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THE ENERGIES OF MULTIPLE X-RAY IONIZATION OF LIGHT ATOMS

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Abstract

The assumption is made that the removal of a K electron has the same effect on the energies of the outer electrons of the atom as the increase of the nuclear charge by one unit. The energy for the successive removal of a K electron and an L electron is computed for elements Na to K on this basis. By means of Wentzel's theory and Hjalmar's measurements of the K spark lines α_3, α_4, α_5, α_6, other multiple ionization levels are computed for the elements Na to S. The square roots of the energies ($\sqrt{\nu/R}$) for the successive removal of the first, second, and third L electrons plotted against atomic numbers give three parallel straight lines indicating that the removal of the first L electron reduces the screening constant (7.27) for the remaining ones by 0.62, and that the removal of the second one causes a further reduction of 0.65. Similar lines are obtained for the two K electrons, the screening constant (1.5) being reduced 0.16 by the removal of the first one. The energies for the successive removal of two electrons from a helium-like ion made up of a nucleus of charge Z and two electrons are computed for these atoms. The plot indicates that the experimental value of the *K absorption limit of phosphorus* is in error.

SEVERAL experimenters have found weak lines accompanying the K emission lines of some of the light elements, which do not correspond to transitions between levels of the ordinary scheme of x-ray levels. They are all of shorter wave-length than the strong lines which they accompany. Wentzel[1] has advanced the theory that these lines are emitted by multiply ionized atoms, and are thus analogous to the spark lines of optical spectra. Adopting Wentzel's notation, $K^p L^q$ will be used to indicate the term value equivalent to the energy of an atom which has had p electrons removed from the K shell and q electrons removed from the L shell. The following equations indicate the transitions which are thought to give rise to the different observed lines, the wave-number of the line being equal to the difference between the wave-numbers of the terms corresponding to the

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[1] G. Wentzel. Ann. der Phys. **66,** 437 (1921); **73** 647 (1924).

two states involved. They are arranged in the order of increasing wave-number.

$$\begin{aligned} \alpha_1 &= K-L \text{ (the ordinary K}\alpha \text{ doublet, unresolved)} \\ \alpha_3 &= KL-L^2 \\ \alpha_4 &= K^2-KL \\ \alpha_5 &= KL^2-L^3 \\ \alpha_6 &= K^2L-KL^2 \end{aligned} \tag{1}$$

Of great importance is the fact that the difference between α_6 and α_4 for one element is equal to the difference between α_3 and α_1 for the element of next higher atomic number. That is,

$$(\alpha_6-\alpha_4)_Z = (\alpha_3-\alpha_1)_{Z+1}$$

Substitution of the term values given by Eqs. (1) gives

$$(K^2L-K^2)_Z-(KL^2-KL)_Z = (KL-K)_{Z+1}-(L^2-L)_{Z+1} \tag{2}$$

Each of these expressions in parentheses is the energy for the removal of one L electron from an atom, those on the left being for atoms of atomic number Z which have already had two K electrons or one K and one L electron removed, respectively, and those on the right for atoms of atomic number $Z+1$ which have already had one K electron or one L electron removed, respectively. The equation indicates that the absence of a K electron in the atoms of atomic number Z is equivalent to the increase of the nuclear charge by one unit, or, in other words, that the screening effect of a K electron is unity and the energy of the L electrons is determined by the difference between the nuclear charge (in electron units) and the number of K electrons surrounding the nucleus. This explanation was given by Wentzel.[1] All of these spark lines result from the jump of one electron from an L orbit (K state of the atom) to a K orbit (L state of the atom), as does the Kα line. The electron orbits involved are, therefore, presumably of the same type as those which give as end states of the Kα transition the L_{21} and L_{22} states of the relativity doublet, which for the atoms of low atomic number are too close together to be separated. These are the orbits which are now thought to be analogous to the p_1 and p_2 orbits of optical doublet spectra. For the total quantum number 2 of the L orbits, they are 2_2 orbits which are approximately circular and do not penetrate within the orbits of the K electrons, hence the perfect screening by the K electrons would be expected. One might expect small differences between an atom with a K electron removed and one with a nuclear charge greater by one because the two would not be exactly equivalent for electrons whose orbits pene-

trate within the K orbits; the mutual screening of the L orbits would be slightly different, and the energy of a non-penetrating orbit slightly different. Wentzel's explanation amounts to assuming that because Eq. (2) is true, the corresponding terms on the two sides of it are individually equal, i.e., that

$$(KL^2-KL)_Z-(L^2-L)_{Z+1}=0 \text{ and } (K^2L-K^2)_Z-(KL-K)_{Z+1}=0$$

Eq. (2) would hold if these two differences were both equal to any other value. The above considerations show, however, that the assumption that they are equal to zero is in agreement with our present ideas concerning the structure of the atom. Furthermore, if the first of these differences were not equal to zero it would be highly improbable that the second one should have the same value. The screening effect of the second electron, the first one being gone, if not perfect, would probably not be exactly equal to that of the first one while both are present.

Making the assumption that the energy of removal of an L electron depends only upon $Z-x$, where x is the number of K electrons present, it is possible to calculate all of these multiple ionization terms from the ordinary K and L terms and the α_3, α_4, α_5 and α_6 lines. The KL term is obtained by the addition of the K term for the atom in question and the L term of the atom of next higher atomic number, corresponding to the successive removal of the K and L electrons. A slight error is introduced because of the change of the energy and screening effect of the added valence electron of the atom of higher atomic number. $(KL)_Z=K_Z+L_{Z+1}$, and then by Eqs. (1), $(K)^2_Z=(KL)_Z+(\alpha_4)_Z$, and $(L^2)_Z=(KL)_Z-(\alpha_3)z$. In a similar way $(KL^2)_Z=K_Z+(L^2)_{Z+1}$, and then $(K^2L)_Z=(KL^2)_Z+(\alpha_6)_Z$ and $(L^3)_Z=(KL^2)_Z-(\alpha_5)_Z$. These last three levels can also be computed in a different way for by our assumption $(K^2L)_2=(K^2)_Z+L_{Z+2}$. The equation which expresses the fact that these two methods of computing these levels give the same results, obtained by equating the two expressions for $(K^2L)_Z$, is $(K^2)_Z+L_{Z+2}=(KL^2)_Z+(\alpha_6)_Z$. It reduces to the equation $(\alpha_6-\alpha_4)_Z=(\alpha_3-\alpha_1)_{Z+1}$ which, as mentioned above, is confirmed by experiment.

The K levels for these elements are given by Fricke's[2] measurements of the K absorption limits. The L absorption limits have not been measured[3] but can be computed from the differences between the wave-

[2] H. Fricke, Phys. Rev. **16**, 202 (1920).

[3] My attention has been called to some new measurements of the L absorption limits, by an improved electrical method, by Holweck (C. R. **180**, 658, 1925). His mean value for Al agrees with the one computed below, but his mean values for the elements from Si to A are 0.2—0.3 greater than the values computed below. The reason for this discrepancy is not apparent.

numbers of the K limits and of the Kα lines measured by Hjalmar[4] and Siegbahn and Dolejšek.[5] If the square roots of these computed L levels be plotted as ordinates with atomic numbers as abscissas a straight line can be drawn through all of the points except the one for phosphorus. The P point also deviates from the similar line for the K levels. If, however, the L level for P be computed from the $\sqrt{L}$ line and a corresponding new K limit computed by adding Kα to it, the point corresponding to this new K limit will lie on the $\sqrt{K}$ line. This would seem to be good evidence that there is an error in the determination of the K absorption limit of P. The L limits for Na, Si, and A and the K limits for Na and Si have been obtained in this way. Table I gives Fricke's measurements of the K limits, the measured Kα lines, the computed K and L terms (terms in parentheses having been obtained by interpolation), and the frequencies of the spark lines (measured by Hjalmar[4]). All levels and frequencies are expressed in ν/R units. Table II gives the

TABLE I

Z	Element	K(Fricke)	$K\alpha$	K(calc)	L(calc.)	α_3	α_1	α_5	α_6
11	Na	.....	76.68	(78.84)	(2.16)	77.21	77.34	.....	.....
12	Mg	95.81	92.35	95.81	3.46	92.99	93.11	93.65	93.83
13	Al	114.67	109.53	114.67	5.14	110.26	110.41	111.05	111.27
14	Si	.....	128.18	(135.19)	(7.01)	129.02	129.18	129.92	130.12
15	P	158.26	148.37	(157.59)	(9.22)	149.33	149.51	.....	.....
16	S	181.81	169.97	181.81	11.84	171.02	171.23	172.68(?)	
17	Cl	207.84	193.14	207.84	14.70	.....	.....	.....	.....
18	A	235.73	.....	235.73	(17.95)	.....	.....	.....	.....
19	K	265.33	243.85	265.33	21.35	.....	.....	.....	.....

TABLE II

Z	Element	K^2	KL	L^2	K^2L	KL^2	L^3
11	Na	159.64	82.30	5.09	164.78	86.80	.....
12	Mg	194.06	100.95	7.96	201.06	107.23	13.58
13	Al	232.09	121.68	11.42	241.33	130.06	19.01
14	Si	273.59	144.41	15.39	285.41	155.29	25.37
15	P	318.94	169.43	20.10	333.64	183.08	.....
16	S	367.74	196.51	25.49	385.69	213.01	40.33(?)

values of the multiple ionization levels computed in the way described above. Wentzel stated that Siegbahn had written to him that he had found an absorption limit for S of wave-length somewhat less than half that of the ordinary K limit. It is presumably the K^2 limit corresponding to the simultaneous removal of the two K electrons. I have been unable

[4] E. Hjalmar, Zeits. f. Phys. **1**, 439 (1920).
[5] M. Siegbahn and V. Dolejšek, Zeits. f. Phys. **10**, 159 (1922).

to find any further published account of that experiment so as to compare the experimental value of the limit with the one given in Table II.

TABLE III

Z	Element	K	$(K)_2$	L	$(L)_2$	$(L)_3$	K_2'	E_2	K_1'
11	Na	78.84	80.80	2.16	2.93	.....	121.19	40.39	.....
12	Mg	95.81	98.25	3.46	4.50	5.62	144.27	46.02	136.20
13	Al	114.67	117.42	5.14	6.28	7.59	169.37	51.95	160.69
14	Si	135.19	138.40	7.01	8.38	9.98	196.50	58.10	187.14
15	P	157.59	161.35	9.22	10.88	.....	225.66	64.31	215.69
16	S	181.81	185.93	11.84	13.65	14.84	256.85	70.92	246.11

$L^2-L=(L)_2$, the energy necessary for removal of the second L electron, and $L^3-L^2=(L)_3$, the energy necessary for removal of the third electron. Similarly, $K^2-K=(K)_2$. These values are given in Table III. As would be expected, $(K)_2>K$, and $(L)_3>(L)_2>L$. If the square roots of these L values be plotted against atomic numbers three parallel straight

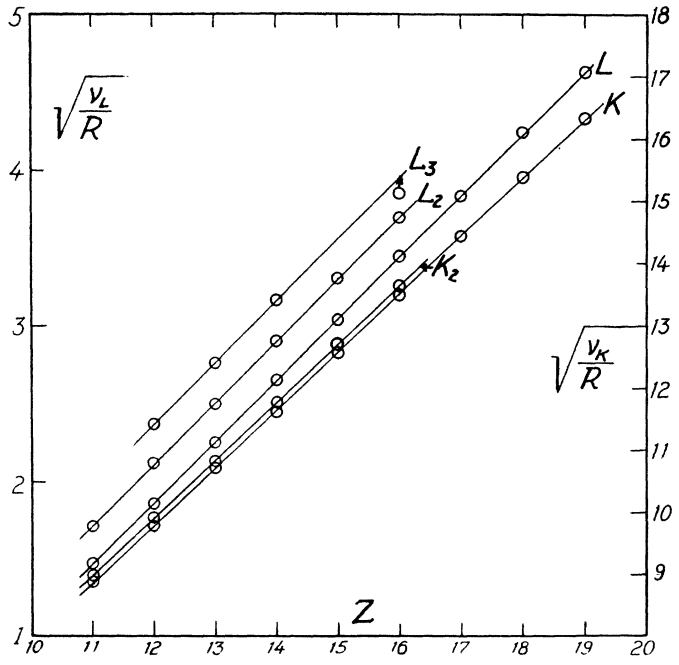

Fig. 1

lines are obtained as shown in Fig. 1. The S point which does not fall on the $\sqrt{(L)_3}$ line was obtained by use of Hjalmar's measurement of the unseparated α_5 and α_6 lines, which he considered doubtful. The $(L)_2$ line has an intercept on the Z axis 0.62 less than that of the L line, that

being the amount of lessening of the screening constant for the second electron by the removal of the first one. Similarly, the removal of the second one reduces the screening constant for the third one by 0.65 more. Similar parallel straight lines are obtained by plotting values of K and $(K)_2$, also shown in Fig. 1. The removal of the first K electron reduces the screening constant for the second one by 0.16.

After the first K electron has been removed, the second one presumably moves in a circular 1_1 orbit around the nucleus. If it were the only electron present the energy necessary for its removal would be Z^2, in ν/R units (neglecting the relativity correction). The presence of the other electrons can have very little effect upon the motion of this electron in its orbit, even though some of the outer electrons probably penetrate within the orbit of this K electron. The times of penetration are such minute fractions of their orbital periods that their effect on the energy of the K electron must be negligible. The energy for the removal of the electron through a cloud of outer electrons fixed in position would be less, however, because of their screening effect and is considerably less in the actual case because of the additional effect of the increased binding of the outer electrons which furnishes more energy. The calculated values of the energies of an electron in a 1_1 orbit for the different nuclei, making the relativity correction, are listed in Table III under K_2'. The difference between K_2' and $(K)_2$ gives E_2. If, as assumed above, the screening of the K electrons is perfect for the outer electrons this decrease in the energy necessary to remove the second electron is the same as the decrease in the energy necessary to remove the first K electron from the atom of next higher atomic number (neglecting the small effect of the added valence electron). That is, the sum of the K term for an atom of atomic number Z and E_2 for an atom of atomic number $Z-1$ will give K_1', the energy which would be necessary to remove the first K electron if there were no outer electrons present. The calculated values of E_2 and K_1' are also listed in Table III. K_1' and K_2' are thus the energies necessary for the successive removal of two electrons from an ion made up of a nucleus of charge Z and two electrons, and correspond to the first and second ionizing potentials of helium. Their values give additional data for the testing of theories of the structure of the helium-like ions. There does not seem to be any simple relation between K_1' and K_2' for these atoms which will also apply to the two successive ionizing potentials of He.

Hjalmar found one additional K spark line, lying between α_1 and α_3, which he designated α_1'. Wentzel suggested that it corresponds to the

transition $KM \rightarrow LM$. Applying the same argument as above, $(KM)_Z = K_Z + M_{Z+1}$ and $(LM)_Z = L_Z + (M_L)_Z$. $(M_L)_Z$, the energy for the removal of an M electron from an atom which has already had an L electron removed, is unknown. The equation $(\alpha_1')_Z = (KM)_Z - (LM)_Z$ becomes

$$(\alpha_1')_Z = K_Z + M_{Z+1} - L_Z - (M_L)_Z$$

which reduces to

$$(\alpha_1' - \alpha_1)_Z = M_{Z+1} - (M_L)_Z \ .$$

The quantity on the left hand side of the equation is positive, so $M_{Z+1} > (M_L)z$. This means that the removal of an L electron does not increase the energy for the subsequent removal of an M electron as much as the removal of a K electron does. That is, the L electron does not screen the nucleus perfectly, which is quite what would be expected. This last discussion will illustrate the complications which are to be encountered in considering the multiple ionization levels corresponding to the L spark lines which have been observed. Because of the imperfect screening by the L electrons there will be no simple relations between these levels and the ordinary single ionization levels, such as we have found for the levels discussed above.

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