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# Shift Energies of Characteristic X-rays and Auger Electrons for Ionized Atoms

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## Synopsis

Shift energies of characteristic X-rays and Auger electrons for several ionized atoms of  $Z=6\sim 17$  have been computed as a function of the degree of ionization, taking Larkins' Hartree-Fock-Slater calculations for neon ( $Z=10$ ) and argon ( $Z=18$ ) as standards. A reasonable agreement is seen with the observed shift energies of X-rays for multiply ionized aluminium.

## 1. Introduction

Recently, various experiments of heavy ion-atom collisions have been extensively carried out in the energy range of  $1\sim 100$  keV/aum. In particular, by measuring the emitted characteristic X-rays or Auger electrons from colliding particles, the ionizations of K, L and/or M shells have been discussed, referring to the theoretical treatments of the Born approximation<sup>1)</sup> and the binary encounter approximation (BEA)<sup>2)</sup>. In these atom-atom encounters, the energies of the X-rays and electrons are found to shift upward and downward, respectively, in comparison with those observed in electron or light ion bombardments. The reason is that atoms are increasingly ionized by heavy and energetic ion incidence, and the binding energies of inner shell electrons become larger than the usual values of singly or slightly ionized atoms.

The electron binding energies are the most fundamental quantities of atoms, and those of multiply ionized atoms are of special interest in recent years. The values can be obtained by the calculation of the Hartree-Fock-Slater (HFS) self-consistent method. Also, Mayers and O'Brien<sup>3)</sup> have shown the procedure through use of a computer. By applying this information, Larkins<sup>4,5)</sup> has calculated the

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energies for ionized neon and argon atoms against the degree of ionization, whereby extra vacancies are assumed to exist successively from the outermost shell.

The calculation according to the HFS method is quite laborious and time-consuming. In addition, the arrangement of vacancies in such violent collisions would be very complicated. Rather, a more reasonable and convenient method is needed in practice to know an overall variation of the binding energy as a function of degree of ionization. In this paper, there is described a simple method of derivation, taking Larkins' results of neon and argon as standards. The energies of characteristic X-rays and Auger electrons together with their shift values are shown for some atoms up to  $Z=17$ .

## 2. Method of Calculation

Slater<sup>6)</sup> has proposed a simple formula of electron binding energy for neutral atoms. It is expressed by the atomic number  $Z$ , screening constant  $s$  and effective quantum number  $n_{\text{eff}}$ , where the values of  $s$  and  $n_{\text{eff}}$  are appropriately decided, referring to the observed binding energies. We start from Slater's modified formula and make assumptions as follows:

- 1) The binding energies for inner shells can be expressed by

$$E_n = 13.56 \left( \frac{Z-s}{n} \right)^2 \quad (\text{eV}), \quad (1)$$

where  $n$  is the principal quantum number ( $n=1, 2, 3, \dots$ ).

- 2) The screening constant  $s$  is a function of ionization rate  $m/Z$  ( $m=0, 1, 2, 3, \dots, Z$ ), and is given by  $s=s^0 f(m/Z)$ , where  $f(m=0)=1$  and  $f(m=Z)=0$ .

- 3) The forms of  $f(m/Z)$  for K and L shells are identical for atoms of  $Z=6\sim 10$ , where neon is a standard atom. Similarly, the  $f(m/Z)$  forms of argon are applicable to the K, L and M shells for atoms of  $Z=11\sim 20$ .

- 4) The value of  $s^0$  is given by putting the observed binding energy into eq. (1).

- 5) For the subshells such as  $L_2$  and  $L_3$ , the forms of  $f(m/Z)$  are the same and  $s^0_{L_2}$  and  $s^0_{L_3}$  are averaged.

Larkins' binding energies of ionized neon for K,  $L_1$  and  $L_{23}$  shells are listed in Table 1, together with the derived  $s_K$ ,  $s_{L_1}$  and  $s_{L_{23}}$  values according to eq. (1). These  $s$  values are plotted in Fig. 1 as a function of the degree of ionization. We find  $s_K$ ,  $s_{L_1}$  and  $s_{L_{23}}$  smoothly decrease against the charge state  $m$ , and are approximated by

$$s_K = s^0_K [1 - 0.60(m/Z) - 0.40(m/Z)^2], \quad (2.1)$$

$$s_{L_1} = s^0_{L_1} [1 - 1.14(m/Z) + 0.14(m/Z)^2], \quad (2.2)$$

Table 1. Binding energies and screening constants for neon as a function of degree of ionization.

The binding energies are the rounded values of Larkins<sup>5)</sup>, which are somewhat different from the observed data<sup>7)</sup>. The energy unit is eV.

$m$	K		L			
	$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_{L23}$	$s_{L23}$
0	869	2.00	49	6.20	20	7.57
+1	895	1.87	69	5.49	41	6.52
+2	926	1.74	91	4.80	66	5.60
+3	963	1.57	116	4.15	93	4.77
+4	1003	1.40	143	3.50	124	3.95
+5	1049	1.20	172	2.88	158	3.18
+6	1098	1.00	204	2.25	—	—

Table 2. Binding energies and screening constants for argon as a function of degree of ionization.

The binding energies are quoted from Larkins<sup>5)</sup> and are rounded, which are somewhat different from the table values<sup>7)</sup>. The energy unit is eV.

$m$	K		L				M			
	$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_{L23}$	$s_{L23}$	$E_{M1}$	$s_{M1}$	$E_{M23}$	$s_{M23}$
0	3915	2.65	325	8.21	249	9.43	33	13.3	15	14.9
+1	3211	2.61	340	7.98	264	9.17	45	12.5	27	13.7
+2	3230	2.57	358	7.73	282	8.89	59	11.8	41	12.8
+3	3250	2.52	377	7.46	301	8.58	73	11.0	57	11.9
+4	3273	2.47	398	7.17	322	8.26	88	10.3	73	11.1
+5	3297	2.41	420	6.87	344	7.92	105	9.7	90	10.3
+6	3324	2.34	444	6.55	368	7.58	122	9.0	—	—

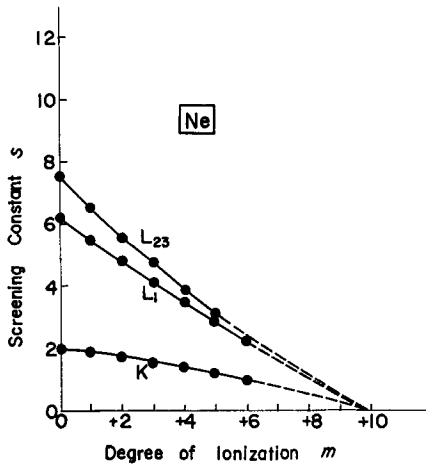


Fig. 1. Derived screening constants for K, L<sub>1</sub> and L<sub>23</sub> shells of neon as a function of degree of ionization.

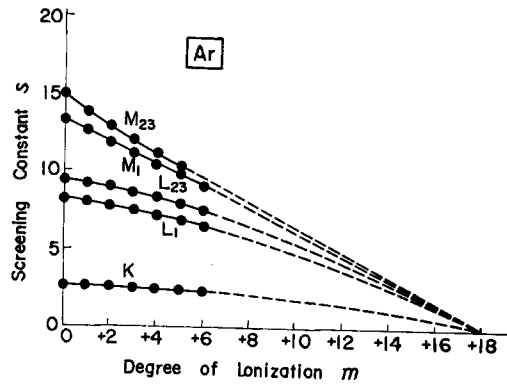


Fig. 2. Derived screening constants for K, L<sub>1</sub>, L<sub>23</sub>, M<sub>1</sub> and M<sub>23</sub> shells of argon as a function of degree of ionization.

and

$$s_{L23} = s_{L23}^0 [1 - 1.32(m/Z) + 0.32(m/Z)^2]. \quad (2.3)$$

For the neon atom,  $s_K^0 = 2.00$ ,  $s_{L1}^0 = 6.20$  and  $s_{L23}^0 = 7.57$  are given as seen in Table 1. Therefore, the essential point of this article is that the  $f(m/Z)$  forms of eqs. (2.1), (2.2) and (2.3) are applicable to carbon, nitrogen, oxygen and fluorine.

Table 2 represents a similar result for argon and the  $s$  values as a function of  $m$ , drawn in Fig. 2. Again, we have the approximate functions of  $f(m/Z)$  around  $m=0\sim 4$  as follows:

$$s_K = s_K^0 [1 - 0.15(m/Z) - 0.85(m/Z)^2], \quad (3.1)$$

$$s_{L1} = s_{L1}^0 [1 - 0.46(m/Z) - 0.54(m/Z)^2], \quad (3.2)$$

$$s_{L23} = s_{L23}^0 [1 - 0.45(m/Z) - 0.55(m/Z)^2], \quad (3.3)$$

$$s_{M1} = s_{M1}^0 [1 - 1.05(m/Z) + 0.05(m/Z)^2], \quad (3.4)$$

and

$$s_{M23} = s_{M23}^0 [1 - 1.15(m/Z) + 0.15(m/Z)^2]. \quad (3.5)$$

For argon,  $s_K^0 = 2.65$ ,  $s_{L1}^0 = 8.21$ ,  $s_{L23}^0 = 9.43$ ,  $s_{M1}^0 = 13.3$  and  $s_{M23}^0 = 14.9$ , and we propose the screening expressions of (3.1)~(3.5) to be equally available to the atoms of  $Z=11\sim 17$ .

Since the binding energies of inner shells are thus computable by using the above equations, the energies of characteristic X-rays and Auger electrons are easily obtained according to the following relations, where the electronic transitions are assumed adiabatic.

Characteristic X-rays:

$$E_X = E_K(m) - E_{L23}(m) \quad \text{for } K_\alpha, \quad (4.1)$$

$$= E_K(m) - E_{M23}(m) \quad \text{for } K_\beta, \quad (4.2)$$

Auger electrons:

$$E_A = E_K(m) - E_{L23}(m) - E_{L23}(m+1) \quad \text{for } K-L_{23}L_{23}, \quad (5.1)$$

$$= E_K(m) - E_{L1}(m) - E_{L23}(m+1) \quad \text{for } K-L_1L_{23}, \quad (5.2)$$

$$= E_K(m) - E_{L1}(m) - E_{L1}(m+1) \quad \text{for } K-L_1L_1. \quad (5.3)$$

From these, we can get the shift energies of X-rays and Auger electrons as a function of the degree of ionization.

### 3. Energies of Characteristic X-rays and Auger Electrons

#### 3.1. Carbon, Nitrogen, Oxygen and Fluorine

Before executing the computation, it is necessary to know the observed data of K, L and M binding energies of normal atoms. The table of Bearden and Burr<sup>7)</sup> seems useful for this purpose. However, since some L binding energies of light atoms still remain ambiguous, the predicted values are adopted.

In Table 3, the binding energies, screening constants, energies of K X-rays

Table 3. Binding energies, screening constants, energies of characteristic X-rays and Auger electrons as a function of charge state for carbon, nitrogen, oxygen and fluorine. The energy unit is eV.

Atom	$m$	K		L				$E_x$	$E_A$		
		$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_{L23}$	$s_{L23}$		$K^-_{L_{23}L_{23}}$	$K^-_{L_1L_{23}}$	$K^-_{L_1L_1}$
$Z=6$ C	0	284	1.42	(15)	3.90	6	4.67	278	260	251	242
	+1	305	1.26	27	3.17	18	3.69	287	252	243	236
	+2	330	1.07	42	2.48	35	2.78	295	240	233	228
	+3	360	0.85	60	1.81	55	1.96	305	227	222	221
	+4	395	0.60	79	1.18	78	1.21	317	—	—	—
$Z=7$ N	0	402	1.57	(19)	4.63	9	5.37	393	370	360	351
	+1	423	1.42	32	3.90	23	4.39	400	358	349	342
	+2	448	1.25	49	3.18	42	3.48	406	342	335	330
	+3	479	1.05	69	2.47	64	2.65	415	323	318	320
	+4	517	0.83	90	1.83	92	1.87	425	310	302	313
	+5	560	0.58	114	1.19	115	1.18	445	—	—	—
$Z=8$ O	0	532	1.74	(24)	5.34	7	6.56	525	504	487	469
	+1	555	1.60	39	4.59	21	5.51	534	493	475	458
	+2	584	1.44	58	3.87	41	4.53	543	478	461	450
	+3	618	1.25	76	3.16	65	3.61	553	460	449	439
	+4	657	1.04	103	2.48	93	2.76	564	441	431	425
	+5	700	0.82	129	1.83	123	1.97	577	423	417	414
	+6	749	0.57	157	1.20	154	1.25	595	—	—	—
$Z=9$ F	0	685	1.89	(31)	5.98	9	7.37	676	652	630	606
	+1	713	1.75	48	5.23	24	6.32	689	643	619	597
	+2	743	1.60	68	4.51	46	5.33	697	625	603	584
	+3	777	1.43	91	3.81	72	4.39	705	603	584	569
	+4	817	1.24	117	3.12	102	3.51	715	580	565	555
	+5	861	1.03	145	2.45	135	2.70	725	557	547	541
	+6	912	0.80	175	1.81	169	1.93	743	533	527	530
	+7	968	0.55	207	1.18	210	1.23	758	—	—	—

The values in brackets are the predicted ones referring to the observed binding energies of large  $Z$  atoms.

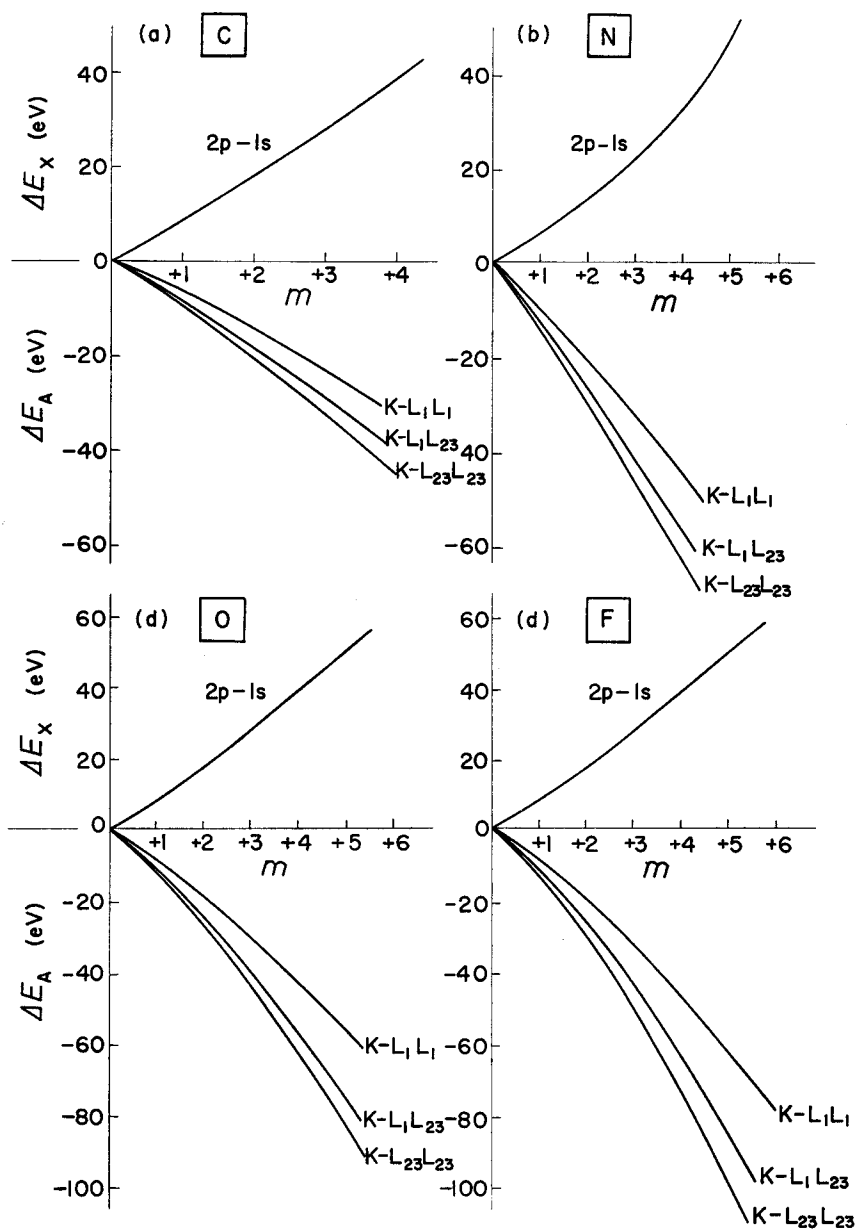


Fig. 3. Shift energies of characteristic X-rays and Auger electrons for carbon, nitrogen, oxygen and fluorine against charge state.

The notations  $\Delta E_X$  and  $\Delta E_A$  mean the shift energies of characteristic X-rays and Auger electrons, respectively.

and Auger electrons for carbon, nitrogen, oxygen and fluorine are listed as a function of the charge state. The shift energies of X-rays and Auger electrons, denoted as  $\Delta E_X$  and  $\Delta E_A$ , respectively, are drawn in Fig. 3.

Table 4. Binding energies, screening constants, energies of characteristic X-rays and Auger electrons for aluminium as a function of charge state. The energy unit is eV.

$m$	K		L				$E_X$	$E_A$		
	$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_{L23}$	$s_{L23}$		K-L <sub>23</sub> L <sub>23</sub>	K-L <sub>1</sub> L <sub>23</sub>	K-L <sub>1</sub> L <sub>1</sub>
0	1560	2.27	118	7.10	73	8.36	1487	1404	1359	1313
+1	1573	2.23	129	6.83	83	8.04	1490	1394	1348	1301
+2	1590	2.17	143	6.50	96	7.67	1494	1382	1335	1287
+3	1614	2.09	160	6.14	112	7.25	1502	1370	1322	1275
+4	1647	1.98	179	5.73	132	6.77	1515	1360	1313	1266
+5	1686	1.85	202	5.28	155	6.23	1531	1347	1300	1255
+6	1731	1.70	229	4.78	184	5.64	1547	1330	1285	1241
+7	1784	1.53	261	4.22	217	5.00	1567	—	—	—

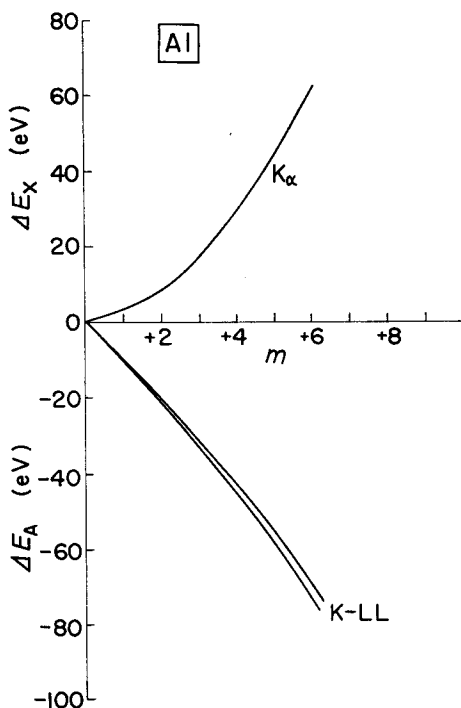


Fig. 4. Shift energies of  $K_\alpha$  X-rays and K-LL Auger electrons for aluminium as a function of charge state.

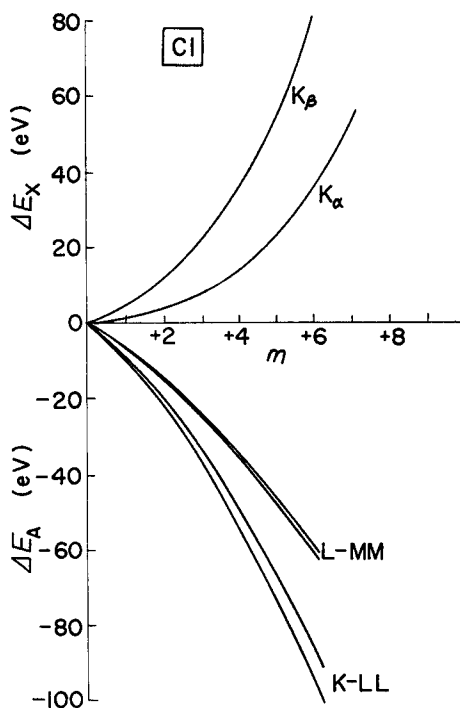


Fig. 5. Shift energies of  $K_\alpha$  and  $K_\beta$  X-rays and K-LL and L-MM Auger electrons for chlorine as a function of charge state.



Table 5. Binding energies, screening constants, energies of characteristic X-rays and Auger electrons for chlorine as a function of charge state. The energy unit is eV.

$m$	K		L				M				$E_X$		$E_A$					
	$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_{L23}$	$s_{L23}$	$E_{M1}$	$s_{M1}$	$E_{M23}$	$s_{M23}$	$K_\alpha$	$K_\beta$	$K-L_{23}L_{23}$	$K-L_1L_{23}$	$K-L_1L_1$	$L_{23}^-$ $M_{23}M_{23}$	$L_{23}^-$ $M_1M_{23}$	$L_{23}^-$ $M_1M_1$
0	2822	2.57	270	8.08	200	9.32	18	13.5	7	14.8	2622	2815	2408	2338	2268	178	167	154
+1	2835	2.54	284	7.85	214	9.06	28	12.7	15	13.9	2621	2820	2390	2320	2251	173	160	146
+2	2855	2.49	300	7.59	231	8.75	40	11.9	26	12.9	2624	2829	2375	2306	2235	166	152	138
+3	2875	2.44	320	7.28	249	8.43	53	11.1	39	11.9	2626	2836	2354	2283	2213	155	141	127
+4	2910	2.35	342	6.96	272	8.05	69	10.2	55	10.9	2638	2855	2341	2271	2202	144	130	116
+5	2942	2.27	366	6.61	297	7.64	87	9.4	73	10.0	2645	2869	2319	2250	2183	130	116	104
+6	2986	2.16	393	6.23	326	7.20	106	8.6	94	9.1	2570	2892	2302	2235	2169	115	103	92
+7	3035	2.04	424	5.81	358	6.73	128	7.8	117	8.2	2677	2918	—	—	—	—	—	—

### 3.2. Aluminium and Chlorine

Since a neutral aluminium atom has three electrons in the M shell, the screening equations of (3.1)~(3.5) should be applied. Unfortunately, the M binding energy cannot be given, and therefore only the K and L screenings are taken into account. The effect due to M ionization will be discussed later. The data for aluminium are shown in Table 4, and the shift energies of X-rays and electrons are presented in Fig. 4.

The results for chlorine are given in Table 5 and in Fig. 5, similarly.

## 4. Discussions

The energies of characteristic X-rays or Auger electrons as a function of the atomic charge state have been seldomly reported, and consequently the propriety of the present computations will be a future problem. However, there is a precious result of the Al+5 MeV Ne experiment<sup>8)</sup>, in which the main and satellite K X-rays have been observed with the use of a crystal spectrometer. The energies corresponding to K, KL, KL<sup>2</sup>, KL<sup>3</sup>, KL<sup>4</sup> and KL<sup>5</sup> vacancies are presented, where the energy shift is about 10 eV per L ionization.

For the aluminium of Table 4, we have just calculated the energies due to the above vacancies, neglecting the contribution of M shell ionization. To introduce the practical effect of M ionization, it would be reasonable to take a half of three M electrons into account. Then, our values are corrected by the amounts corresponding to +1.5 ionization, which show larger shift energies than before.

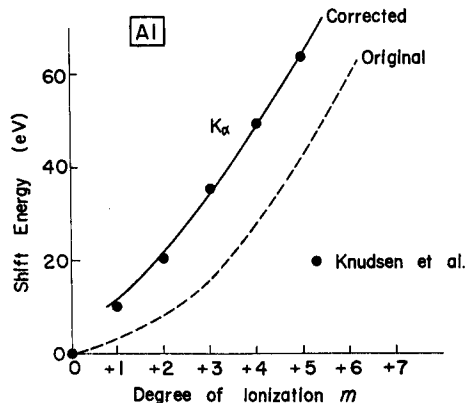


Fig. 6. Calculated and observed energy shifts of K<sub>α</sub> X-rays for aluminium as a function of degree of ionization.

The solid line is a corrected curve of the original one by considering the ionization of M shell electrons. The marks are the observed data of Knudsen et al.<sup>8)</sup>

The original and corrected energies are given by a broken line and solid line, respectively, in Fig. 6. The experimental values are also plotted in the figure and a good agreement is seen. In practice, the  $K_{\beta}$  X-rays of weak intensity have been approved, which supports the remaining M electrons in ionized aluminium.

In the Al+Ne experiment of Knudsen *et al.*, the strongest satellite X-rays are found around  $KL^2$  and  $KL^3$ , which means 3.5 vacancies as an average in the K and L shells of target aluminium. Those of M shell are estimated as 1.5 vacancies, as stated above. Therefore, we conclude that the mean charge state of aluminium by the bombardment of 5 MeV neon is +5.

Larkins<sup>4,5</sup> has also carried out the calculations of the energies for doubly K ionized neon and argon atoms. Applying the results of his experiments, the screening constants are given against the degree of ionization, as listed in Table 6, from which the appropriate screening functions are derived and the shift energies can be computed similarly. However, the magnitudes in this case are expected to be larger than those in singly K vacant atoms.

Table 6. Binding energies and screening constants for doubly K ionized neon and argon as a function of degree of ionization.

The binding energies in unit of eV are of Larkins<sup>4,5</sup>.

$m$	Neon				Argon							
	K		L		K		L				M	
	$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_K$	$s_K$	$E_{L1}$	$s_{L1}$	$E_{L23}$	$s_{L23}$	$E_{M1}$	$s_{M1}$
0	992	1.45	72	5.39	3434	2.09	366	7.61	292	8.72	48	12.4
+1	1025	1.31	94	4.73	3454	2.04	384	7.36	311	8.42	62	11.6
+2	1063	1.15	119	4.08	3475	1.99	404	7.08	330	8.13	76	10.9
+3	1105	0.87	145	3.46	3499	1.94	425	6.80	351	7.82	91	10.2
+4	1152	0.78	174	2.84	3524	1.88	448	6.50	375	7.48	107	9.6
+5	1203	0.58	205	2.22	3552	1.82	473	6.19	399	7.15	125	8.9
+6	1258	0.37	239	1.60	3581	1.75	499	5.87	426	6.79	143	8.3

Quite recently, we have done the C+C<sup>2+</sup> and N+N<sup>2+</sup> collision experiments in the energy range of 1~5 MeV, and the Auger electrons from target carbon and nitrogen have been observed. The Auger spectra are heavily distorted compared with those by electron or light ion bombardment, and the average energies show gradual shifts downwardly as the energies of heavy ions increase. At 4 MeV, the shifts for carbon and nitrogen are found to be about 30 eV. Referring to Table 3, we can predict that the average degrees of L ionization for target carbon and nitrogen are roughly +3 and +2.5, respectively.

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