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Energy Shifts and Transition Probabilities of L_γ X Rays from Bismuth with Multiple N Vacancies

Takeshi MUKOYAMA* and Shin ITO**

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The transition energies and probabilities of L_γ rays from bismuth atom with N-shell vacancies are calculated by the use of a Dirac-Fock computer program. The transition energies are obtained as the difference between total energies of the initial and final states. The L-x-ray emission rates are calculated in the relaxed-orbital approximation and all the possible multipoles are included. The calculations have been made for $L_{\gamma 1}$, $L_{\gamma 4}$ and $L_{\gamma 4'}$ x rays. The energy shifts for these x rays and the transition probabilities are listed and plotted as a function of the number of N-shell vacancies.

KEY WORDS: L_γ x rays in Bi/ Energy shifts and transition probabilities/ Multiple N-shell vacancies/

I. INTRODUCTION

It is well known that when the x-ray spectra in ion-atom collisions are observed with Si(Li) detectors, their peaks are broadened and shifted to higher-energy side of the diagram lines.[1] This is due to the satellite x rays emitted from the target with multiple vacancies. If there are outer-shell vacancies in addition to an inner-shell vacancy, they are not filled before the radiative transition takes place to the inner-shell vacancy and act as spectators for inner-shell x-ray emission. The existence of such outer-shell vacancies increases the binding energies of the inner-shell electron because of reduction in the screening effect for the nuclear charge and causes the energy shifts of x-ray lines. These satellite peaks can be partially resolved by the use of high-energy-resolution crystal spectrometers.[2]

In the case of the experiment with a Si(Li) detector, these satellite lines are, in general, not resolved from the diagram line due to poor energy resolution of the detector and the x-ray spectra show a single broadened line with a shifted centroid to higher-energy side. The magnitude of the energy shift and the change in the x-ray intensity depend on the number of spectator vacancies, i.e. the degree of multiple ionization. Theoretical estimation of x-ray energies for atoms with multiple vacancies can be obtained as the difference between total electron energies of the initial and final atomic states.[3]

Extensive experimental studies on energy shifts and transition probabilities of K x rays with multiple L- and M-shell vacancies by heavy-ion bombardments have been performed and the number of vacancies produced was deduced from comparison with the theoretical calculations.[4] However, in the case of L x rays, both experimental and theoretical investigations of energy shifts and change in transition rates for multiple-vacancy states are rather scarce. Uchai *et al.*[5] measured L-x-ray spectra from seven elements in the $70 \leqq Z \leqq 90$ range

* 向山 毅 : Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Kyoto, 606.
** 伊藤 真 : Radioisotope Research Center, Kyoto University, Kyoto, 606.

by 1-MeV/amu Ag-ion bombardments. They found that the observed L-x-ray intensity ratios are consistent with the theoretical values for a single L-shell vacancy,[6] if a statistical scaling factor[7] is multiplied. On the other hand, energy shifts of L x rays for a single M- or N-shell vacancy have been calculated by Parente *et al.*[8] and those for multiple M-shell vacancies have been published by Uchai *et al.*[9]

Recently we have studied $L\gamma$ x rays from Bi bombarded by O and Ne ions.[10] The degree of N-shell multiple ionization was estimated from the energy shifts of the L-x-ray transitions from O shells. However, there have been reported no theoretical calculations of L-x-ray energies and emission rates for atoms with multiple N-shell vacancies. In the present work, we present the transition energies and emission rates of $L\gamma_1$, $L\gamma_4$, and $L\gamma_{4'}$ x rays in Bi atoms with multiple N-shell vacancies. The Dirac-Fock computer program of Desclaux[11] is used for this purpose and the x-ray energies are obtained as the difference between the total energies of the initial and final configurations. The x-ray emission probabilities are calculated relativistically in the relaxed-orbital approximation and all the possible multipoles are included.

II. CALCULATION

Calculations have been made for the $L\gamma_1$ ($N_4 \rightarrow L_2$), $L\gamma_4$ ($O_3 \rightarrow L_1$), and $L\gamma_{4'}$ ($O_2 \rightarrow L_1$) x rays. The configuration-averaged total energies and electronic wave functions for Bi atoms with various configurations are obtained with the Dirac-Fock method.[11] For $L\gamma_4$ and $L\gamma_{4'}$ x rays, the electronic configurations with up to 20 spectator vacancies in the N_5, N_6 and N_7 shells are considered, while in the case of $L\gamma_1$ x rays those with up to 3 vacancies in the N_4 shell are treated. In the former case, outer N-subshell electrons are removed first, i.e. first from the N_7 shell, then form the N_6 shell, and finally from the N_5 shell. The effect of finite nuclear size is taken into account by treating the nucleus as a uniformly charged sphere.

The transition energies of the $L\gamma$ x rays are calculated from the difference between the total energies of the initial and final states. The energy shifts are determined by subtracting each L-x-ray energy without N-shell spectator vacancies from the corresponding values with multiple vacancies.

The calculations of the x-ray emission rates are made in the relaxed-orbital approximation, i.e. the different atomic potentials are used in the initial and final states. However, for simplicity, the exchange and overlap effects in the x-ray transition probability[12] are neglected. The relativistic formulation with the retardation effect for the x-ray transition probability[13] is used. All the multipoles possible in the transition are included.

III. RESULTS AND DISCUSSION

All the numerical computations in the present work have been performed on the FACOM M-780 computer in the Data Processing Center of Kyoto University. In Table I, the calculated L-x-ray energies and transition probabilities for a single vacancy, i.e. without spectator N vacancies, are listed and compared with the tabulated values. The present results for the transition energies are in agreement with the values of Bearden[14] within 0.2%. On the other hand, the difference between the present transition probabilities and those of Scofield[6] is 1.2% for $L\gamma_1$ x rays, about 5% for $L\gamma_{4'}$ rays, and about 3% for $L\gamma_4$ x rays. This discrepancy

Table I. Comparison of L-x-ray energies and transition probabilities with a single vacancy in Bi.

X ray	Energy (keV)		Probability (eV/$\hbar$)	
	Present	Bearden[a]	Present	Scofield[b]
$L_{\gamma 1}$	15.237	15.2477	0.4161	0.411
$L_{\gamma 4'}$	16.296	16.2709	0.02409	0.02532
$L_{\gamma 4}$	16.321	16.2947	0.02835	0.02928

[a] Ref. 14. [b] Ref. 6.

Table II. Energy shift ΔE and transition probability Γ of $L_{\gamma 1}$ x rays with multiple N_4-shell vacancies in Bi.

n	Initial	Final	Energy (keV)	ΔE (eV)	Γ (eV/$\hbar$)[a]
0	L_2^{-1}	N_4^{-1}	15.237	—	0.4161
1	$L_2^{-1}N_4^{-1}$	N_4^{-2}	15.247	10	0.4205
2	$L_2^{-1}N_4^{-2}$	N_4^{-3}	15.257	20	0.4261
3	$L_2^{-1}N_4^{-3}$	N_4^{-4}	15.268	31	0.4318

[a] Transition probability is calculated for the fully-occupied N_4 shell. The actual probability should be corrected for the number of N_4-shell electrons.

Table III. Energy shift ΔE and transition probability Γ of $L_{\gamma 4'}$ x rays with multiple N-shell vacancies in Bi.

n	Intial	Final	Energy (keV)	ΔE (eV)	Γ (eV/$\hbar$)
0	L_1^{-1}	O_2^{-1}	16.296	—	0.02409
1	$L_1^{-1}N_7^{-1}$	$N_7^{-1}O_2^{-1}$	16.310	13	0.02522
2	$L_1^{-1}N_7^{-2}$	$N_7^{-2}O_2^{-1}$	16.324	27	0.02638
3	$L_1^{-1}N_7^{-3}$	$N_7^{-3}O_2^{-1}$	16.339	42	0.02757
4	$L_1^{-1}N_7^{-4}$	$N_7^{-4}O_2^{-1}$	16.354	58	0.02878
5	$L_1^{-1}N_7^{-5}$	$N_7^{-5}O_2^{-1}$	16.371	75	0.03002
6	$L_1^{-1}N_7^{-6}$	$N_7^{-6}O_2^{-1}$	16.389	93	0.03128
7	$L_1^{-1}N_7^{-7}$	$N_7^{-7}O_2^{-1}$	16.407	111	0.03255
8	$L_1^{-1}N_7^{-8}$	$N_7^{-8}O_2^{-1}$	16.427	130	0.03385
9	$L_1^{-1}N_6^{-1}N_7^{-8}$	$N_6^{-1}N_7^{-8}O_2^{-1}$	16.448	151	0.03513
10	$L_1^{-1}N_6^{-2}N_7^{-8}$	$N_6^{-2}N_7^{-8}O_2^{-1}$	16.470	173	0.03643
11	$L_1^{-1}N_6^{-3}N_7^{-8}$	$N_6^{-3}N_7^{-8}O_2^{-1}$	16.493	196	0.03775
12	$L_1^{-1}N_6^{-4}N_7^{-8}$	$N_6^{-4}N_7^{-8}O_2^{-1}$	16.516	220	0.03909
13	$L_1^{-1}N_6^{-5}N_7^{-8}$	$N_6^{-5}N_7^{-8}O_2^{-1}$	16.541	244	0.04044
14	$L_1^{-1}N_6^{-6}N_7^{-8}$	$N_6^{-6}N_7^{-8}O_2^{-1}$	16.566	270	0.04181
15	$L_1^{-1}N_5^{-1}N_6^{-6}N_7^{-8}$	$N_5^{-1}N_6^{-6}N_7^{-8}O_2^{-1}$	16.595	299	0.04322
16	$L_1^{-1}N_5^{-2}N_6^{-6}N_7^{-8}$	$N_5^{-2}N_6^{-6}N_7^{-8}O_2^{-1}$	16.625	329	0.04464
17	$L_1^{-1}N_5^{-3}N_6^{-6}N_7^{-8}$	$N_5^{-3}N_6^{-6}N_7^{-8}O_2^{-1}$	16.656	359	0.04606
18	$L_1^{-1}N_5^{-4}N_6^{-6}N_7^{-8}$	$N_5^{-4}N_6^{-6}N_7^{-8}O_2^{-1}$	16.687	390	0.04750
19	$L_1^{-1}N_5^{-5}N_6^{-6}N_7^{-8}$	$N_5^{-5}N_6^{-6}N_7^{-8}O_2^{-1}$	16.718	421	0.04898
20	$L_1^{-1}N_5^{-6}N_6^{-6}N_7^{-8}$	$N_5^{-6}N_6^{-6}N_7^{-8}O_2^{-1}$	16.750	454	0.05040

can be ascribed to the following three reasons. First, Scofield used the Dirac-Fock-Slater method to calculate the atomic wave functions, while we used the Dirac-Fock method. Second, his calculations are made in the *frozen-orbital* approximation where the same atomic potential corresponding to the ground state is used for both initial and final states. The present work is based on the relaxed-orbital approximation and the presence of the vacancies in the initial and final states was correctly taken into consideration. Third, we used the x-ray transition energies obtained in the present work, instead of the values estimated from the tabulated atomic binding energies.

Table II lists the energy shift, ΔE, and the transition probability, Γ, of $L_{\gamma 1}$ x rays as a function of the number of N_4-shell vacancies, n. The vacancy configurations for the initial and final states are also shown as well as the x-ray transition energies. The transition probabilities are obtained by assuming that the N_4 shell is fully occupied in the initial state. It is clear from the table that the energy shift and transition probability are a linear function of n. The energy shift per N_4 vacancy is about 10 eV.

In Tables III and IV, the transition energies, energy shifts, and transition probabilities are listed as a function of the number of N-shell vacancies for $L_{\gamma 4'}$ and $L_{\gamma 4}$ x rays, respectively. The initial and final vacancy states are indicated in the tables. The results for the energy shifts are plotted in Fig. 1 as a function of n. The positions where the N_5 and N_6 vacancies start are shown by the arrows. Figure 2 shows the similar plot for the x-ray transition probabilities.

Table IV. Energy shift ΔE and transition probability Γ of $L_{\gamma 4}$ x rays with multiple N-shell vacancies. in Bi.

n	Intial	Final	Energy (keV)	ΔE (eV)	Γ (eV/$\hbar$)
0	L_1^{-1}	O_3^{-1}	16.321	—	0.02836
1	$L_1^{-1}N_7^{-1}$	$N_7^{-1}O_3^{-1}$	16.336	15	0.02985
2	$L_1^{-1}N_7^{-2}$	$N_7^{-2}O_3^{-1}$	16.351	30	0.03140
3	$L_1^{-1}N_7^{-3}$	$N_7^{-3}O_3^{-1}$	16.367	46	0.03298
4	$L_1^{-1}N_7^{-4}$	$N_7^{-4}O_3^{-1}$	16.385	64	0.03461
5	$L_1^{-1}N_7^{-5}$	$N_7^{-5}O_3^{-1}$	16.403	82	0.03627
6	$L_1^{-1}N_7^{-6}$	$N_7^{-6}O_3^{-1}$	16.422	101	0.03797
7	$L_1^{-1}N_7^{-7}$	$N_7^{-7}O_3^{-1}$	16.442	121	0.03970
8	$L_1^{-1}N_7^{-8}$	$N_7^{-8}O_3^{-1}$	16.463	142	0.04147
9	$L_1^{-1}N_6^{-1}N_7^{-8}$	$N_6^{-1}N_7^{-8}O_3^{-1}$	16.485	164	0.04330
10	$L_1^{-1}N_6^{-2}N_7^{-8}$	$N_6^{-2}N_7^{-8}O_3^{-1}$	16.509	188	0.04515
11	$L_1^{-1}N_6^{-3}N_7^{-8}$	$N_6^{-3}N_7^{-8}O_3^{-1}$	16.533	212	0.04704
12	$L_1^{-1}N_6^{-4}N_7^{-8}$	$N_6^{-4}N_7^{-8}O_3^{-1}$	16.558	237	0.04895
13	$L_1^{-1}N_6^{-5}N_7^{-8}$	$N_6^{-5}N_7^{-8}O_3^{-1}$	16.584	263	0.05089
14	$L_1^{-1}N_6^{-6}N_7^{-8}$	$N_6^{-6}N_7^{-8}O_3^{-1}$	16.610	289	0.05285
15	$L_1^{-1}N_5^{-1}N_6^{-6}N_7^{-8}$	$N_5^{-1}N_6^{-6}N_7^{-8}O_3^{-1}$	16.641	320	0.05481
16	$L_1^{-1}N_5^{-2}N_6^{-6}N_7^{-8}$	$N_5^{-2}N_6^{-6}N_7^{-8}O_3^{-1}$	16.673	352	0.05679
17	$L_1^{-1}N_5^{-3}N_6^{-6}N_7^{-8}$	$N_5^{-3}N_6^{-6}N_7^{-8}O_3^{-1}$	16.706	385	0.05879
18	$L_1^{-1}N_5^{-4}N_6^{-6}N_7^{-8}$	$N_5^{-4}N_6^{-6}N_7^{-8}O_3^{-1}$	16.738	417	0.06081
19	$L_1^{-1}N_5^{-5}N_6^{-6}N_7^{-8}$	$N_5^{-5}N_6^{-6}N_7^{-8}O_3^{-1}$	16.772	451	0.06285
20	$L_1^{-1}N_5^{-6}N_6^{-6}N_7^{-8}$	$N_5^{-6}N_6^{-6}N_7^{-8}O_3^{-1}$	16.806	485	0.06491

It can be seen from the tables and Fig. 1 that when the number of N-shell vacancies is small, the energy shift for $L_{\gamma 4}$ and $L_{\gamma 4'}$ x rays is almost proportional to n, about 15 eV per vacancy. However, as n becomes larger, the energy shift per vacancy increases and energy shift deviates from the linear function of n. On the other hand, Fig. 2 indicates that the transition probabilities are approximately a linear function of n in the whole region considered here.

In the present work, we assumed that in N-shell multiple ionization the N_7-shell electrons are removed first. This assumption seems to be realistic, because in most cases the N_7-shell ionization probability is higher than the N_5-shell one. However, it is interesting to test the dependence of order of removal of N-subshell electrons on the energy shift and transition probability of $L_{\gamma 4}$ and $L_{\gamma 4'}$ x rays. For this purpose, we considered the case where the N_5-shell electrons are removed first instead of the N_7-shell electrons. In Table V, the energy shifts and

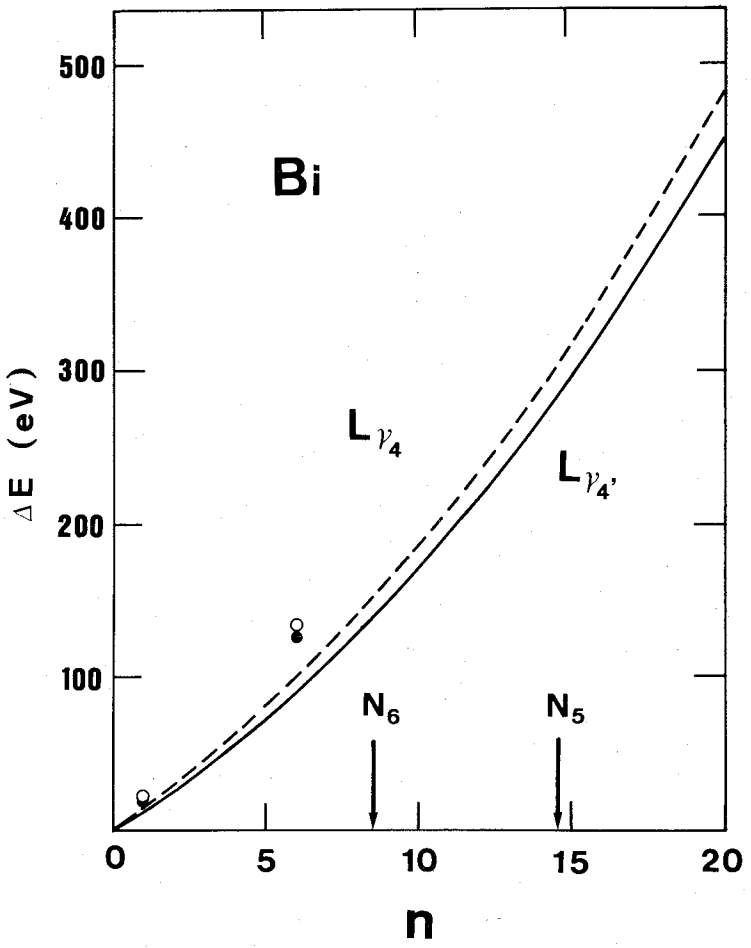

Fig. 1. Energy shift, ΔE, of L_γ x rays as a function of the number of N-shell vacancies, n. The solid line indicates the shift for $L_{\gamma 4'}$ x rays, while the dashed line represents the shift for $L_{\gamma 4}$ x rays. The positions where the N_5 and N_6 shells start to be removed are shown by the arrows. The solid and open circles indicate the values when the N_5 electrons are removed instead of the N_7 electrons.

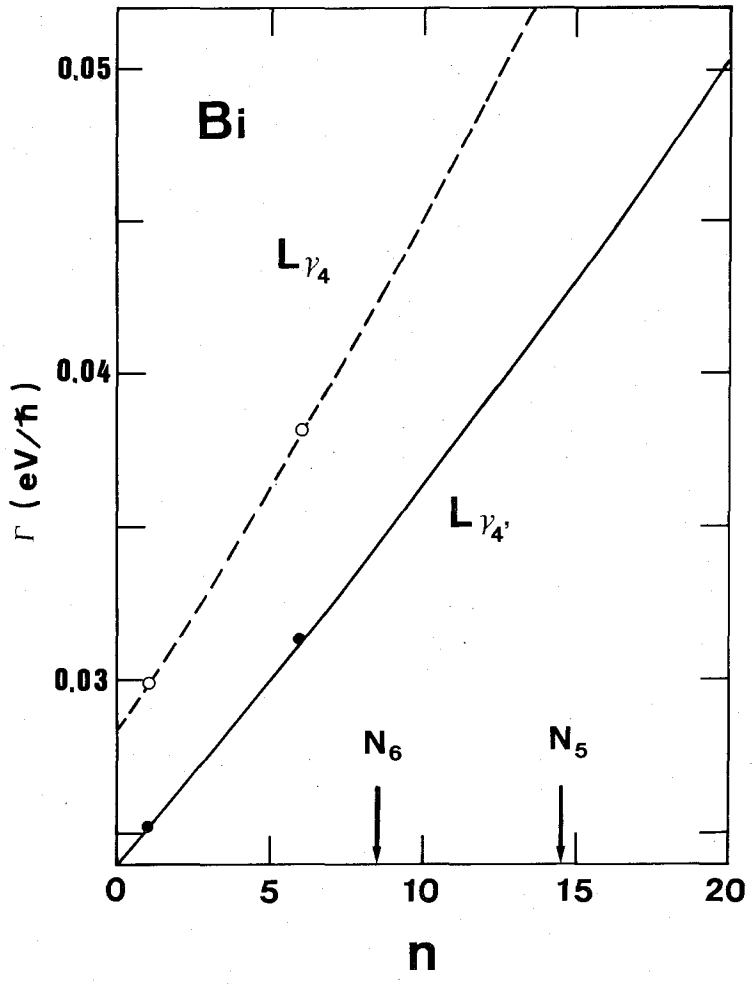

Fig. 2. Transition probability, Γ, of L_γ x rays as a function of n. See caption of Fig. 1.

transition probabilities of $L_{\gamma 4}$ and $L_{\gamma 4'}$ x rays with single and 6 vacancies in the N_5 shell are compared with the corresponding values for the N_7-shell vacancies. The results are also shown in Figs. 1 and 2 by the open and solid circles. It is seen that the energy shifts for the N_5-shell vacancies is about 20 eV per vacancy and larger than that for the N_7-shell vacancy. The transition probability is almost same for both cases and independent of the order of removal of N-subshell electrons.

These results can be explained as follows. In the case of transition probabilities, the dominant contributions to the matrix element comes from the radial distance near to the mean L_1-shell radius. The probability is determined from the behavior of the electron wave functions in this region and the position of the N-shell vacancy has little influence. On the other hand, the x-ray energies are determined from the difference in the electronic total energies in the initial and final states. The energy of the final state, where the vacancy is present in the O shell, depends on the position of the N-shell vacancy.

In summary, we have calculated the energy shifts and transition probabilities of L_γ x rays

Table V. Dependence of order of removal of N-subshell electrons on energy shift ΔE and transition probaility Γ of $L_{\gamma 4}$ and $L_{\gamma 4'}$ x rays in Bi.

x ray	n	Initial	Final	ΔE (eV)	Γ (eV/$\hbar$)
$L_{\gamma 4'}$	1	$L_1^{-1}N_7^{-1}$	$N_7^{-1}O_2^{-1}$	13	0.02522
	6	$L_1^{-1}N_7^{-6}$	$N_7^{-6}O_2^{-1}$	93	0.03128
	1	$L_1^{-1}N_5^{-1}$	$N_5^{-1}O_2^{-1}$	20	0.02526
	6	$L_1^{-1}N_5^{-6}$	$N_5^{-6}O_2^{-1}$	126	0.03141
$L_{\gamma 4}$	1	$L_1^{-1}N_7^{-1}$	$N_7^{-1}O_3^{-1}$	15	0.02985
	6	$L_1^{-1}N_7^{-6}$	$N_7^{-6}O_3^{-1}$	101	0.03797
	1	$L_1^{-1}N_5^{-1}$	$N_5^{-1}O_3^{-1}$	21	0.02991
	6	$L_1^{-1}N_5^{-6}$	$N_5^{-6}O_3^{-1}$	135	0.03819

in Bi atoms with multiple N-shell vacancies. For small number of vacancies, the energy shift per vacancy is about 10 eV for $L_{\gamma 1}$ x rays and about 15 eV for $L_{\gamma 4}$ and $L_{\gamma 4'}$ x rays. The energy shift per N-shell vacancy increases with increasing the number of vacancies. The transition probability is approximately a linear function of the number of vacancies.

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