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Vacancy Cascade Following Inner-Shell Ionization

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The charge distributions of ions following inner-shell ionization of rare gases have been calculated by the Monte Carlo method. Electron shakeoff accompanying formation of vacancy is taken into account. The recent tabulated values for x-ray emission rates, Auger transition rates, and electron shakeoff probabilities are used. The calculated results are compared with the experimental data for photoionization and electron capture decay of Ar and Kr. Good agreement between the measured and calculated charge distributions is achieved.

KEY WORDS: Vacancy cascade/ Charge distribution/ Inner-shell ionization/

I. INTRODUCTION

When a vacancy is produced in the inner shell of an atom as a result of photon irradiation, charged-particle impact or nuclear decay, such as electron capture and internal conversion, this vacancy is filled by x-ray emission or Auger effect. In the former process, one electron from an outer shell falls into the inner-shell hole and the radiation whose energy corresponds to the energy difference between the initial and final states is emitted. On the other hand, the Auger effect is the radiationless transition in which the excess energy due to the single-electron transition from the outer shell to the inner-shell vacancy is transferred to the second electron in the same atom, being ejected into the continuum. As the result of the x-ray emission the inner-shell vacancy only moves to the outer shell, while in the Auger effect an additional vacancy is created.

The new outer-shell vacancies produced by filling the inner-shell hole are filled via cascades of successive radiative and Auger transitions until the vacancies reach to the outer-most shell. In the outer shells, the Auger effect is much more probable than the radiative transition and most vacancies are filled by the Auger process. Thus the atom with inner-shell vacancies in the initial state is highly ionized in its final state due to the vacancy cascade.

In general, such highly ionized states cannot survive for an appreciable time for measurements in solids and chemical compounds because the electrons to neutralize the atom by filling the vacancies are available from the surrounding atoms. However, in the case of a free atom, such as rare gases, the highly charged states resulting from inner-shell ionization are not destroyed and can be observed experimentally. The experimental studies on the vacancy cascade are made by measuring the charge distribution of ions with a charge spectrometer.

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Early experimental works[1] for vacancy cascade were made on rare gases with inner-shell vacancies produced through radioactive decays, i. e. electon capture and internal conversion. Later, Carlson and Krause carried out the extensive studies on charge spectra following photoionization.[2-5] More recently Lightner *et al.* measured relative abundance of multiply charged ions of rare gases by low-energy x rays.[6]

The theoretical estimation of the vacancy cascade process has been made by Carlson and Krause, treating successive radiative and Auger transitions by the use of Monte Carlo simulation.[2,5] They showed that the electron shakeoff process plays an important role to determine the final charge distribution. This process is the electron-ejection mechanism due to sudden change in the central potential of the atom and takes place when a new vacancy is created. The calculated charge spectra for Ar and Kr including electron shakeoff are in good agreement with the experimental data. Recently Mirakhmedov and Parilis[7] have performed the similar calculations for Kr taking into account the change in Auger and radiative transition energies. With increasing number of vacancies during the cascade, some Auger channels turn out to be energetically forbidden. They obtained the charge spectrum of ions together with the energy spectra of x rays and Auger electrons emitted during the vacancy cascade.

At present, some atomic data used in these calculations, such as x-ray emission rates, Auger transition rates, and shakeoff probabilities, are old and less reliable. In recent years relativistic calculations for these values with more realistic atomic models have been reported. It is worthwhile to recalculate the charge distributions of ions following inner-shell ionization by the use of the new atomic data. In the present work, we have performed the Monte Carlo calculations of the charge spectra of ions following photoionization of Ar and Kr as well as those following electron capture decay of ^{37}Ar and ^{79}Kr.

II. METHOD OF CALCULATION

The vacancy cascade is simulated by the Monte Carlo method. Three processes are considered: x-ray emission, Auger transition, and electron shakeoff. When an initial vacancy is created, the computer selects in each step possible processes according to their relative rates by means of random numbers.

At the initial ionization state, we treat the electron shakeoff process separately. The probability of this process is generally small, but when this process takes place at the initial stage, the additional vacancies produced are multiplied during the cascade and have considerable influence on the final charge distribution. Considering this fact, we estinate the charge distribution for the shakeoff from the distributions of the singly ionized initial states concerned. For example, the spectrum of the K-shell vacancy with L_1-shell shakeoff is constructed from the spectrum of K-shell vacancy and that of the L_1-shell vacancy. Then the final charge distribution is obtained as a weighted sum of all prossible cases according to the relative intensities of the initial states.

In each step, first we determine whether the transition is radiative or not.

When it is radiative, the next vacancy is selected. In the case of Auger transition, two vacancy states are chosen and the number of vacancies is increased by one. For each vacancy, it is tested whether the shakeoff process takes place. If the electron shakeoff occurs, the atomic shell from which the shakeoff electron is ejected is selected and the number of vacancies is increased by one. This procedure is repeated until the vacancies reach to the outer-most shell and no transition takes place. Then the number of vacancies is recorded and the computer program generates the next history. After 10, 000 histories, the charge distribution of ions is computed.

Throughout the present work, we use the atomic transition rates in a singly ionized atom, but modify their values to be proportional to the number of electrons available to a particular transition. In addition, we neglect two- or multi-electron shakeoff process and double Auger transition.

III. RESULTS AND DISCUSSION

All the calculations in the present work have been done on the FACOM M-382 computer in the Data Processing Center of Kyoto University.

The radiative transition rates for Ar and Kr are taken from the tabulated values obtained by the relativistic Hartree-Fock-Slater (RHFS) calculations of Scofield.(8) We use the K- and L-shell Auger rates calculated by Chen *et al.*(9) with the RHFS wave functions and the nonrelativistic values of McGuire(10) for M subshells. The shakeoff probabilities as a result of removal of an electron are taken from the table of Carlson and Nestor,(11) based on the RHFS model.

In the case of electron-capture decay, the atomic data for the daughter atom, Cl and Br, are used. Since the Auger rates for Cl are not included in Ref. 9, we obtained the values by interpolation of the table prepared by Kostroun *et al.*(12) for K shell and that by McGuire(13) for L shell. The L_2- and L_3-shell Auger transition rates for Br are also not published in Ref. 9 and we used the values for Kr. The shakeoff probabilities for removal of an electron are assumed to be the same as those for the parent atom. At the initial ionization, the inner-shell vacancy is produced by electron capture. In this case, there is the change in the nuclear charge, as well as the change in the central potential. The shakeoff probabilities accompanying electron capture are different from those resulting from the removal of electron and are taken from the calculated results of Crasemann *et al*,(14) using the Hartree-Fock wave functions.

In the present work, all the subshells in the atom, except for the out-most shell, are considered. The outer-most shell, i. e. M shell in Ar and N shell in Kr, is treated as one shell. When the nonrelativistic values of the atomic parameters are used, the values for the particular subshell is estimated according to the occupation number of electrons in each subshell.

Figure 1 shows a typical vacancy cascade for filling the initial K-shell vacancy in Kr atom. The first transition is the $K_{\alpha 1}$ x-ray emission and the vacancy moves to the L_3 shell. This is the only radiative transition in this cascade and the rest are the Auger processes. For example, the second transition is the L_3-M_1M_3 Auger

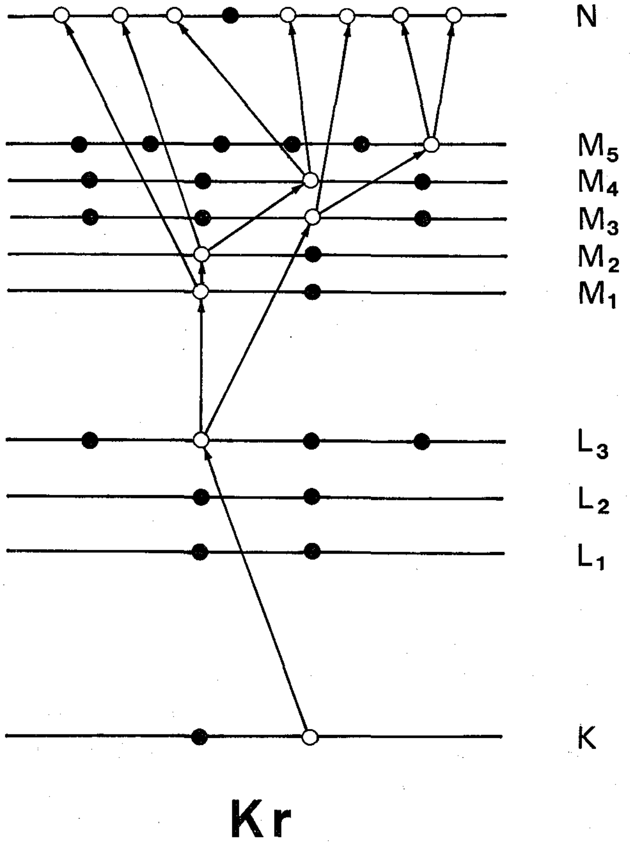

Fig. 1. Typical example of the vacancy cascade for filling the initial K-shell vacancy of Kr atom. The solid circle indicates the electron and the open circle represents the vacancy. Arrows show the direction of the vacancy cascade.

Table I. Relative abundance of ions resulting from an inner-shell vacancy of Ar atom with and without electron shakeoff.

Charge	K		L_1		L_2		L_3	
	A	B	A	B	A	B	A	B
1	0.7	0.9	0	0	0	0	0	0
2	8.6	11.2	3.7	4.4	85.0	100.0	85.1	100.0
3	10.3	10.3	82.5	95.6	14.8	0	14.8	0
4	43.2	53.1	13.6	0	0.2	0	0.1	0
5	26.1	18.6	0.2	0	0	0	0	0
6	9.3	5.9	0	0	0	0	0	0
7	1.6	0	0	0	0	0	0	0
8	0.2	0	0	0	0	0	0	0

A : With shakeoff.
B : Without shakeoff.

Table II. Comparison of experimental and calculated charge distribution of Ar ions following photoionization. Relative abundance is normalized as $\sum_{n=2}^{8} I(n) = 100$, where n is the charge of ion and $I(n)$ is the relative abundance.

n	Experiment[a]	Calculation		Experiment[d]	Calculation	
		A[b]	B[c]		A	B
1	2.0±1.0	1.6	1.4		2.1	2.1
2	10.6±0.5	10.7	10.7	10.1±1.6	8.7	10.6
3	13.8±0.5	14.8	14.3	16.4±1.6	16.9	14.5
4	36.0±0.8	40.4	39.9	33.4±1.6	40.5	40.0
5	26.4±0.8	23.9	23.0	25.5±2.0	23.7	22.8
6	10.1±0.7	8.5	9.4	11.1±1.6	8.5	9.4
7	2.7±0.5	1.5	2.2	3.5±1.1	1.5	2.2
8	0.4±0.2	0.2	0.5		0.2	0.5

a) X rays from Ti target, Ref. 2.
b) Present work.
c) Ref. 2.
d) X rays from Mo target, Ref. 2.

process. At the final stage of the cascade, the charge of the ion is +7 and 6 Auger electrons have been ejected.

In order to demonstrate the importance of the shakeoff process during the cascade, the relative abundance of ions resulting from K-, L_1-, L_2-, and L_3-shell vacancy creation in Ar atom has been calculated with and without electron shakeoff. The obtained results are listed in Table I. As has been shown by Carlson and Krause,[2] inclusion of the shakeoff process leads to a broad charge distribution, which seems to be more realistic in comparison with the experiment. All the following calculations in the present work have been performed taking into account the electron shakeoff.

Table II shows comparison of the calculated values for photoionization of Ar atom by x rays with the experimental results of Carlson and Krause.[2] Their calculated values are also listed in the table. They used x rays from the Ti target and from the Mo target. In the former case, the relative abundance of initial vacancies is 90.3% for K shell, 5.8% for L_1 shell, 1.0% for L_2 shell, 2.0% for L_3 shell, and 0.9% for M shell.[15] On the other hand, for the Mo target we adopted the values used in Ref. 2; 89.1% for K shell, 8.9% for L_1 shell, 0.2% for L_2 shell, 0.4% for L_3 shell, and 1.4% for M shell. The comparison of the present results for the Ti target with the experimental data[2] is shown in Fig. 2.

Similar comparison with the results of Carlson and Krause[5] for Kr atom is made in Table III and Fig. 3. In this case, the initial vacancy distribution is taken from Ref. 5; 86.5% for K shell, 8.3% for L_1 shell, 1.23% for L_2 shell, 2.47% for L_3 shell, 0.7% for M_1 shell, 0.13% for M_2 shell, 0.27% for M_3 shell, 0.08% for M_4 shell, 0.12% for M_5 shell, and 0.2% for N shell. In Table III, the calculated values of Mirakhmedov and Parilis,[7] including the effect of the change in the

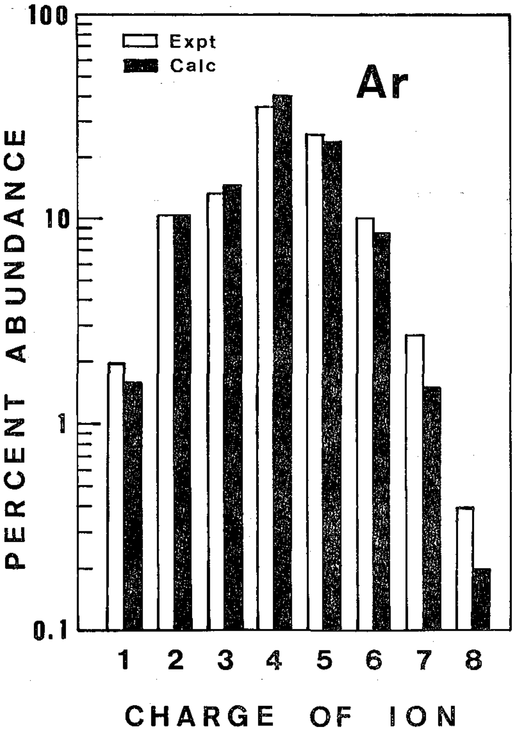

Fig. 2. Comparison of the measured and calculated charge spectra following photoionization of Ar atom. The experimental data are taken from Ref. 2.

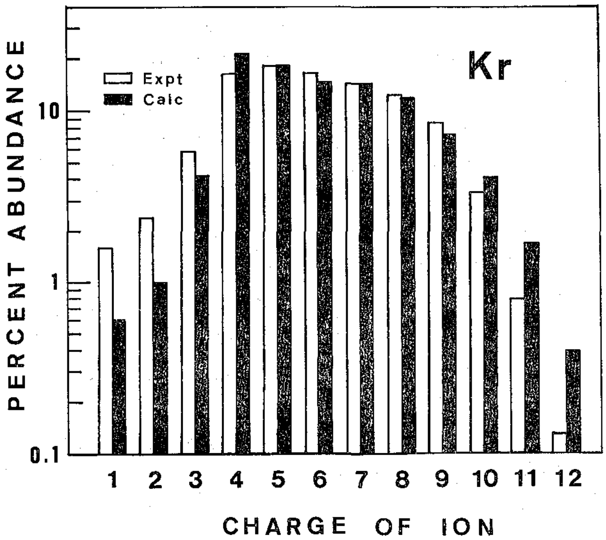

Fig. 3. Comparison of the measured and calculated charge spectra following photoionization of Kr atom. The experimental data are taken from Ref. 5.

Table III. Comparison of experimental and calculated charge distribution of Kr ions following photoionization.

Charge	Experiment a)	Calculation A b)	Calculation B c)	Calculation C d)
1	1.6±0.5	0.6	0.7	0.64
2	2.4±0.4	1.0	1.3	0.80
3	5.8±0.5	4.2	5.1	5.19
4	16.2±0.5	21.6	19.0	20.50
5	18.1±0.5	18.2	20.6	23.24
6	16.5±0.7	14.6	14.2	21.28
7	14.1±0.6	14.3	11.1	11.28
8	12.4±0.6	12.0	13.6	10.31
9	8.6±0.7	7.3	9.4	5.06
10	3.4±0.5	4.1	3.9	1.69
11	0.8±0.2	1.7	1.0	0.08
12	0.13±0.10	0.4	0.13	0.02
13		0.01	0.02	0.01

a) Ref. 5.
b) Present work.
c) Ref. 5.
d) Ref. 7.

transition energies, are listed for comparison.

It is clear that the present results are in good agreement with the experimental values and the calculated ones of Carlson and Krause.[2,5] However, in Ar the present values are slightly smaller than the experimental data for highly ionized states. This is probably due to neglection of double Auger effect in the present calculations. According to the experimental results of Carlson and Krause,[16] the intensity of the $L_{2,3}$-MMM double Auger process in Ar is about 10 % relative to all radiationless transitions.

In the case of Kr, the calculated charge spectrum is lower for singly- and doubly-ionized states and higher for highly-ionized states than the experimental one. The calculations of Mirakhmedov and Parilis[7] cannot reproduce the experimental distribution in highly-charged states.

The calculated charge spectrum following electron-capture decay of ^{37}Ar is listed in Table IV and compared with the experimental data of Snell and Pleasonton[17] and the calculated values of Carlson and Krause.[2] The initial vacancy distribution was estimated by the electron-capture ratios, $P_L/P_K = 0.098$[18] and $P_M/P_L = 0.104$,[19] as 90.2 % for K shell, 8.9 % for L_1 shell, and 0.9 % for M shell. The agreement with experiment and other theoretical calculation is quite good, although there is a slight underestimation for highly-ionized states, as has been seen in the case of photoionization.

Table V shows comparison of experimental and calculated charge distributions of Br ions after electron-capture decay of ^{79}Kr. The experimental measurements were carried out by Snell *et al.*[20] There is a positron-emission branch in this nuclide. The

Table IV. Comparison of experimental and calculated charge distribution of Cl ions following electron-capture decay of ^{37}Ar.

n	Experiment[a)]	Calculation A[b)]	Calculation B[c)]
0		1.2	0.9
1	6.2 ± 0.1	10.0	9.5
2	15.7 ± 0.4	19.0	15.9
3	39.2 ± 0.5	30.4	45.8
4	26.7 ± 0.4	29.4	20.9
5	10.2 ± 0.2	10.9	7.2
6	1.8 ± 0.1	0.2	0.6
7	0.4 ± 0.1	0.1	0.05

a) Ref. 17.

b) Present work, normalized to $\sum_{n=1}^{7} I(n) = 100$.

c) Ref. 2, normalized in the manner similar to the present result.

Table V. Comparison of experimental and calculated charge distribution of Br ions following electron-capture decay of ^{79}Kr.

n	Experiment[a)]	Calculation A[b)]	Calculation B[c)]
−1	7.7	7.6	6.6
0	3.7	2.1	2.6
1	4.0	1.2	1.7
2	4.7	4.6	5.5
3	12.7	10.0	18.4
4	16.0	15.3	16.7
5	14.3	13.8	11.9
6	13.6	14.4	9.6
7	11.3	13.4	14.1
8	7.7	9.5	8.8
9	3.3	4.9	3.2
10	0.68	2.4	0.8
11	0.13	0.7	0.1
12	0.054	0.10	
13	0.014	0.03	

a) Ref. 20.
b) Present work.
c) Ref. 5.

experimental data in the table were obtained after consideration of this effect, assuming the electron-capture/β^+ ratio to be 9.3.[21] The charge −1 in the table corresponds to the pure β^+ decay without electron shakeoff. The shakeoff probabilities accompanying β^+ decay are assumed to be same as those in β^- decay and taken from table of Carlson *et al.*22), obtained by the use of the RHFS wave functions. The initial distribution of vacancy was estimated for each subshell from these shakeoff probabilities. In the electron-capture decay, the initial vacancy distribution was obtained from the experimental capture ratio, $P_L/P_K=0.108$,23) and from the theoretical ratios of P_M/P_K, $P_NP/_K$, based on the atomic parameters given in Ref. 24. The relative abundance of the initial vacancies used in the calculations is 89.2 % for K shell, 9.6 % for L_1 shell, 1.1 % for M_1 shell, and 0.1 % for N_1 shell. It can be seen from the table that the present results are in agreement with the experimental data and other theoretical values.

IV. CONCLUSION

The charge distributions of ions of rare gases following photoionization and electron capture have been calculated by the Monte Carlo method, using the recently published atomic data. The calculated results are in good agreement with the experimental values and other theoretical calculations. However, there is a slight deviation for highly-ionized states. Inclusion of multi-electron transitions, such as multiple shakeoff and double Auger process, may improve this discrepancy. Both experimental and theoretical values for these processes are scarse and not reliable. It is hoped to perform more systematic and precise studies on these processes in order to elucidate the discrepancy between theory and experiment in the vacancy cascade.

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