Niels Bohr and Dirk Coster, "Roentgen Spectra and the Periodic System of the Elements"

In a paper published in this journal,[2] one of the authors developed the principal aspects of a theory of atomic structure. On the basis of this theory, it seems possible to give an interpretation of optical as well as Roentgen spectra that is intimately related to an interpretation of the periodic system of the elements. Following the publication of this paper, the Roentgen-spectroscopic experimental material suitable for testing the theoretical concepts was considerably enriched through an investigation by the other author, and its relationship to theory was discussed in a recently published paper.[3] This brought to light several interesting results. In the present joint paper, the comparison of the experimental material with the theory is gone into somewhat more thoroughly than was the case in the studies cited, taking into consideration particularly the relevance of Roentgen spectra for the interpretation of the periodic system.

Theoretical Concepts of Atomic Structure

The theory is based on a classification of the electron orbits in the atom by means of comparison with the stationary states of an electron which executes a central motion. The orbits are designated by the symbol n_k. n represents the so-called "main quantum number," which, in the limiting case where the central motion becomes a simple periodic Kepler motion,[4] is the only factor determining the energy, as may be seen in the Balmer formula for the hydrogen spectrum. As is well known, the "azimuthal quantum number" k, whose effect on the energy depends on the deviation of the motion from a simple periodic one, defines the angular momentum of the electron about the center of the orbit. The introduction of this quantum number, of course, is the basis of Sommerfeld's theory of the fine structure of the hydrogen lines; this

fine structure is due to the circumstance that, because of the relativity modification of the laws of mechanics, even the orbit of a single electron about a positive atomic nucleus is not strictly periodic, but can be described as a Kepler ellipse which executes a slow rotation in its plane. A survey of the number of electrons in the normal atom which, according to the theory, belong to the different types of n_k orbits, is given in Table 1. Concepts of atomic structure are expressed here which, apart from the characteristic new features, exhibit many similarities to the concepts that form the basis of the investigations on Roentgen spectra by Sommerfeld and Vegard.

It will be apparent that the electron orbits are arranged in groups that belong to the same value of the main quantum number n. The formation of these groups, in going to elements of higher atomic number, is related to the regularities that occur in the periodic system. One essential feature in this is that the groups are in turn divided into subgroups, which correspond to the different values of the azimuthal quantum number k. The reason for the typical deviations from simple periodicity in the system of the elements (families of the iron and platinum metals as well as of the rare earths) is assumed to be (1) the gradual addition of new types of electron orbits with the same main quantum number as that of the groups of electron orbits already present in preceding elements, which causes (2) the progressive stepwise formation of these groups. A survey of the periodic system that exhibits these features especially clearly is given in Figure 2,[5] where the elements belonging to the same period of the system are arranged in vertical columns. Elements in successive columns that can be regarded as homologous in their chemical as well as their optical characteristics are connected by straight lines. Series of successive element

TABLE 8–1.

Δ^{n}_{k}	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2
1 H	1																					
2 He	2																					
3 Li	2	1																				
4 Be	2	2																				
5 B	2	2	(1)																			
10 Ne	2	4	4																			
11 Na	2	4	4	1																		
12 Mg	2	4	4	2																		
13 Al	2	4	4	2	1																	
18 A	2	4	4	4	4																	
19 K	2	4	4	4	4		1															
20 Ca	2	4	4	4	4		2															
21 Sc	2	4	4	4	4	1	(2)															
22 Ti	2	4	4	4	4	2	(2)															
29 Cu	2	4	4	6	6	6	1															
30 Zn	2	4	4	6	6	6	2															
31 Ga	2	4	4	6	6	6	2	1														
36 Kr	2	4	4	6	6	6	4	4														
37 Rb	2	4	4	6	6	6	4	4			1											
38 Sr	2	4	4	6	6	6	4	4			2											
39 Y	2	4	4	6	6	6	4	4	1		(2)											
40 Zr	2	4	4	6	6	6	4	4	2		(2)											
47 Ag	2	4	4	6	6	6	6	6	6		1											
48 Cd	2	4	4	6	6	6	6	6	6		2											
49 In	2	4	4	6	6	6	6	6	6		2	1										
54 X	2	4	4	6	6	6	6	6	6		4	4										
55 Cs	2	4	4	6	6	6	6	6	6		4	4			1							
56 Ba	2	4	4	6	6	6	6	6	6		4	4			2							
57 La	2	4	4	6	6	6	6	6	6		4	4	1		(2)							
58 Ce	2	4	4	6	6	6	6	6	6		4	4	1		(2)							
59 Pr	2	4	4	6	6	6	6	6	6	2	4	4	1		(2)							
71 Lu	2	4	4	6	6	6	8	8	8	8	4	4	1		(2)							
72 —	2	4	4	6	6	6	8	8	8	8	4	4	2		(2)							
79 Au	2	4	4	6	6	6	8	8	8	8	6	6	6		1							
80 Hg	2	4	4	6	6	6	8	8	8	8	6	6	6		2							
81 Tl	2	4	4	6	6	6	8	8	8	8	6	6	6		2	1						
86 Nt	2	4	4	6	6	6	8	8	8	8	6	6	6		4	4						
87 —	2	4	4	6	6	6	8	8	8	8	6	6	6		4	4					1	
88 Ra	2	4	4	6	6	6	8	8	8	8	6	6	6		4	4					2	
89 Ac	2	4	4	6	6	6	8	8	8	8	6	6	6		4	4	1				(2)	
90 Th	2	4	4	6	6	6	8	8	8	8	6	6	6		4	4	2				(2)	
118 Y	2	4	4	6	6	6	8	8	8	8	8	8	8	8	6	6	6				4	4

Note: By 1925 the even distribution of the electrons over the subgroups was abandoned on the basis of the Roentgen spectra; the new rule provided a stepwise increase by 4 electrons. Thus, element 86, now designated by Em = Emanation instead of Nt = Niton, was represented by the following electron arrangement:

$$2 \mid 2\ 6 \mid 2\ 6\ 10 \mid 2\ 6\ 10\ 14 \mid 2\ 6\ 10 \mid 2\ 6$$

The boldly projected element 118 would presumably be characterized as follows:

$$2 \mid 2\ 6 \mid 2\ 6\ 10 \mid 2\ 6\ 10\ 14 \mid 2\ 6\ 10\ 14 \mid 2\ 6\ 10 \mid 2\ 6$$

Figure 2. The new periodic table of the elements.

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1H
2He

3Li —11Na
4Be —12Mg
5B  —13Al
6C  —14Si
7N  —15P
8O  —16S
9F  —17Cl
10Ne—18A

19K ——37Rb          55Cs ——— 87 –
20Ca——38Sr          56Ba ——— 88Ra
[21Sc——39Y]         [57La    89Ac]
[22Ti——40Zr]        [58Ce    90Th]
[23V ——41Nb]        [59Pr    91Pa]
[24Cr——42Mo]        [60Nd    92U]
[25Mn——43 –]        [61 –]
[26Fe——44Ru]        [62Sm]
[27Co——45Rh]        [63Eu]
[28Ni——46Pd]        [64Gd]
29Cu——47Ag          [65Tb]
30Zn——48Cd          [66Dy]
31Ga——49In          [67Ho]
32Ge——50Sn          [68Er]
33As——51Sb          [69Tm]
34Se——52Te          [70Yb]
35Br——53I           71Lu
36Kr——54X           72 –
                    73Ta
                    74W
                    75 –
                    76Os
                    77Ir
                    78Pt
                    79Au
                    80Hg
                    81Tl
                    82Pb
                    83Bi
                    84Po
                    85 –
                    86Rn ———118 –
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that assume a special position in that their inner groups are being built up are enclosed in square brackets.

The arrangement of Table 1 is based, in its main features, on considerations of a general nature which are explained in the paper mentioned above. In the working out of details, an intensive investigation of series spectra plays an essential part. In these spectra, again, although the gradual formation of inner electron groups is clearly reflected, the direct information that can be obtained from the series spectra concerns primarily the gradual addition of those electron orbits of new types by which the steps of the formation are introduced. Correspondingly, in Table 1, essentially only those elements are indicated that are the initial steps of the formation; besides, whenever the spectral material does not allow one to draw a unique conclusion regarding the number of electrons in the outermost groups, the numbers of electrons

which correspond to the highest quantum orbits are shown in parentheses. The further formation of the groups is indicated only by its final result; but the description of the completely formed groups, also, still contains many uncertainties at this time, especially in regard to the finer interaction of electron motions within the same main group and its subgroups. Without entering into this question further here, we merely want to point out that the general assumptions on the nature of this interactlon, introduced in the paper mentioned above and discussed there in more detail, provide a criterion, based on the correspondence principle, for a theoretical understanding of the typical laws that govern emission and absorption spectra in the Roentgen region, and whose main features were explained by Kossel's for mal theory.
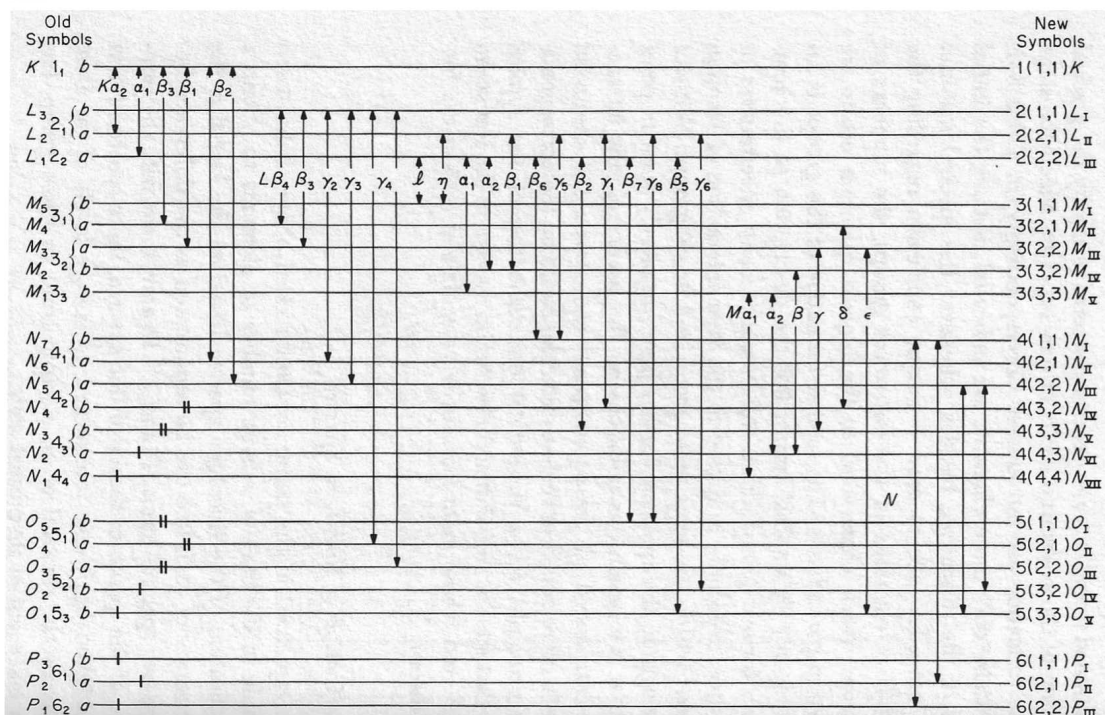
Classification of Roentgen Spectra

As explained in the paper by Coster cited above, it has been possible in the case of a large number of elements to obtain a classification of the Roentgen spectra based on the fact that the frequency ν of each line can be represented as the difference between two spectral terms, T′ and T″. In agreement with the principles of the quantum theory of line spectra, these spectral terms—multiplied by h—are interpreted as energy levels of an atom which, by the removal of an electron from an inner group, has been taken out of its normal state.

Figure 3 gives a survey of the characteristic Roentgen spectrum to be expected for the inert gas radon (86). The spectral lines are indicated in the usual manner by vertical arrows, while the horizontal lines represent the levels. Only those lines are shown that were actually measured for several elements in the vicinity of this inert gas. At the same time, the figure gives a survey of the spectrum of the elements in the vicinity of the rare gases xenon and krypton. The levels that disappear in going to elements of lower atomic number between radon (86) and xenon (54) are shown in the figure by one vertical line, and the levels that disappear in addition between xenon (54) and krypton (36) are designated by two lines.

Figure 3.

4

As indicated in the figure, the symbols used to designate the levels have been changed from those used in the preceding papers. First, the sublevels that belong to the same group of levels are designated by Roman numerals in the sequence in which they gradually occur with increasing atomic number in the Roentgen spectra of the elements. Further, each level has attached to it a numerical symbol of the form n (k_1, k_2). Later, we shall discuss in more detail the relationship of these symbols to the theory of atomic structure. Here, we only want to point out that the levels that were used in Figure 3 for representing the spectra of each of the three inert gases are all characterized by those values of n and the k's that, in Table 1 above, occur as values of the quantum numbers n and k for the electron orbits in the atoms of these elements. We observe further that the occurrence of lines that correspond to combinations between the

levels is governed by the rule that the number k_1 always changes by one unit in the transition process, while k_2 either changes by one or remains constant. These rules are equivalent to the rules that were expressed in Coster's earlier work by means of the old symbols, and formally they correspond precisely to the rules that were formulated in the same time by Wentzel. The numerical values introduced for k_1 and k_2 are equal to the values of the numbers n and m used by this author for the classification of the levels. However, we shall interpret their theoretical significance in a somewhat different way.

Determination of Energy Levels from the Experimental Material

The results of the presently available measurements of Roentgen spectra allow us to calculate the energy levels of a large number of elements with considerable precision. ...

[1] [Copied from Eduard Farber, Ed., *Milestones of Modern Chemistry*, Basic Books, New York, 1966, pp 122-130. Translation by Elisabeth F. Lanzl. —CJG]

[2] N. Bohr, *ibid*., Vol. 9 (1922), p. 1.

[3] D. Coster, *Philosophical Magazine*, Vol. 43 (1922), p. 1070; Vol. 44 (1922), p. 546.

[4] [As in the sun's planets. —Ed.]

[5] [Cf. N. Bohr, *Three Essays on Spectra and Atomic Structure*, p. 132, Fig. 5, where a more detailed explanation of this figure can be found. Not taken into account either in the schematic representation or in the figure is the note by Dauvillier, *C. R.*, May, 1922, mentioned in the supplement to these essays, on the observation of some weak lines in the Roentgen spectrum of an element of atomic number 72 in a mixture

of rare earths, for this observation can hardly be regarded as definitely proved. The presence of an element between Lu (71), whose highest valence is 3, and Ta (73), whose highest valence is 5, with chemical properties similar to Lu, would represent a deviation from the otherwise general rule that the highest valence in the transition from one element to the following one never increases by more than one unit—a rule that has a direct explanation in the generally assumed concepts of atomic structure (cf. also C. R. Bury, *Journal of the American Chemical Society*, Vol. 43 [1921], p. 1602). [This footnote appears to be by the editor of *Milestones in Modern Chemistry*, not in the original paper. — CJG]]