1.8
$L_1 L_3 M_5$	103.	85.	2	2.5	2.9
$L_1 L_3 N_4$	11.	8.7	3 + 4	5.1	4.0
$L_1 L_3 N_5$		10.9	5	4.0	1.4
$L_1 L_3 N_{6,7}$	6.7	20.5	7	3.4	7.5
$L_1 L_3 O_{2,3}$	1.3	1.0	8	2.5	2.1
$L_1 L_3 O_{4,5}$	1.6	4.0	9	5.1	1.7
$L_3 M_1 M_3$	3.3	2.3	11 + 12	2.0	6.4
$L_3 M_2 M_3$	4.1	4.9	13	1.4	1.1
$L_3 M_2 M_5$	2.3	3.8	14	3.0	5.0
$L_3 M_3 M_3$	8.0	7.5	15	1.8	7.6
$L_3 M_3 M_4$	9.2	7.4	16	5.2	0.7
$L_3 M_3 M_5$	9.9	12.4	17	1.6	4.1
$L_3 M_4 M_4$	1.9	1.1	18	14.	13.6
$L_3 M_4 M_5$	22.	21.	20	2.8	3.0
$L_3 M_5 M_5$	13.	15.	21	2.0	2.1
$L_3 M_1 N_1$	1.7	0.77	22	9.5	9.4
$L_2 L_3 N_1$	46.	10.3	23	5.5	8.2
$L_2 L_3 N_2$	35. (46)	55.	Remainder	27.	24.3
$L_2 L_3 N_3$	101. (35)	25.			
$L_2 L_3 N_4$	45. (101)	99.			
$L_2 L_3 N_5$	(45)	27.			
$L_2 L_3 N_{6,7}$	8.	13.			
$L_2 L_3 O_2$	12.	12.			
$L_2 L_3 O_{4,5}$	4.7	24.			

unreasonable. The L_1 Coster-Kronig and L_3 Auger electron peaks are isolated but the L_2 Coster-Kronig peaks overlap the M Auger spectrum. The groups in the second column are combinations of electron peaks arising from various L-shell transitions. To compute the intensity values we used the normalization found from the isolated L_1 Coster-Kronig and L_3 Auger peaks in column 1, but were forced to discard the L_2 normalization. Groups 21 and 22 are identified as the $L_2\ M_4\ M_4$ and $L_2\ M_4\ M_5$ transitions respectively and we normalized the computed L_2 intensities to these peaks. The groups intensities were not further normalized and the agreement is not unreasonable. Again we justify the procedure because normalizing the L_2 intensities to the total L_2 Coster-Kronig intensity measurements leads to unreasonable results and because the L_2 Coster-Kronig peaks overlap the M Auger spectrum.

Mehlhorn [10] has measured the L_1 Coster-Kronig electron intensity spectrum from Argon. The computed results with three different sets of continuum electron energies, Rubenstein's results [11] and Mehlhorn's measured values are shown in Table III. Rubenstein's 2 s ionization energy is 287 eV, we use 355 eV, and the measured value is 326 eV. In Table III we list the calculated and experimental results normalized to a $L_1\ L_{23}\ M_{23}$ total intensity of 100. On this relative basis, of our three calculations the one called model agrees best with the data. However, it is clear that all the calculations either overestimate the total $L_1\ L_{23}\ M_1$ intensity or underestimate the total $L_1\ L_{23}\ M_{23}$ intensity. Fortunately, Mehlhorn has

TABLE III

Electron intensities and half-widths for L_1 Coster-Kronig decay in Ar

Term	Model $Ec(2\text{ p}, 3\text{ s}) = 15.6$ eV $Ec(2\text{ p}, 3\text{ p}) = 30.3$ eV	EXP* $Ec(2\text{ p}, 3\text{ s}) = 29.5$ eV $Ec(2\text{ p}, 3\text{ p}) = 44.0$ eV	ESCA $Ec(2\text{ p}, 3\text{ s}) = 40.0$ eV $Ec(2\text{ p}, 3\text{ P}) = 56.0$ eV	Ref. 11	Exp[10]
$L_1 L_{23} M_1$	70.2	95.6	122.0	102.0	26.3
$L_1 L_{23} M_{2,3}(S')$	17.6	23.8	30.4	17,8	22.9
(^3S)	13.3	17.0	20.2	11.5	10.4
$('D)$	16.3	12.8	9.5	15.2	15.2
$(^3D_1)$	10.5	9.3	8.0	11.1	10.4
$(^3D_2)$	17.6	15.4	13.3	18.5	17.1
$(^3D_3)$	24.6	21.6	18.6	25.9	24.1
$\Gamma(L_1 L_{23} M_1)$ (eV)	1.64	1.45	1.33	1.40	0.38
$\Gamma(L_1 L_{23} M_{23})$ (eV)	2.34	1.53	1.09	1.37	1.46

measured the half-width ($\Gamma = \hbar A_T$, where Γ is the halfwidth and A_T is the total transition rate), with which we can compute experimental absolute transition rates. This is also included in Table III. Some important features appear : (1) the total $L_1 L_{23} M_1$ intensity is relatively insensitive to variation of L_1 ionization threshold and E_c ; (2) the total $L_1 L_{23} M_{23}$ intensity is very sensitive to such variation ; (3) the calculation EXP* with observed continuum electron energy agrees best with the measured $L_1 L_{23} M_{23}$ halfwidth ; (4) all the calculations of the $L_1 L_{23} M_1$ halfwidth are much greater than the experimental value. Clearly the calculations overestimate the $L_1 L_{23} M_1$ total Coster-Kronig intensity. This may indicate that the difference between calculated and experimental intensity ratios (Fig. 5) in the *KLL* electron spectrum for $9 \leqslant Z \leqslant 12$ is due to an overestimate in the calculation of the $KL_1 L_{23}$ intensity ratio.

IV. **Conclusions.** — At the present time the calculations on Auger and radiative decay processes has been done for the *K* and *L* shell. We plan to extend the calculations to the *M* shell in the immediate future but there is almost no data, either on yields or electron spectra with which comparisons can be made. We would like to encourage such measurements. However, even without measurements, valuable information could be obtained from a critical evaluation of published Auger electron intensity halfwidths, as was shown by Mehlhorn.

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