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L-shell Auger and Coster-Kronig spectra from relativistic theory

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The intensities of L-shell Auger and Coster-Kronig transitions in heavy atoms have been calculated relativistically. A detailed comparison is made with measured Auger spectra of Pt and U. The pertinent transition energies were computed from relativistic wave functions with inclusion of the Breit interaction, self-energy, a vacuum-polarization correction, and complete atomic relaxation. Multiplet splitting is found to distribute Auger electrons from certain transitions among several lines. The analysis leads to reassignment of a number of lines in the measured spectra. Lines originally identified as L_2-L_3N_i in the U spectrum are shown to arise from $M_{4,5}$ Auger transitions instead. The effect of relativity on L_3-MM Auger-transition intensity ratios is studied; in some cases, these ratios are found to be affected by as much as 50% by the inclusion of relativity, while in others the ratios change little. This variation in response can be traced to the different factors through which relativity influences radiationless transition probabilities.

I. INTRODUCTION

Auger spectra that arise in the deexcitation of K-shell vacancies have been studied extensively, in theory and experiment.[1,2] Good agreement is attained between calculated and measured energies and intensities if configuration interaction in light atoms and relativistic effects in heavy atoms are included. In the medium range of atomic numbers, intermediate coupling with configuration interaction has been found to improve agreement between theory and experiment.[2,3]

By contrast, few measurements of L-shell Auger spectra have been performed, perhaps due to the great complexity of these spectra which contain numerous and often overlapping lines. On the theoretical side, some nonrelativistic calculations of L Auger spectra in j-j coupling exist,[1,2,4] but no relativistic calculations have been carried out heretofore.

We have computed theoretical relativistic L-shell Auger transition rates to the various final double-hole configurations in j-j coupling, for heavy elements.[5] In the present paper, we test these relativistic rates in conjunction with calculated relativistic L-shell Auger transition energies,[6] by analyzing available experimental data.[7,8] We further investigate the importance of relativity in the intensities of L Auger transitions, over the range of atomic numbers $70 \leq Z \leq 96$.

II. COMPARISON OF CALCULATED AND MEASURED L AUGER SPECTRA OF Pt AND U

The Auger and Coster-Kronig rates were calculated in j-j coupling from perturbation theory, assuming frozen orbitals, using relativistic Dirac-Hartree-Slater (DHS) wave functions. A detailed description of the theory is given elsewhere.[9]

A test of the present calculations of radiationless-transition probabilities and relativistic computations of transition energies[6] is made possible by the detailed experimental studies of the platinum and the uranium L Auger spectra due to Toburen and Albridge[7] and Zender *et al.*,[8] respectively. The magnitude of relativistic effects in the theory can furthermore be assessed by comparing the present calculations with the nonrelativistic work of McGuire.[4]

A. Platinum

The L-shell Auger spectrum of Pt is detailed in Table I. To facilitate comparison with experiment, we have numbered the lines as in the work of Toburen and Albridge.[7] The theoretical Auger-electron energies were computed with the program described in Ref. 6. Relativistic Dirac-Hartree-Slater wave functions served as zeroth-order eigenfunctions to compute the expectation of the total Hamiltonian. A first-order correction to the local approximation was thus included. Complete relaxation was taken into account. The Breit interaction, the self-energy, and a vacuum-polarization correction were included. The multiplet splitting of some of the lines is also incorporated in Table I.

The theoretical transition rates were normalized to the total experimental intensity of the group of lines from L_3-M_1M_2 through L_3-M_3M_5 (lines 1a through 4c). The transition rates for Hg from the

TABLE I. L Auger spectrum of Pt.

Line number[a]	Transition	J	Energy (keV) Calculated[b]	Energy (keV) Measured[a]	Relative intensity Calculated[b]		Relative intensity Measured[a]
1*a*	L_3-M_1M_2	1	5.151	5.124	0.119	0.12	1.5 ± 0.8
		0	5.170		0.001		
1*b*	L_3-M_2M_2	0	5.417	5.442	0.01		1.0 ± 0.8
1*c*	L_3-M_1M_3	1	5.516	5.520	3.81	6.8	4.1 ± 0.35
		2	5.553		2.99		
2	L_3-M_2M_3	2	5.804	5.783	7.97	11.5	12 ± 0.3
		1	5.814		3.53		
3*a*	L_3-M_1M_4	2	5.972	6.014	0.72	2.3	2.3 ± 1.5
		1	5.981		0.15		
	L_3-M_1M_5	2	6.048		0.68		
		3	6.062		0.75		
3*b*	L_3-M_3M_3	0	6.172	6.176	3.68	14.6	17.1 ± 1.5
		2	6.192		10.92		
3*c*	L_3-M_2M_4	1	6.236	6.266	0.47	0.6	0.7 ± 0.7
		2	6.271		0.13		
	L_3-M_2M_5	3	6.327	6.313	3.73	4.8	3.7 ± 1.0
		2	6.334		1.07		
4*a*	L_2-M_1M_1	0	6.571	6.580	0.1		1.0 ± 0.8
4*b*	L_3-M_3M_4	0	6.630	6.623	0.89	15.4	14.9 ± 1.0
		1	6.630		3.16		
		2	6.641		3.62		
		3	6.629		7.73		
4*c*	L_3-M_3M_5	1	6.695	6.693	6.07	21.0	18.9 ± 0.9
		2	6.724		2.21		
		3	6.705		12.67		
		4	6.735		0.05		
5*a*	L_2-M_1M_2	1	6.857	6.751	2.69	3.3	2.2 ± 1.6
		0	6.876		0.61		
5*b*	L_3-M_4M_4	0	7.055	7.057	0.31	2.2	(1.4) } 13.0 ± 3
		2	7.078		1.89	} 5.7	
5*c*	L_2-M_2M_2	0	7.123	7.114	3.5		(11.6)
5*d*	L_3-M_4M_5	1	7.150	7.170	0.47	42.1	34.6 ± 4
		2	7.154		4.22		
		3	7.165		4.94		
		4	7.149		28.71		
	L_1-M_1M_1	0	7.187		3.75		
5*e*	L_3-M_5M_5	0	7.212	7.224	1.26	27.6	18.4 ± 2.2
		2	7.233		5.89		
		4	7.242		19.87		
	L_2-M_1M_3	1	7.222		0.45		
		2	7.259		0.14		
6*a*	L_1-M_1M_2	1	7.473	7.462	1.92	2.01	1.0 ± 0.7
		0	7.492				
	L_3-M_1N_1	0	7.471		0.09		
		1	7.482		0.0004		
6*b*	L_1-M_1M_2	0	7.492	7.507	0.59	9.4	7.8 ± 0.6
	L_2-M_2M_3	2	7.510		5.61		
		1	7.520		3.19		
7*a*	L_3-M_1N_2	1	7.594	7.652	0.03	3.2	2.8 ± 0.8
		0	7.595		0.00		
	L_2-M_1M_4	2	7.678		0.71		
		1	7.687		0.16		
	L_3-M_1N_3	1	7.685		1.01		
		2	7.688		0.73		
	L_1-M_2M_2	0	7.739		0.007		
	L_3-M_2N_1		7.755		0.04		
	L_2-M_1M_5	2	7.754		0.10		
		3	7.768		0.43		

TABLE I. (*Continued*)

Line number[a]	Transition	J	Energy (keV) Calculated[b]	Energy (keV) Measured[a]	Relative intensity Calculated[b]		Relative intensity Measured[a]
7*b*	L_1-M_1M_3	1	7.838	7.833	2.09		1.9 ± 0.3
7*c*	L_1-M_1M_3	2	7.875		2.01		
	L_3-M_2N_2	0	7.866		0.004		
		1	7.878		0.002		
	L_3-M_1N_4		7.877	7.883	0.081	2.4	2.7 ± 0.3
	L_2-M_3M_3	0	7.878		0.11		
		2	7.898		0.082		
	L_3-M_1N_5		7.895		0.12		
7*d*	L_2-M_2M_4	1	7.942	7.940	4.0		4.0 ± 0.7
		2	7.977	7.966	0.76	2.6	1.0 ± 0.4
	L_3-M_2N_3		7.965		1.8		
7*e*	L_2-M_2M_5	3	8.033	8.030	4.55	6.9	6.0 ± 0.6
		2	8.040		2.35		
8*a*	L_1-M_2M_3	2	8.126		0.05		
		1	8.136		0.006		
	L_3-M_3N_1	1	8.133	8.124	0.93	2.0	2.0 ± 0.7
		2	8.136		0.81		
	L_3-M_1N_6		8.141		0.07		
	L_3-M_1N_7		8.145		0.13		
8*b*	L_3-M_2N_4		8.156	8.192	0.13	0.9	1.1 ± 0.6
	L_3-M_2N_5		8.173		0.77		
	L_3-M_3N_2		8.253	8.249	2.5		2.0 ± 0.7
	L_1-M_1M_4	2	8.294	8.299	2.73	3.4	4.9 ± 0.5
		1	8.303		0.67		
	L_2-M_3M_4	0	8.338		0.18		
		1	8.336		0.33		
		2	8.346		0.38		
		3	8.335	8.342	3.50	10.1	7.7 ± 0.5
	L_3-M_3N_3	0	8.335		1.42		
		1	8.350		0.024		
		2	8.343		4.20		
		3	8.350		0.054		
	L_1-M_1M_5	2	8.370	8.370	3.25	4.0	1.6 ± 0.4
		3	8.384		0.75		
	L_3-M_2N_6		8.420		0.07		
	L_3-M_2N_7		8.423		0.19		
	L_2-M_3M_5	1	8.401	8.433	0.29	0.9	2.0 ± 0.4
		2	8.430		0.002		
		3	8.411		0.34		
		4	8.441		0.009		
9	L_1-M_3M_3	0	8.494		0.12		
		2	8.514	8.535	0.003	7.5	5.1 ± 1.0
	L_3-M_3N_4		8.536		3.15		
	L_3-M_3N_5		8.554		4.23		
	L_1-M_2M_4	1	8.558		0.17		
		2	8.593	8.593	0.004	0.4	0.7 ± 0.2
	L_3-M_4N_1		8.584		0.22		
10*a*	L_1-M_2M_5	3	8.649		1.34		
		2	8.656	8.645	0.01	1.7	1.0 ± 0.3
	L_3-M_5N_1		8.664		0.35		
	L_3-M_4N_2		8.702	8.742	0.14	0.66	0.3 ± 0.2
	L_2-M_4M_4	0	8.760		0.52		
10*b*		2	8.784		3.77		
	L_3-M_5N_2		8.782		0.99		
	L_3-M_4N_3		8.795	8.780	2.28	7.68	5.9 ± 0.8
	L_3-M_3N_6		8.799		0.29		
	L_3-M_3N_7		8.803		0.35		

TABLE I. (*Continued*)

Line number[a]	Transition	J	Energy (keV) Calculated[b]	Energy (keV) Measured[a]	Relative intensity Calculated[b]	Relative intensity Calculated[b] (group)	Relative intensity Measured[a]
10c	L_2-M_4M_5	1	8.856		0.22		
		2	8.860		0.34		
		3	8.871	8.852	1.85	20.2	15.2 ± 0.7
		4	8.855		14.28		
	L_3-M_5N_3		8.875		3.50		
	L_2-M_5M_5	0	8.918	8.917	0.1		0.2 ± 0.15
		2	8.940		0.41		
		4	8.948		0.32		
	L_1-M_3M_4	0	8.952	8.957	0.02	1.4	1.7 ± 0.4
		1	8.952		0.03		
		2	8.963		0.03		
		3	8.951		0.41		
	L_3-M_4N_4	0	8.974		0.13		
10d	L_3-M_4N_4	1	8.989		0.003		
		2	8.982		0.66		
		3	8.989		0.02		
	L_3-M_4N_5		9.002	9.002	5.89	6.8	6.4 ± 0.5
	L_1-M_3M_5	1	9.017		0.01		
		3	9.027		0.19		
10e		2	9.046		0.02		
		4	9.057	9.070	0.09	16.1	11.3 ± 0.4
	L_3-M_5N_4		9.065		7.06		
	L_3-M_5N_5		9.083		8.94		
	L_2-M_1N_1		9.185		0.03		
	L_3-M_4N_6		9.250	9.216	0.15	0.68	0.65 ± 0.6
	L_3-M_4N_7		9.252		0.50		
11a	L_2-M_1N_2		9.300		0.52		
	L_3-M_5N_6		9.329	9.336	1.57	3.6	2.1 ± 1.0
	L_3-M_5N_7		9.334		1.51		
11b	L_2-M_2N_1		9.461	9.466	0.86	6.3	6.9 ± 0.6
	L_1-M_4M_5		9.477		5.48		

[a] Reference 7.
[b] Present work.

present calculations were used in the comparison; these are not expected to differ appreciably from those for Pt in relative magnitude. The measurements had been made with a source of radioactive ^{195}Au which decays to ^{195}Pt; the experimental vacancy distribution[7] L_1:L_2:L_3 = 0.840.56 : 1.09 was used in calculating predicted relative line intensities.

The line identification in Table I is based on the present theoretical work. From lines 1a through 5e, this identification coincides with that originally given by Toburen and Albridge.[7] That early analysis was based on energies calculated from a simple "$Z+1$ rule." From line 6a on, sometimes drastic changes in the identification of line components are dictated by the new calculations. For example, according to Toburen and Albridge, line 7b comprises the entire L_1-M_1M_3 transition. The calculated relative intensity of this transition is 4.1, or twice the measured intensity of 1.9 ± 0.3. Line 7c was identified by Toburen and Albridge[7] as consisting of the L_2-M_3M_3 and L_3-M_2N_2 transitions; these transitions have a calculated total intensity of 0.2 while the measured intensity of line 7c is 2.7 ± 0.3. The new energy calculations permit us to resolve these discrepancies; they show that line 7b consists of only that component of the L_1-M_1M_3 transition that is coupled to $J=1$ in the final state, with a theoretical energy of 7.838 keV (measured energy 7.833 keV). The $J=2$ component of the L_1-M_1M_3 transition, with a calculated energy of 7.875 keV, blends into line 7c. The latter line contains the L_3-M_1N_4 and the L_3-M_1N_5 transitions as well, in addition to those ascribed to it by Toburen and Albridge, giving it a total theoretical relative intensity of 2.4; this agrees with the measured intensity of 2.7 ± 0.3.

Major intensity discrepancies that arise from the original Toburen-Albridge identification,[7] including those described in the preceding example are listed in Table II. These discrepancies have been removed in the light of the new relativistic

TABLE II. Summary of discrepancies that arise if the original Auger-line identifications of Ref. 7 are retained.

Line number or assignment	Relative intensity Theory[a]	Experiment[b]
7b	4.1	1.9 ± 0.3
7c	0.2	2.7 ± 0.3
8a	0.1	2.0 ± 0.7
8b	2.8	1.1 ± 0.6
L_3-M_3N_3, L_1-M_1M_5	9.7	1.6 ± 0.4
9	0.1	5.1 ± 1.0
L_3-$M_2O_{4,5}$, L_3-M_3N_4, L_1-M_2M_4, L_3-M_3N_5, L_3-M_4N_1	7.8	0.7 ± 0.2
L_3-M_5N_3	3.5	0.2 ± 0.15

[a] Present work.
[b] Reference 7.

energy and intensity calculations. It should be noted that often, as in the example described above, the j-j configurational average energies are not sufficient to make unambiguous assignments. We illustrate this importance of multiplet splitting by a further example. The calculated L_2-M_2M_4 average energy is 7.964 keV, and the L_3-M_2N_3 average energy is 7.965 keV. The measured spectrum contains two lines in this energy region, at 7.940 and 7.966 keV (Table I). Only after including the multiplet splitting do we find that the first of the observed lines must be due to the $J=1$ component of the L_2-M_2M_4 transition, with a calculated energy of 7.942 keV, while the $J=2$ component of this transition (7.977 keV) blends with the L_3-M_2N_3 Auger electrons (7.965 keV) to produce the line that is observed at 7.966 keV. A number of such cases can be found in Table I, where multiplet splitting distributes the Auger electrons from one given transition among several lines in the measured spectrum. We find that satisfactory agreement between the calculated and measured spectra is generally attained on the basis of the analysis given in Table I.

B. Uranium

The theoretical intensities in the uranium L Coster-Kronig and Auger spectra were normalized to the measured relative intensities from the work of Zender *et al.*[8] by matching the total intensity of the group of transitions from L_3-M_1M_3 through L_3-M_5M_5 (Table III); we used the experimental[8] initial L-vacancy distribution after Coster-Kronig transitions, viz., $L_1:L_2:L_3=0.20:0.27:0.51$. This method of normalization circumvents difficulties that could arise from the overlap of spectra revealed by the energy calculations: the L_1-L_3M_4 and L_1-L_3M_5 lines are mixed with certain M-shell Auger lines; the L_2-M_4M_4 lines are mixed with those from L_3-$M_4O_{4,5}$ transitions, and the L_2-M_4M_5 lines overlap with L_3-$M_5O_{4,5}$ lines.

The L_1 Coster-Kronig and L Auger spectra of U are listed in Table III. Theoretical energies were computed relativistically as described in Sec. II A for Pt. The energy separation between line groups is quite large in these spectra; hence multiplet splitting does not change any of the original[8] assignments. A number of changes in the earlier analysis[8] of these spectra are, however, indicated in the light of the new theoretical energies and intensities.

We note the following revisions of the analysis of Zender *et al.*,[8] incorporated in Table III: The L_2-M_1M_2 line coincides with the L_3-M_1N_1 line; the L_2-M_2M_2 and L_3-M_1N_3 transitions must be added to group 1, the L_1-M_1M_2 transition to group 2, the L_1-M_2M_5 transition to Group 18, the L_3-$M_4O_{4,5}$ transitions to group 21, and the L_3-$M_5O_{4,5}$ transitions to group 22. Changes in the original identification include the reassignment of the L_3-M_3N_5 transition to group 9 (instead of group 11) and of the L_1-M_1M_5 transition to group 16 (instead of group 15). Generally good agreement is then attained between theoretical and measured spectra, except that the calculated intensities of the strong L_1-L_3M_4 and L_1-L_3M_5 Coster-Kronig transitions appear to be too low. This discrepancy may arise in part from the fact that some M Auger lines cannot be resolved experimentally from these Coster-Kronig lines.

The difficulty of experimentally resolving the U L_2 Coster-Kronig spectra from M-shell Auger spectra has already been noted by McGuire.[4] In fact, we find that the tentative assignment[8] of the lines from L_2-L_3N_1 through L_2-L_3N_4 in the experimental spectrum is incorrect. The results of relativistic DHS energy calculations,[6] included in Table IV, show that these lines should be identified as M_5-$N_{4,5}N_{6,7}$, M_4-$N_{4,5}N_{6,7}$, M_5-$N_{6,7}N_{6,7}$, and M_4-$N_{6,7}N_{6,7}$.

In order to calculate the theoretical relative intensity of these $M_{4,5}$ Auger lines, we need the initial $M_{4,5}$ vacancy distribution. We use the experimental L vacancy distribution,[8] L-M x-ray transition rates from the work of Scofield,[10] our L fluorescence yields,[9] the L_1-L_3M Coster-Kronig transition rates from the present study, and the M-shell Auger transition rates of McGuire.[4] We find $M_4:M_5=0.56:0.81$ for the initial vacancy distribution, where M vacancies created by M-shell internal conversion have been neglected. With the M_4 and M_5 Auger transition rates computed by McGuire,[4] and using the same normalization as

TABLE III. L-shell Coster-Kronig and Auger spectra of uranium.

Line number[a]	Transition	Energy (keV) Calculated[b]	Energy (keV) Measured[a]	Relative intensity Calculated[b]		Relative intensity Measured[a]
	L_1-L_3M_4	0.724	0.68 ± 0.03	51.3		73 ± 20
	L_1-L_3M_5	0.911	0.92 ± 0.04	64.0		103 ± 20
	L_1-L_3N_1	3.084		4.1		mixed with L_2-L_3O_1 and L_2-L_3O_2
	L_1-L_3N_2	3.251		1.7		
	L_1-L_3N_3	3.490	3.48 ± 0.06	2.3		
	L_1-L_3N_4	3.754	3.77 ± 0.02	7.6	16.8	11 ± 2
	L_1-L_3N_5	3.800		9.2		
	L_1-L_3N_6	4.156	4.15 ± 0.02	5.2	11.5	6.7 ± 1.1
	L_1-L_3N_7	4.168		6.3		
	L_1-L_3O_1	4.236		1.0		
	L_1-L_3O_2	4.303	4.35 ± 0.03	0.4	0.9	1.3 ± 0.6
	L_1-L_3O_3	4.361		0.5		
	L_1-L_3O_4	4.460	4.47 ± 0.03	1.4	3.1	1.6 ± 0.6
	L_1-L_3O_5	4.473		1.7		
	L_3-M_1M_3	7.207	7.20 ± 0.02	3.9		3.3 ± 0.8
	L_3-M_2M_3	7.574	7.54 ± 0.02	6.6		4.1 ± 1.6
	L_3-M_2M_5	8.322	8.32 ± 0.02	2.1		2.3 ± 0.8
	L_3-M_3M_3	8.456	8.45 ± 0.01	7.8		8.0 ± 1.0
	L_3-M_3M_4	9.033	9.01 ± 0.01	8.3		9.2 ± 1.3
	L_3-M_3M_5	9.215	9.18 ± 0.01	10.5		9.9 ± 1.4
	L_3-M_4M_4	9.603	9.66 ± 0.03	1.1	1.2	2.1 ± 1.2
	L_2-M_1M_1	9.700		0.06		
	L_3-M_4M_5	9.780	9.75 ± 0.01	20.3		22 ± 2
	L_3-M_5M_5	9.959	9.93 ± 0.01	13.4		13 ± 1.4
	L_3-M_1N_1	10.094	10.11 ± 0.02	0.04	2.0	1.7 ± 0.3
	L_2-M_1M_2	10.094		1.97		
1	L_2-M_2M_2	10.451	10.49 ± 0.02	2.11	4.1	3.6 ± 0.8
	L_3-M_2N_1	10.471		0.01		
	L_3-M_1N_3	10.497		0.63		
	L_1-M_1M_1	10.522		1.36		
2	L_3-M_2N_3	10.875	10.90 ± 0.02	1.1	4.0	2.5 ± 0.6
	L_1-M_1M_2	10.916		2.8		
3 & 4	L_3-M_2N_5	11.185	11.3 ± 0.1	0.3	6.0	5.1 ± 1.3
	L_1-M_2M_2	11.273		0.00		
	L_3-M_1O_1			0.01		
	L_3-M_1O_2			0.00		
	L_2-M_2M_3	11.348		4.62		
	L_3-M_3N_1	11.351		1.04		
5	L_3-$M_1O_{4,5}$		11.53 ± 0.03	0.04		4.0 ± 1.0
	L_3-M_3N_2	11.520		1.54		
	L_2-M_1M_4	11.545		0.39		
	L_3-$M_2N_{6,7}$	11.542		0.22		
7	L_2-M_1M_5	11.723	11.79 ± 0.04	0.14	7.7	3.4 ± 2
	L_3-M_3N_3	11.757		3.3		
	L_1-M_1M_3	11.802		4.02		
	L_1-M_1O_3			0.25		
8	L_3-$M_2O_{4,5}$		11.91 ± 0.04	0.07	2.6	2.5 ± 1.2
	L_2-M_2M_4	11.930		2.43		
	L_3-M_4N_1	11.932		0.14		
9	L_3-M_3N_4	12.021	12.03 ± 0.04	1.9	4.3	5.1 ± 2.0
	L_3-M_3N_5	12.065		2.37		
11 & 12	L_2-M_2M_5	12.096	12.13 ± 0.05	3.06	3.5	2.0 ± 1.1
	L_3-M_4N_2	12.101		0.08		
	L_3-M_5N_1	12.108		0.31		
	L_1-M_2M_3	12.169		0.06		
13	L_3-M_5N_2	12.277			0.5	1.4 ± 0.8
14	L_1-M_1M_4	12.367	12.38 ± 0.05	2.75	4.5	3.0 ± 1.5
	L_3-M_4N_3	12.337		1.28		
	L_3-$M_3N_{6,7}$	12.422		0.46		

TABLE III. (*Continued*)

Line number[a]	Transition	Energy (keV) Calculated[b]	Energy (keV) Measured[a]	Relative intensity Calculated[b]		Relative intensity Measured[a]
15	L_3-M_3O_1			0.27	2.1	1.8 ± 1.0
	L_3-M_5N_3	12.513	12.51 ± 0.04	1.83		
16	L_1-M_1M_5	12.545	12.58 ± 0.04	3.45	4.2	5.2 ± 3.0
	L_3-M_3O_2			0.37		
	L_3-M_4N_4	12.604		0.41		
17	L_3-M_3O_3		12.64 ± 0.03	0.75	4.0	1.6 ± 0.9
	L_3-M_4N_5	12.645		3.22		
18	L_1-M_2M_4	12.752	12.8 ± 0.1	0.19	13.0	14 ± 2
	L_3-$M_3O_{4,5}$			0.83		
	L_2-M_3M_4	12.806		1.83		
	L_3-M_5N_4	12.778		3.87		
	L_3-M_5N_5	12.823		4.91		
	L_1-M_2M_5	12.918		1.33		
20	L_3-M_4O_1		13.14 ± 0.03	0.04	2.2	2.8 ± 0.5
	L_3-M_4O_2			0.02		
	L_3-$M_5N_{6,7}$	13.180		2.14		
21	L_2-M_4M_4	13.376	13.34 ± 0.04	1.79	2.4	2.0 ± 0.5
	L_3-$M_4O_{4,5}$	13.336[c]		0.66		
22	L_2-M_4M_5	13.553	13.51 ± 0.03	6.67	8.3	9.5 ± 2.2
	L_3-$M_5O_{4,5}$	13.512[c]		1.65		
	L_1-M_4M_4	14.198		0.17	6.1	5.5 ± 0.9
	L_3-N_1N_1	14.215		0.00		
	L_2-M_2N_1	14.244		0.53		
	L_2-M_1N_3	14.270		0.04		
	L_1-M_4M_5	14.375		4.43		
	L_3-N_1N_2	14.393		0.00		
	L_2-M_2N_2	14.416		0.92		

[a] Reference 8.
[b] Present work.
[c] Energies estimated by the $Z+1$ rule.

TABLE IV. Theoretical L_2-L_3N_i Coster-Kronig and $M_{4,5}$ Auger electron energies and transition rates for U compared with measurements.

Transition	Energy (keV) Theory[a]	Energy (keV) Experiment[b]	Relative intensity Theory[a]	Relative intensity Experiment[b]
L_2-L_3N_1	2.262	2.35 ± 0.02	0.41	
M_5-N_4N_6	2.334		63.3	46 ± 9
M_5-N_4N_7	2.342			
M_5-N_5N_6	2.374			
M_5-N_5N_7	2.388			
L_2-L_3N_2	2.430		3.4	
M_4-N_4N_6	2.510	2.51 ± 0.03	41.2	35 ± 9
M_4-N_4N_7	2.518			
M_4-N_5N_6	2.550			
M_4-N_5N_7	2.564			
L_2-L_3N_3	2.668		0.8	
M_5-N_6N_6	2.725	2.72 ± 0.02	111.0	101 ± 20
M_5-N_6N_7	2.735			
M_5-N_7N_7	2.748			
L_2-L_3N_4	2.933		3.0	
M_4-N_6N_6	2.901	2.87 ± 0.02	72.0	45 ± 11
M_4-N_6N_7	2.912			
M_4-N_7N_7	2.924			

[a] Present work. [b] Reference 8.

for the L spectra, we find the M Auger-line intensities listed in Table IV. Comparison of the theoretical intensities and energies with the measured values, also included in Table IV, clearly suggests that the lines originally identified as L_2-L_3N_i are, in fact, the $M_{4,5}$ Auger lines. The theoretical intensities of the L_2-L_3N_i Coster-Kronig transitions are so low that the corresponding lines probably were much too weak to be observed.

III. L_3-*MM* AUGER-TRANSITION RATIOS

Finally, we consider certain theoretical L_3-MM Auger-transition intensity ratios, as functions of atomic number, and compare them with experiment (Figs. 1–3). These ratios are free of uncertainties in the initial L-vacancy distributions. It appears that the present relativistic DHS results agree considerably better with experiment[7,8,11-17] than the predictions from nonrelativistic theory.[4] Figures 1–3 show that some of the intensity ratios, such as L_3-M_5M_5/L_3-M_4M_5, are not very sensitive to relativistic effects, while other intensity ratios (such as L_3-M_2M_3/L_3-M_3M_5) can change by as much as 50% when relativity is taken into account.

The fact that the inclusion of relativity fails to affect some Auger-transition probability ratios while others are substantially altered appears, at first, to be surprising. We note, however, that relativistic effects in Auger rates can proceed from several different sources: (i) the difference between relativistic and nonrelativistic wave functions; (ii) the inclusion of retardation in the electrostatic interaction; and (iii) the contribution

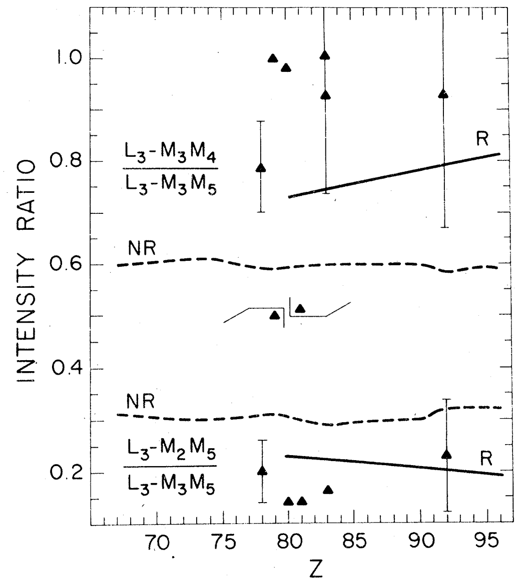

FIG. 2. Auger transition-probability ratios L_3-M_3M_4/L_3-M_3M_5 and L_3-M_2M_5/L_3-M_3M_5 as functions of atomic number. Predictions of the present, relativistic theory are plotted as solid curves; the results from nonrelativistic calculations (Ref. 4) are indicated by the broken curves. Experimental data are from Refs. 7, 8, and 11–17.

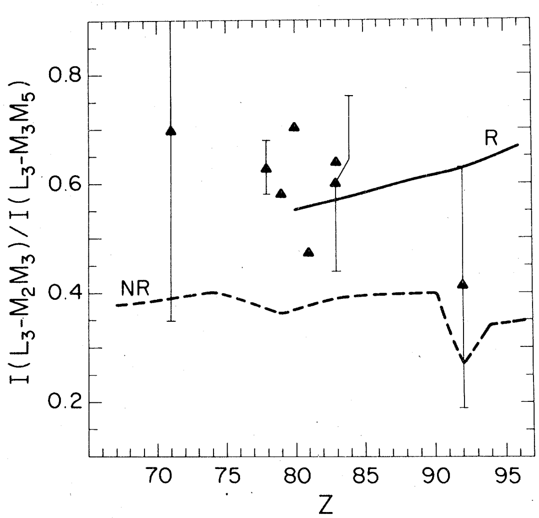

FIG. 1. Ratio of the L_3-M_2M_3 Auger transition probability to the L_3-M_3M_5 transition probability as a function of atomic number. The solid curve is the prediction of the present relativistic theory, and the broken curve is calculated from nonrelativistic theory (Ref. 4). Experimental results are from Refs. 7, 8, and 11–17.

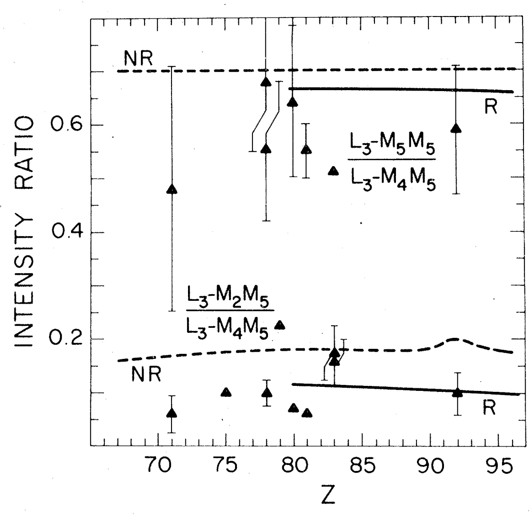

FIG. 3. Ratios of L_3-M_5M_5 to L_3-M_4M_5 and L_3-M_2M_5 to L_3-M_4M_5 Auger-transition probabilities as functions of atomic number. Relativistic predictions from the present work are indicated by the solid curves; the results of nonrelativistic calculations from Ref. 4 are shown by broken curves. Experimental data are from Refs. 7, 8, and 11–17.

from the retarded current-current interaction. The net effect on the transition rates depends on how these components add up. By comparing our retarded Coulomb matrix elements from relativistic calculations with nonrelativistic Coulomb matrix elements from Herman-Skillman (Hartree-Slater) wave functions, we are led to the following observations.

(i) For some transitions, such as L_3-M_3M_5, L_3-M_4M_5, and L_3-M_5M_5, the change in the contribution from the electrostatic interaction is more or less compensated by the contribution from the retarded current-current interaction, whence these transitions are not sensitive to the inclusion of relativity.

(ii) For L_2-M_4M_5 transitions, relativity reduces the Coulomb term. The contribution from the retarded current-current interaction is out of phase with the Coulomb term; this further reduces the transition rate.

(iii) For some transitions (e.g., L_3-M_2M_3, L_3-M_2M_5, and L_3-M_3M_4), the relativistic effect on the direct matrix elements is opposite from the effect on the exchange matrix elements. The direct and exchange matrix elements are out of phase for these transitions, therefore, the rates become very sensitive to the inclusion of relativity.

IV. CONCLUSION

Theoretical L-shell Auger and Coster-Kronig spectra of atoms with atomic numbers $70 \leq Z \leq 96$ have been computed relativistically. A detailed comparison with the measured L Auger spectra of Pt and U shows reasonable agreement, both in energies (to within 25 eV) and in relative intensities (to within 25% for strong lines). Analysis of the spectra shows that energy estimates from the $Z+1$ rule are often insufficient for line identification, and that multiplet splitting can distribute Auger electrons from one transition among several lines in the observed spectrum. Relativity is found to affect the intensity ratio of some L_3-MM Auger transitions in heavy atoms by as much as 50%.

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