Langmuir has suggested[8] that in the cyanide radical the carbon and nitrogen atoms possess in common an outer shell of electrons. If in accordance with this hypothesis the cyanide radical be regarded as a single atom for crystal structure purposes, potassium cyanide can be given the holohedral sodium chloride structure with four molecules in the unit; but if this be done, the values of $\sqrt{A^2 + B^2}$ for (711) and (320) will, on the same assumptions used previously, be 24 and 128, respectively, and this would make the intensity of the (320) reflection $(128/24)^2$ or 28 times as strong as that of the (711) reflection. This great discrepancy might be overcome by assuming the reflecting power of the cyanide radical to drop off much more rapidly than that of the potassium atom with decreasing values of d/n; but there seems to be little present justification for such an assumption.

VII. Summary.

The crystal structure of potassium cyanide has been studied with X-rays making use of the Laue photographic method, the spectrometric method, and the powder method. The X-ray data show conclusively that the structure of this substance approximates the sodium chloride structure. Consequently, the potassium atoms were placed at the sodium atom positions and the carbon and nitrogen atoms near the chlorine atom positions. The positions of carbon and nitrogen atoms which give the best agreement with the data place these atoms 1.15×10^{-8} cm. apart, equidistant from the position of the chlorine atom. The structure is represented in Fig. 2.

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NOTES.

Correlation of Atomic Structure and Spectra.—In the July number of THIS JOURNAL there is a very interesting article by Bury[1] on a modification of the Lewis-Langmuir hypothesis of atomic structure. The sole change in this modification is that the fourth of Langmuir's postulates is altered to read as follows.

"The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus, successive layers can contain 2, 8, 18 and 32 electrons. Groups of 8 and 18 electrons in a layer are stable even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure."

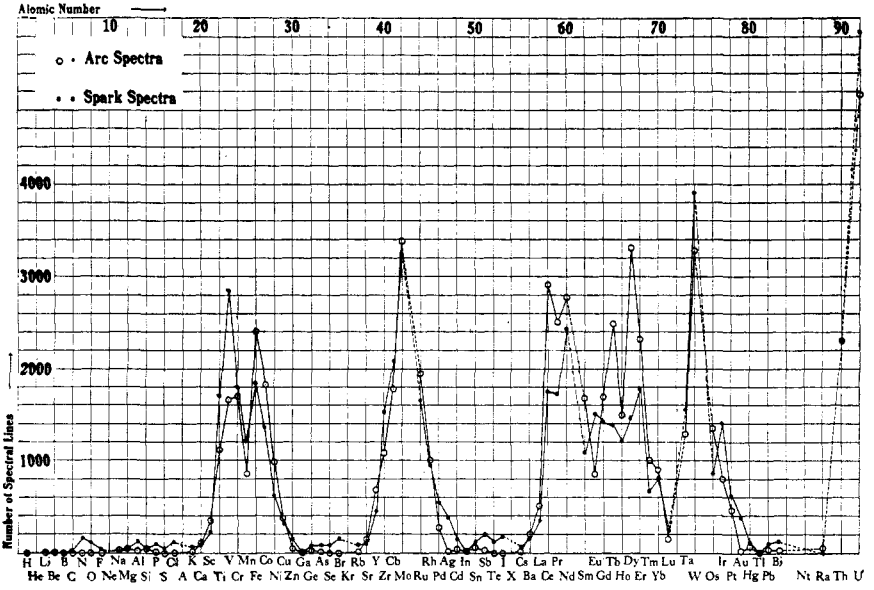
The only physical substantiation of this hypothesis which Bury stresses

[8] Langmuir, THIS JOURNAL, **41**, 905 (1919).

[1] C. R. Bury, *ibid.*, **43**, 1602 (1921).

is the relation of atomic diameter of elements in a group of the periodic table with the number of electron shells in these elements. It seems that other data might also be employed which would test the plausibility of this hypothesis, namely, the data on the number of lines in the arc or spark spectra.

By plotting the atomic weights (or better the atomic numbers) as abscissas and the number of spectral lines as ordinates, Exner and Haschek[2] obtained periodic curves both for the spark and the arc spectra, the essentials of which are reproduced in Fig. 1. In the general form of the



curves, both are very similar and present the following main features. There are peaks between the elements Sc and Cu, Y and Pd, Ta and Pt. Th and U rise toward a peak at the end. There is also a plateau including most of the rare earths, that is, between Ce and Lu. The rest of the elements have relatively few lines.

Now, if it is assumed that it is only the electrons in the outer shell of the atom that are responsible for the spectral lines, then it may be supposed that in a general way, there is a relationship between the number of these electrons and the number of lines in the spectrum. Of course theoretically an infinite number of lines may be emitted by an element, but practically there are enormous differences between elements in this respect. By including only those lines given in Exner and Haschek's tables,[3] the rela-

[2] Exner and Haschek, "Die Spektren der Elemente bei Normalem Druck," Franz Deuticke, Leipzig, 1911, Vol. 1, p. 36.

[3] Exner and Haschek, Ref. 2, vols. 2 and 3.

tive numbers of lines in the spectra of the elements are placed on a more equable basis for comparison. If all lines except those between the wave lengths λ = 3,000 and 6,000 Å. were omitted, the comparative results would be essentially the same except that the plateau of the rare earths would be lowered due to their great richness of lines in the ultraviolet. A list of all the lines found either in the spark or in the arc spectra would be preferable to either alone. However, it is almost impossible to make such a compilation from Exner and Haschek's tables.

The number of lines in the arc and spark spectra of three groups of elements will be discussed herein with relation to the views of Bury and Langmuir on atomic structure,—namely (1) the elements of groups in the periodic table, (2) the transition elements and (3) the rare earth elements.

TABLE I

Element	Group	Arrangement of Electrons		Number of Line	
		Bury	Langmuir	Arc	Spark
Be	II*a*	2.2	2.2	9	10
Mg	II*a*	2.8.2	2.8.2	52	58
Ca	II*b*	2.8.8.2	2.8.8.2	114	84
Zn	II*a*	2.8.18.2	2.8.8.12	35	134
Sr	II*b*	2.8.18.8.2	2.8.8.18.2	146	89
Cd	II*a*	2.8.18.18.2	2.8.8.18.12	38	129
Ba	II*b*	2.8.18.18.8.2	2.8.8.18.18.2	207	148
Hg	II*a*	2.8.18.32.18.2	2.8.8.18.18.26	78	99
B	III*a*	2.3	2.3	2	3
Al	III*a*	2.8.3	2.8.3	28	115
Sc	III*b*	2.8.8.3	2.8.8.3	342	204
Ga	III*a*	2.8.18.3	2.8.8.13	14	14
Y	III*b*	2.8.18.8.3	2.8.8.18.3	684	430
In	III*a*	2.8.18.18.3	2.8.8.18.13	28	30
La	III*b*	2.8.18.18.8.3	2.8.8.18.18.3	512	356
Tl	III*a*	2.8.18.32.18.3	2.8.8.18.18.27	22	18

According to Bury, the elements of Group II of the periodic table all have two electrons in the outer shell, while Langmuir's hypothesis allows the members of the calcium series 2 electrons apiece but the beryllium series 2, 12 or 26. If the values for the number of lines given by Exner and Haschek are indeed comparable and if there is a qualitative relation between the number of such lines and the number of electrons in the outer shell, it will be seen in Table I that Bury's modification gives a better approximation to the facts observed by Exner and Haschek than the original hypothesis of Langmuir. Thus calcium and zinc according to Bury's arrangement of electrons should give approximately the same number of lines, while with Langmuir's arrangement, Zn would be expected to give six times as many as Ca. Considering that probably there is an increase of lines with increasing complexity of the core as shown by

the first three members of the group where both hypotheses agree, the number of lines given by alternating members of the group is remarkably uniform.

Group III of the periodic table is also included in Table I. It seems to be a general tendency for the *b* sub-group to give more lines than the *a* sub-group instead of the reverse as expected by Langmuir's hypothesis. In this connection it will be noted that in the *a* sub-group, after the first two members, there are 18 electrons in the outer shell of the core while in the *b* sub-group there are only 8 according to Bury. Naturally 3 electrons in the valence shell can arrange themselves more uniformly over 18 electrons than over 8. To substantiate this, Al, an *a* sub-group member with only 8 electrons in the second shell, has the largest number of lines of any member of its sub-group.

The transition elements, Bury suggests, have a variety of electron structures to account for their varying valences, an electron or electrons being pushed into an incompleted inner shell when the number of electrons in the outer shell becomes large. In Table II, the elements from K to Ge are arranged according to their atomic numbers. A transition group is included between these elements. Bury suggests that the number of varying structures increases roughly from Ti to Mn as a maximum and then decreases to Cu. If Bury's idea is correct, then each element having more than one form should give an entirely different spectrum for each

TABLE II

Element	Arrangement of Electrons		No. of Lines	
	Bury	Langmuir	Arc	Spark
K	2.8.8.1	2.8.8.1	18	61
Ca	2.8.8.2	2.8.8.2	114	84
Sc	2.8.8.3	2.8.8.3	342	204
Ti	2.8.8.4; 2.8. 9.3; 2.8.10.2	2.8.8.4	1123	1705
V	2.8.8.5; 2.8. 9.4; 2.8.10.3; 2.8.11.2	2.8.8.5	1642	2837
Cr	2.8.8.6; 2.8.11.3; 2.8.12.2	2.8.8.6	1697	1806
Mn	2.8.8.7; 2.8. 9.6; 2.8.11.4; 2.8.12.3; 2.8.13.2	2.8.8.7	865	1216
Fe	2.8.10.6; 2.8.12.4; 2.8.13.3; 2.8.14.2	2.8.8.8	2392	1838
Co	2.8.13.4; 2.8.14.3; 2.8.15.2	2.8.8.9	1830	1360
Ni	2.8.14.4; 2.8.15.3; 2.8.16.2	2.8.8.10	976	623
Cu	2.8.17.2; 2.8.18.1	2.8.8.11	368	328
Zn	2.8.18.2	2.8.8.12	35	134
Ga	2.8.18.3	2.8.8.13	14	14
Ge	2.8.18.4	2.8.8.14	27	62

different arrangement of electrons. These spectra superimposed on each other would result in a very complicated spectrum, rich in lines. This view predicts an increase in the number of lines to Mn and then a decrease. Moreover, there is a chance for lack of symmetry in the core of transition elements having the third shell containing between 8 and 18 electrons. These stable groups are probably symmetrically placed

in the shell, but this is not possible for such a structure as 2.8.13.3 for Fe. This irregularity would affect the positions of the valence electrons with consequent increase of the number of lines that may be produced. Langmuir's structure of the elements between K and Ge gives each element one more electron in the outer shell for each increase in atomic number. Thus it would be expected that the complexity of the spectra would increase all the way to Ge without a noticeable break. The number of lines does increase to Cr and Fe which are on either side of Mn which ought to be the true maximum, and then decreases steadily to Ga. This behavior accords with Bury's modification with the exception of Mn which is not vital.

There are similar peaks at the other transition groups. Thus between Y and Pd there is a very well defined peak with Mo at its maximum. The numbers of lines in the spectra of the elements of this transition group, *i. e.*, Y. Zr, Cb, Ru, Rh, and Pd fall almost exactly on the line drawn from Sr up to Mo and down to Ag. W forms the maximum of the peak of the third transition group and Th and U form the beginning of a fourth peak. Thus all the main peaks in Exner and Haschek's curves are accounted for by Bury's arrangement of electrons.

There remains only the plateau of the rare earth metals to be discussed. Langmuir's explanation of the structure of the elements of the rare earth metals shows the first member, La, with 3 electrons in the outer shell and then with each increase of one in the atomic number, an additional electron is added to the same shell. Lu thus is pictured with 17 electrons in the outer shell. The spectral curve should therefore become more and more complicated throughout the whole group without a drop at the end. It should blend into the third transition group without a break. Bury's explanation is that all the elements of this group may have a valence of 3, the excess electrons being added to an inner incompleted shell rather than to the outer shell. The first member and the last member of the group, La and Lu, have stable groups in the inner shells, but the intermediate elements have the fourth shell composed of from 19 to 31 electrons. It seems possible that there might be a choice of positions for the extra electrons in the inner shell which would give different kernels within the valence shell and thus cause such elements to be capable of producing a distinct set of lines for each arrangement. The non-symmetry of many of these structures would also tend to increase the number of lines. With the exception of La and Lu, the rare earth metals do give very complicated spectra with very large numbers of lines. The exceptions are interesting. La and Lu have stable systems in the inner shells and so would not be expected to give varying electron structures with consequent abundance of spectral lines.

Any relation of a property of the elements, such as the number of spectral lines, to the atomic number may lead to predictions concerning those elements as yet un-

known. There are six places vacant in the table of elements arranged according to atomic number, namely Nos. 43, 61, 72, 75, 85 and 87. Of these, No. 72 possibly is Urbain's celtium. But Bury's arrangement gives the electron structure 2.8.18.32.8.4 for this element which is consequently tetravalent, while Urbain describes celtium as being intermediate in chemical character between Lu and Sc, both trivalent elements. A further investigation of the chemical properties and the X-ray spectrum of celtium is therefore desirable.

Elements 43, 61 and 75 lie in approximately symmetrical positions on the curve of number of spectral lines plotted against atomic number. This relationship probably does not mean much in connection with No. 61, but may signify more in respect to Nos. 43 and 75. Thus they both would be expected to give very complicated spectra having large numbers of lines. Moreover, according to Bury, both would have similar electron structures, *i. e.*, 2.8.18.8.7 and 2.8.18.32.8.7. Since Bury thinks that in the second and third transition groups the electrons pass into an inner layer less readily than in that of the first long period, these elements Nos. 43 and 75 might be expected, if they really exist, to form compounds where they have high valences. Thus, in a search, one might look for them as cations rather than as anions.

Summary.

It is shown that Bury's modification of Langmuir's hypothesis is at least consistent with the facts derived from a study of the number of lines in the arc and spark spectra of the elements as given in Exner and Haschek's tables.

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Correction.—Owing apparently to carelessness in proof-reading for which I am personally responsible, several very small errors exist in the tables of results in the paper by Baxter, Tani and Chapin[1] on the atomic weight of lanthanum. My attention has been called to this matter by Dr. Moles of the Laboratorio de Investigaciones Fisicas in Madrid. In order to avoid confusion the tables are reprinted below with the corrected figures starred. Fortunately, the changes do not affect the ultimate result in the least.

Ratio $LaCl_3 : 3Ag$	At. Wt. La	Ratio $LaCl_3 : 3AgCl$	At. Wt. La
0.757888	138.912*	0.570543	138.969
0.757841	138.897	0.570394	138.905
0.757878	138.909	0.570391	138.904
0.757915	138.921	0.570331	138.878*
0.757930	138.925	0.570413*	138.913*
0.757917*	138.921*	0.570447*	138.927*
		0.570368	138.893
Av. 0.757895*	Av. 138.914*	Av. 0.570413*	Av. 138.913*

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[1] Baxter, Tani and Chapin, THIS JOURNAL, **43**, 1804 (1921).