X-rays and Atomic Structure at the Early Stage of the Old Quantum Theory

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I. Introduction

In the previous paper\(^1\) we concluded that at the earlier stage of the development of the theory of atomic constitution, namely in the decade of 1910's, chemical considerations have played the cardinal part. Atomic models capable of explaining the chemical properties, which were proposed and developed by Kossel, Lewis, and others, exhibited right properties as far as the general features were concerned. Especially they gave the correct number of electrons in each ring- or shell-grouping of electrons inside atom.

In the course of this investigation, we were compelled to trace the development of the theories of characteristic X-ray spectra and to assess properly the role played by these theories in the history of the theory of atomic constitution in the same period (in the 1910's). We indeed found that although works on X-ray spectra made some contributions which could not be looked over, they were subordinate to the chemical approach.

The following is the result that we have obtained concerning the part played by the studies of characteristic X-rays in elucidating the structure of the Bohr atom.\(^2\)

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\(^2\) After the author finished the preliminary note\(^2\) on this subject, she received the issue of \textit{ISIS}\(^3\) in which J. L. Heibron published a paper on the theory of X-rays and the structure of atom in the same period as hers. Making use of, in addition to the published papers, unpublished various documents, he traced in detail the process of the rise and fall of the ring atom model mainly in consequence of the evolution of the theories of X-ray spectra. The author, however, considers the cause of the decline of ring atom model not only in X-ray spectra but also in the chemical properties of atom. It should be noticed that the relation of the X-ray investigations with the chemical considerations is outside the scope of Heilbron's paper.
II. Bohr and Moseley

In 1912 J.J. Thomson proposed a tentative theory about the origin of characteristic X-rays that they were emitted when a tightly bounded intra-atomic electron group was removed from the atom and a subsequent recombination took place\(^4\). He wrote: “Suppose that besides the corpuscles which can be dislodged from the atom by the expenditure of an amount of energy measured by a few volts, there are in the atom other systems which require for their dissociation a much greater amount of energy, say an amount measured by thousands of volts. When the residue and the corpuscle unite and reproduce the original system, this amount of energy will have to be radiated away. The maximum energy would be in the neighbourhood of wave-length \(10^{-8}\) cm., i.e. the radiation would be Röntgen radiation”. In the second paper of 1913\(^5\) Bohr, as did J.J. Thomson, supposed that “the characteristic Röntgen radiation is sent out during the settling down of the system if electrons in inner rings are removed by some agency, e.g. by impact of cathode particles”. On this supposition he could show that the characteristic X-radiation of the K-type might be ascribed to the innermost ring. He determined the minimum velocity of cathode ray particles which was necessary to produce the K-radiation by calculating the energy required to remove one of the electrons from the innermost ring. For the approximation, he took, instead of the actual atom, a simple model system consisting of a bound electron rotating in a circular orbit around the positive nucleus of charge \(Ne\) The value calculated for the minimum velocity approximately agreed with Whiddington’s experimental results on the velocity of cathode ray particles capable of producing the K X-rays.

In the same year Moseley\(^6\) examined systematically the characteristic X-rays emitted by various elements, and obtained the well known empirical formula bearing his name which could be expressed as the relation between the frequency of X-rays and the atomic number:

\[
\begin{align*}
V_{K\alpha} &= R(Z - 1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right), \\
V_{L\alpha} &= R(Z - 7.4)^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right),
\end{align*}
\]

(1)
where $R$ is the Rydberg constant, $Z$ the atomic number, $V_{K\alpha}(V_{L\alpha})$ the frequency of $K\alpha (L\alpha)$-line.

Moseley’s work was received as strongly supporting the hypothesis that the atomic number of an element was the number of its nuclear charge, that is, the number of electrons in its atom. For example, Rutherford stated that “the strongest and most convincing evidence in support of this hypothesis will be found in a paper by Moseley in *The Philosophical Magazine* of this month.” Similar opinion was also expressed by an author of a review article on the recent works on the structure of atom. This hypothesis, together with the experimental fact that the position of a certain line, say $K\alpha$, for the successive elements of the periodic system revealed a regular progressive shift, seemed to support strongly the view that the origin of the characteristic X-ray spectra must be located in the immediate neighbourhood of the nucleus, that is, in the innermost part of the atom. At the same time it became to be believed that the study of the characteristic X-ray spectra would shed much light on the structure of the innermost part of atom.

Furthermore, the similarity of Moseley’s formula with Bohr’s formula for the hydrogen spectrum motivated attempts to find an explanation of X-ray spectra on the basis of Bohr’s atomic theory. In fact, Moseley himself proposed an explanation of his formula that the $K\alpha$-line was emitted during a translational movement of the innermost ring as a whole between two states in which the angular momentum of each electron was equal to $\frac{h}{2\pi}$ and $\frac{h}{2\pi}$ respectively. Assuming that the fact that rather $Z-1$, not $Z$ itself, appeared in his formula was a reflection of the effect of other electrons in the same ring, Moseley deduced that the number of electrons in the ring concerned was equal to 4. However, Moseley realized that, as Bohr later pointed out, his own theory seemed to face a difficulty in the energy consideration. In fact, the approximate agreement of Bohr’s calculation with Whiddington’s measurements of the energy required to produce the characteristic X-rays was generally interpreted as strongly indicating that the X-ray spectrum was due to a displacement of a single electron, not the whole ring. If the ring as a whole was to displace, the energy should be several times larger.

*) About Moseley’s work, J. L. Heilbron wrote a separate article. For the detailed account of Moseley’s papers, the reader is referred to Heilbron’s article.
III. Kossel and Sommerfeld.

Now, of succeeding investigations on the characteristic X-rays, two important theories must be considered in detail: one was presented by Kossel in 1914 and the other by Sommerfeld in 1916. These authors both seem to have paid particular attention to Bohr's theory of atomic constitution since immediately after its emergence.

In 1914, Kossel made investigation on the absorption of X-rays passing through material layers and obtained the absorption curves in the two regions of wavelength, the regions of K-series and L-series, for several metals. Each curve showed a sharp absorption near the wave length of the second line of each series (that is, the $K_\beta$-line or $L_\beta$-line), which could be related to production of the emission lines. Kossel asserted that this result could be explained by means of Bohr's model, and proposed a new theory of the mechanism of emission of characteristic X-ray which was different from Moseley's one. Whereas Moseley thought that the transition from one state to another of the innermost electron ring as a whole gave rise to the emission of characteristic X-rays, Kossel adopted Bohr's view on the origin of the characteristic X-rays as described earlier, according to which they were emitted by the displacement of an electron from the innermost ring.

Kossel thought, according to Bohr, that a vacant place might be produced in the innermost ring (K-ring) by the removal of an electron from it when the atom was bombarded by cathode rays or X-rays. He argued that if the vacancy was to be filled up by an electron from outside the atom, the frequency of radiation emitted by this electron would not be smaller than the minimum frequency (Grenzfrequenz) of the incident X-rays that was necessary to produce the characteristic line. But no X-ray line of a frequency not smaller than the Grenzfrequenz had been observed. The strongest line, the $K_\alpha$-line, had a wave length that was longer than that corresponding to the Grenzfrequenz and was the longest among observed K-lines. The $K_\alpha$-line, therefore, had to be assumed to correspond to the emission of the smallest amount of energy. Thus Kossel supposed that the $K_\alpha$-line would be produced when a vacant place in the K-ring was filled up by one of the electrons in the second ring, not by an electron from
outside the atom. The state of atom, in which the second ring has given away an
electron, is identical to the state in which an electron on the second ring (L-ring)
has been removed from it directly by X-rays. Thus the same would then occur,
Kossel thought, to the L-ring with a vacant place as that occurred to K-ring. The
wave length of the L-line would correspond to the smallest energy emitted as
L-lines. In analogy with the Kα-line, the Lα-line would be ascribed to the
transition of an electron from the third ring to the second. Successive transitions
of electrons between two adjacent rings would thus give rise to emission of Kα-,
Lα-, Mα-, ..., lines, if Mα-, ..., lines were to exist at all.

Guided by such a consideration, Kossel was led to the conclusion that the
sum of the energies emitted by each transition of electron never exceeds the
energy required to remove one electron from the innermost ring to outside the
atom, which corresponds to the K-Grenzfrequenz. In fact, making use of his
absorption curves and Moseley’s formula, Kossel confirmed the relation:

\[ \nu_{K_g} = \nu_{K_\alpha} + \nu_{L_g} \]  

where \( \nu_{K_g} \) is the K-Grenzfrequenz corresponding to the energy required to
remove an electron from the first ring (K-ring), \( \nu_{K_\alpha} \) is the frequency of Kα-line
the jumping of an electron from the third (L-ring) to the first
ring, and \( \nu_{L_g} \) is the L-Grenzfrequenz.

Kossel then assumed that in addition to the transitions mentioned above,
another type of transition that the vacant place in the K-ring would be filled up
by an electron from an outer ring, say from the third, or forth, or ... ring might
occur. On this assumption it was expected that the energy emitted by the
transition from the third to the first ring would be equal to the sum of the energy
corresponding to the Lα-radiation (transition from the third to the second ring)
and that corresponding to the Kα-radiation (transition from the second to the first
ring): \( h \nu_{K_\alpha} + h \nu_{L_\alpha} \). By making use of Moseley’s measurement of frequencies for
the Kα and Kβ and calculating the value of the frequency of Lα with the help of
Moseley’s formula, Kossel could show that for the elements from Ca to Zn this
sum of the energies actually corresponded to the Kβ-radiation:
\[ \nu_{K\beta} = \nu_{K\alpha} + \nu_{L\alpha} \]  

(3)

He expected the relation \( \nu_{K\delta} = \nu_{K\alpha} + \nu_{L\beta} \) for the combination of the first, second, and forth rings, and also similar relations for other combinations of rings.\(^*\).

Kossel’s results above was generally received as adding support to Bohr’s ring atom and as indicating that the combination principle established in optical region is valid also for the characteristic X-rays. For example, an author of a review article on the works on the structure of atom expressed similar opinion.\(^{15}\) Kossel himself noted in his 1914 paper\(^{16}\) that his relation (2) was closely analogous to Rydberg-Schuster rule, according to which, in optical spectral series, the difference of the frequency of the limiting line of P series and that of S or D series is equal to the frequency of the first line of P series. Referring to Kossel’s view, Bohr in his 1915 paper “On the Quantum Theory of Radiation and the Structure of the Atom”\(^{17}\) said: “It will be seen that these relations correspond exactly to the ordinary principle of combination of spectral lines”. And referring to some experimental results obtained recently agreeing with Kossel’s results, Bohr said” ...

\(^*\) Heilbron asserted that “of course Kossel’s main thesis was not these relations but the assertion that ionization precedes X-ray emission. It is here, I believe, that we may well see the influence of Lenard. During all of Kossel’s time at Heidelberg, Lenard was on crusade for his view that spectral emission occurs only during the recapture of an electron by an ionized atom, ... . By the time of Kossel’s gradation, Lenard’s view that ionization must precede emission had been widely accepted; J. J. Thomson, among others, held it, and there is good evidence that Bohr did so as well. But in 1913 Bohr specifically abandoned this mechanism, at least for optical spectra; and it seems very likely that part of the reason he and Moseley were unable to hit on Kossel’s simple X-ray model was that they had already firmly rejected it for the optical case. Kossel, however, ... , did not part with it so readily”. This Heilbron’s argument, however, is not acceptable to the present author. She as well believes with Heilbron that Lenard’s view had been widely accepted in the period considered. As was mentioned above, J. J. Thomson held it. But in 1913 Bohr too did so, at least for X-ray spectra. This is sufficiently evidenced by Bohr’s calculation of the minimum velocity of cathode ray particles required to produce K-radiation. The author does not think that Kossel sticked on the view that ionization must precede emission. As will be shown later Kossel expected that in addition to the process of ionization another process would be responsible to the emission of X-rays, in which an electron was excited from the innermost ring to an possible outer ring.
it will be seen that even if Kossel's considerations will need modification in order to account in detail for the high frequency spectra, they seem to offer a basis for a further development”.

However, the validity of Kossel's relations (3) and others between frequencies of X-ray lines, and consequently that of the combination principle of X-ray lines, became soon to be suspected by Sommerfeld. In his 1916 paper\(^1\) which will be considered later, Sommerfeld pointed out that his expressions of X-ray spectral terms showed that no frequency of L-lines was derived from such combination of the frequencies of K-lines as the Kossel relation, \(\nu_{L\alpha} = \nu_{K\beta} - \nu_{K\alpha}\), and to support this view cited the experimental result obtained recently by Siegbahn for M-series the first two lines of which were not derived from any combination of L-lines. Being aware of Sommerfeld's suspicion above, Kossel noted that the value of K Grentzfrequenz expected from the assumption that the combination principle would hold for the X-ray lines, which had been believed to be equal to the first term of Moseley's formula for K\(_{\alpha}\)-line, was somewhat greater than the observed value of Wagner. Nevertheless Kossel believed that these defects might be cleared away by minor additional assumptions and in 1916 said that his view was increasingly supported by various experimental data.\(^2\) Predicting the duplicity of the second ring (L-ring) from the presence of two absorption edges in the absorption curve in the L-region obtained by Wagner, Kossel expected from his relation (2) that K\(_{\alpha}\)-line too should split into doublet with components of frequencies,

\[
\nu_{K\alpha} = \nu_{Kg} - \nu_{Lg}
\]

and

\[
\nu_{K\alpha'} = \nu_{Kg} - \nu_{Lg},
\]

respectively, and showed that the value of the splitting \(\Delta\nu\) of K\(_{\alpha}\)-doublets observed for Pt and Au by Malmer was equal to the value of the distance between two absorption edges in the L-region:
\[ \Delta \nu = \nu_{K\alpha} - \nu_{L\alpha} = \nu_{Lg} - \nu_{Lg}. \]  

He could further show that this was approximately equal to \( \nu_{L\beta} - \nu_{L\alpha} \). Finding in the existence of doublets an analogy between the X-ray and the optical spectra, Kossel was convinced of the validity of his relations. But Kossel’s effort in clearing away the defects of his relations was soon to turn out fruitless. Final solution of these difficulties was not obtained before the development of the correspondence principle and of the further studies in the fine structure of X-ray spectral lines.

In 1915 Sommerfeld presented the celebrated paper\(^{20}\) in which he extended the quantum condition of Bohr to the system with several degrees of freedom. As is well known, Sommerfeld dealt with Keplerian orbits by means of the generalized quantum conditions

\[ \int_0^{2\pi} p_{\phi} d\phi = n \hbar, \quad \text{and} \quad \int p_r dr = n' \hbar, \]  

where \( n \) and \( n' \) are whole numbers, \( p_{\phi} \) and \( p_r \) the momenta corresponding to the polar co-ordinates \( \phi \) and \( r \), and gave satisfactory explanation of the fine structure of hydrogen type spectrum by taking into account the relativistic variation of the mass of electron\(^{21}\).

Sommerfeld also succeeded in applying his theory of fine structure to the explanation of X-ray doublets.\(^{22}\) The possibility of applying his theory to K- and L-doublets was suggested to him by Kossel’s empirical relations of the splittings of \( K\alpha \) and \( L \)-doublets which implied that the \( L \)-ring consisted of two rings. At the same time, Sommerfeld noticed the similarity of Moseley’s formula for \( K\alpha \)-line with Bohr’s formula for hydrogen type spectrum. That the terms in Moseley’s formula have the same form as those in Bohr’s formula except that \( Z \) is replaced by \( Z-1 \) suggested him that the electrons, at least, on the innermost two rings would be describing hydrogen like orbits. He thus thought that the relativistic theory of the fine structure of hydrogen type spectra might be applied to K- and L-doublets. If the relativistic correction was taken into account, it would become possible to get a more precise expression for the terms of X-ray spectrum.

Substituting the effective nuclear charge in Sommerfeld’s expression \( W = - \)
\[ \frac{\text{Rh}Z^2}{(n+n')^2} \left[ 1 + \frac{\alpha^2 Z^2}{(n+n')^2} \left( \frac{1}{4} + \frac{n'}{n} \right) \right] \]

where \( \alpha = \frac{2me^2}{hc} \), of the energy of electron moving on the orbit characterized by the principal quantum number \((n+n')\), Sommerfeld got expressions of two L-terms, which were characterized by \(n = 2, n' = 0\) (circular orbit) and \(n = 1, n' = 1\) (elliptical orbit) respectively, and of K-term:

\[
\begin{align*}
L &= R \cdot \frac{(Z - \ell)^2}{2^2} \left( 1 + \frac{\alpha^2}{4} \frac{(Z - \ell)^2}{2^2} \right), \\
L' &= R \cdot \frac{(Z - \ell)^2}{2^2} \left( 1 + \frac{5\alpha^2}{4} \frac{(Z - \ell)^2}{2^2} \right), \\
K &= R \cdot \frac{(Z - k)^2}{1^2} \left( 1 + \frac{\alpha^2}{4} \frac{(Z - k)^2}{1^2} \right).
\end{align*}
\]

(6)

The difference between the optical spectra and the characteristic X-ray spectra lies in that while the former is produced by the displacement of the electron outside "the electron cloud", the latter is produced by the displacement of electrons other than "light electron", which takes part in the emission of spectral lines, the electron cloud.

Concluding his considerations outlined above, Sommerfeld pictured the atom as follows\(^2\): The difference between the optical spectra and the characteristic X-ray spectra lies in that while the former is produced by the displacement of the electron outside "the electron cloud", the latter is produced by the displacement of electron other than "light electron", which takes part in the emission of spectral lines, the electron cloud.
ment of the electron in the innermost part inside the electron cloud. The similarity of the spectral terms for $K_{\alpha}$-line with the hydrogen type terms suggests that the electrons describing the first (K) and the second (L) orbits are hardly disturbed by the electron cloud. This explains the fact that the larger the quantum number is in the case of optical spectra and the smaller in the case of X-ray spectra, i.e. the more distant from the electron cloud are the electrons taking part in the emission of spectra, the more approaches the spectrum formula to the hydrogen type formula.

Thus Sommerfeld's atom in the normal state consists of the inner electrons belonging to K- and L-orbits separated from the electron cloud (whereas M, N ... orbits penetrate into the electron cloud), the electron cloud, and the outer electrons taking part in the emission of the optical spectra.

IV. Germination of the Conception of "Closed Shell"

Now, it should be noticed here that through the works of Kossel and of Bohr, one of the most important conceptions for understanding the constitution of atom was germinated. It was the idea of completion of the electron ring, namely that of the closed shell as we now understand.

It can be seen from Kossel's discussion that he presupposes that the vacant place in an electron ring must immediately be filled up by another electron from an outer ring. This implies the idea of completion, that is, the assumption that each of electron rings has tendency to contain a certain definite number of electrons. But Kossel did not yet realize this idea. In his paper of 1914 Kossel expected that the transition of an electron from the innermost ring not only to outside the atom but also to an outer, the second or the third ring, etc. of the atom would take place. He however concluded from his absorption curves which showed no peak of absorption corresponding to the $K_{\alpha}$-emission line that the transition of electron at least from the innermost ring to the second ring did not occur so frequently as the ionization process.

*) Kossel thought that this conclusion could not be applied to the transition to much outer rings.

2) He continued searching for absorption lines corresponding to these processes and in 1919 he concluded the existance of such absorptions from the results obtained by Stenström.
It seems to be Bohr who first understood clearly the idea of completion.\(^{28}\) Bohr noticed the previous results of W. H. Bragg which had showed that, in order to produce any line of the K-radiation of an element, the frequency of the exciting radiation had to be greater than the frequency of all the lines in the K-radiation. He stated that this lack of the reverse process to that of emission, in contrast to the ordinary optical resonance absorption, might be simply explained on the basis of Kossel's view: "The simple reverse of the process corresponding to the emission of, for instance, K\(\alpha\) would necessitate the direct transfer of an electron from ring 1 to 2, but this will obviously not be possible unless at the beginning of the process there was a vacant place in the latter ring."\(^{29}\) It is therefore necessary for the emission of any line in the K-radiation that an electron should first be completely removed from the atom. Bohr's argument here clearly presupposes that each electron ring could contain only certain limited number of electrons.

From the similar considerations as Bohr's, Kossel in 1916 stated that in the non-excited state the inner rings would reject the electrons coming from the outer rings or outside the atom, and that this conception, providing us with a concrete image of atom according to which the inner rings were "completely occupied" by the electrons, was important for the understanding of the conditions of stability of the electron arrangement.\(^{30}\)

The idea of completion which was almost simultaneously deduced also from the chemical considerations by Kossel himself\(^{31}\) logically implied the exclusion principle, but no one at the time noticed this. It might be interesting to know how this idea, connected with the development of the study of the fine structure of spectra and with the chemical considerations, was developed to the exclusion principle. However, except Bohr and Kossel, no investigator who attempted to estimate the numbers of the electrons in the inner rings did pay attention to the idea of completion.

V. The Numbers of the Electrons on the Inner Rings
It seems to us today as if Kossel and Sommerfeld provided physicists with the basis on which the emission of the characteristic X-rays could sufficiently be explained in terms of the Bohr atom. But the situation was not so simple. In those
days it was not so easy to form the picture of atom that, in the ground state (or the normal state as Bohr called), consisted of electrons distributed on several rings characterized by different quantum numbers. According to Bohr's original assumption, in the normal state of the atom all the electrons had indeed the same angular momentum \( \frac{\hbar}{2\pi} \), that is, they were distributed on rings with the same quantum number 1.

Furthermore Kossel's mechanism that the X-rays were emitted when a vacant place in an inner ring produced by the removal of an electron from it to outside the atom or to an possible outer ring was filled up by an electron from an outer ring was not generally accepted. Neglecting the effect of electrons on the outer rings, if such rings existed at all, many dealt with the emission of X-rays by assuming only the transition of one or more electrons between inner two adjacent rings.

This can be seen from various attempts made in those days to determine the numbers of electrons on rings.

On the assumption of ring arrangement of electrons, it was possible to estimate the numbers of electrons on the inner rings if one calculated, with approximation, the frequencies of spectral lines taking into account the influence of other electrons on the same ring and of electrons on the other inner rings and then compared the values thus obtained with the observed frequencies of X-ray spectra. In fact, numerous investigators, such as Debye, Vegard, Sommerfeld and so on, turned themselves to this problem.

As was mentioned in the section II, Moseley had attempted to determine the number of electrons in the first ring. In somewhat different way the simple case of an atom having solely one ring was dealt with by Debye in 1917.\(^{32}\) Debye assumed that \( p \) electrons, each of which had the angular momentum \( \frac{\hbar}{2\pi} \), moved at equal angular intervals on a circular orbit around a nucleus of charge \( eZ \). He supposed that the electrons on the outer ring, if these existed at all, would be so distant from the first ring that they had no influence on it. The total energy of the ring was expressed as \( -\hbar R p (Z - S_p)^2 \), where \( S_p = \frac{1}{p} \sum_{i=1}^{p-1} \frac{1}{4i} \sin \pi i \frac{p}{P} \). It was supposed that when an electron was excited to another possible ring, the angular momentum of each remaining electron was preserved while these remaining
electrons would be rearranged so as to be situated again at equal angular intervals. The $K_\alpha$ line was supposed to be emitted when an electron excited to the nearest possible ring with an angular momentum $\frac{2h}{2\pi}$, then fell onto the original ring. The total energy of the excited system was calculated to be $-hR \left\{ (p-1) (Z-S_p)^2 + \frac{1}{2} (Z-p+1)^2 \right\}$. According to Bohr's frequency condition, the frequency of the $K_\alpha$ line is $\nu = hR \left\{ (p-1) (Z-S_p)^2 + \frac{1}{2} (Z-p+1)^2 \right\}$. By comparison of this equation with the measurement of $K_\alpha$ lines for the elements from Na ($Z = 11$) to Nd ($Z = 60$), it was shown that by putting $p = 3$ a good agreement was obtained for the small values of $Z$. Furthermore by taking into account the relativistic variation of the electron mass Debye could show that for larger $Z$'s, too, a good agreement was obtained with $p = 3$. Debye thus concluded that in atoms of all elements (except for the first few elements in the periodic table) the innermost ring had three electrons on it.

In the same year, claiming the extention of Debye's consideration, Vegard assumed a process that a group of $q$ electrons were excited from the innermost ring with $p$ electrons to the second ring, and then $q$ energy quanta were emitted simultaneously by the falling down of all the $q$ electrons to the original ring. This process comprises both Debye's solution of $p = 3$ and $q = 1$ and Moseley's assumption $p = 4$, $q = 4$. Vegard could show that both assumptions led to the frequencies of $K_\alpha$ lines which agreed equally well with the observations, although he considered the assumption of Debye to have an advantage in its physical implication.

Vegard then proceeded to explain the $L$-lines in the following way. In view of the fact that the sharp absorption in the $L$ region corresponded to a wave length somewhat shorter than that of $L_\alpha$ emission line, though it was found near the latter, it was necessary, argued Vegard, to assume that there existed electrons on the second ring ($L$-ring) in the normal state of the atom and that the $L_\alpha$ line was produced when an electron excited from the second ring to the third returned to the original second ring. It could not be assumed, as done by Debye, that the $L_\alpha$-line was emitted when an electron excited from the first ring to the third fell
onto the second ring.

Furthermore Vegard assumed that this second ring should be characterized by the quantum number 2. He showed that from calculation of the frequency of $L_\alpha$-line by assuming that the $L_\alpha$-line was emitted by a transition of electrons between two adjacent inner rings and that electrons on these two rings were equally considered to have the same angular momentum $\frac{h}{2\pi}$, empirical formula of Moseley's type for the frequency of $L_\alpha$-line was never deduced. This result necessitated to alter in some way Bohr's assumption that in the normal state all the electrons had the same angular momentum $\frac{h}{2\pi}$.

Thus Vegard assumed that $L_\alpha$-line was produced when an electron excited from the second ring of quantum number 2 to third ring of quantum number 3 fell onto the original ring. And he could get the solution that if one, according to Debye, takes 3 as the number of electrons on the first ring, there should be 7 electrons in the second ring in order to obtain the expression for $L_\alpha$-line which agrees with the observations.

Here it must be noted that Vegard in his calculation pointed out that in the normal state of atom there must be several rings with the quantum number larger than 1 (or "multiple-quanta" rings or orbits as were called in those days). He was the first to mention the existence of the multiple-quanta rings.¹) Bohr in his 1913 paper assumed that all the electrons in the normal state had the same angular momentum $\frac{h}{2\pi}$. He, however, accepted Kossel's explanation of X-ray spectra in which the existence of the multiple-quanta rings in the normal state of the atom was tacitly suggested. Sommerfeld's atom consisted of the multiple-quanta orbits of electrons. Therefore it might as well be possible that Bohr would have realized the existence of the multiple-quanta rings in the normal state before Vegard pointed it out**). As far as we know, however, it was not until 1921 that Bohr explicitly mentioned it, when he wrote in a letter to the editor of *Nature*: "The assumption of the presence in the normal state of the atom of such multiple-

¹) Heilbron asserted that the modification of "Bohr's one-quantum ring atom" was the main contribution of the study of X-ray spectra to the theory of atomic structure during the period under consideration.

**) According to Heilbron, before Kossel and Sommerfeld, namely in the end of 1913, Bohr still believed that in the normal state the atom had not multiple-quanta orbits.
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quanta orbits has already been introduced in various recent theories, as, for instance, in Sommerfeld's work on the high-frequency spectra ...'34) In any case, the fact that Vegard for the first time pointed out explicitly the possibility of the presence of multiple-quanta rings in the normal stage of atom seems to show that Bohr's conception of atom was generally received literally, even after the works of Kossel and Sommerfeld, as stating that the atom in the normal state has only rings of quantum number 1 (or one quantum rings as were called in those days) and the so-called multiple-quanta rings exist only in the excited state.

In 1918 Sommerfeld reinterpreted his theory of X-ray spectra so as to conform his elliptical electron orbits to the ring configuration, and on Sommerfeld's theory Kroo estimated the numbers of electrons on the first two rings.

Sommerfeld thought that the screening effect to the nuclear charge in his formula (6) could be explained rather by the assumption of ring arrangement of electrons than by his own atom which had electrons moving on circular and elliptical orbits, and attempted to conform the existence of the elliptical orbits of electrons to the ring configuration by assuming that the electrons moving on their own elliptical orbits could be imagined as being situated at any instance at equal angular intervals on a circle with the nucleus at the center.35) Sommerfeld called such a configuration "Ellipsenverein". Then he could discuss generally the energy of the system consisting of many electron rings. Showing that the energy of interaction between rings might be neglected in dealing with, at least, the $K_\alpha$ -emission, Sommerfeld concluded that the frequency of $K_\alpha$ - line could be calculated in the similar way as Debye and Vegard, i.e. Sommerfeld assumed that the electrons on rings inside the ring concerned were concentrated at the nucleus, other electrons on the same ring were situated at the same angular intervals, and electrons on outer rings could be neglected.

On this theory of Sommerfeld Kroo calculated the frequency of the $K_\alpha$-line.36) The atom in the normal state was assumed to consist of $k$ electron ring of quantum number 1 and of $\ell$ electron ring of quantum number 2. He also assumed that $K_\alpha$ is emitted when an electron excited from the first to the second ring falls onto the first ring. Putting $k = 3$ and $\ell = 8$, that is, comparing the energies of the excited state with 2 electrons on K-ring and 9 electrons on L-ring and the
final state with 3 electrons on K-ring and 8 electrons on L-ring, he obtained an
expression of the frequency of Kα-line which well agreed with the observation.

Estimations of the numbers of electrons on inner rings were not successful on
the basis of the ring model. As was mentioned in the previous paper\textsuperscript{37}), the fact
that the result was not in conformity with the numbers of electrons expected
from the periodic system of elements, forced Reiche to suspect whole conception
of the distribution of coplanar rings and to suppose that the electrons would take
spacially symmetrical configurations\textsuperscript{*}).

Furthermore it is seen that in these works the idea of the completion of the
ring was not taken into account. If it were taken into account, it would be
impossible that the excited state has larger number of electrons on L-ring than in
the normal state. Therefore, the scheme by Kroo for the emission of Kα

\begin{array}{c|c|c}
 & \text{K-ring} & \text{L-ring} \\
\hline
\text{Normal state} & 3 & 8 \\
\text{Initial state} & 2 & 9 \\
\text{Final state} & 3 & 8 \\
\end{array}

would have to be replaced by the scheme:

\begin{array}{c|c|c}
 & \text{K-ring} & \text{L-ring} \\
\hline
\text{Normal state} & 3 & 9 \\
\text{Initial state} & 2 & 9 \\
\text{Final state} & 3 & 8 \\
\end{array}

Whether the idea of completion may be taken into account or not, there will
be no essential difference in the calculation but there would be a difference in the
interpretation of the results obtained. In order to conform the results to the
conclusion based on chemical considerations, Sommerfeld interpreted the Debye's

\textsuperscript{*}) The same suspicion was also raised by the works on the X-ray spectra on the more
complex assumptions on the electron arrangement and by the investigations on the
crystal structure. For the detailed account of this, the reader is referred to Heilbron's
article.
conclusion in such a way that the initial state in which there were 2 electrons in the first ring and 1 electron in the second was the normal state of the atom and the final state in which there were 3 electrons in the first ring was the state of supersaturation.38)

The emphasis should however be placed on the fact that through these works on the arrangement of electrons, the presence of the multiple-quanta rings in the normal state of atom gradually became to be recognized clearly and at the same time the importance of the "energy levels" in the considerations of the constitution of atom was begun to be realized.

VI. Conclusion

After Bohr and Moseley it became to be believed that the study of the characteristic X-ray spectra should shed much light on the structure of the innermost part of atom, by the reason that while the optical spectra and the chemical properties of the atom were supposed to be the manifestation of the behaviour of outermost electrons in atom, the X-ray spectra were supposed to be originated from the innermost electrons in atom. On the basis of the assumption of the ring arrangement of electrons various attempts were made to determine the numbers of electrons in the innermost rings by comparing the calculated frequencies of the characteristic X-rays with the observations. At the end of the 1910's the results of such investigations, however, turned out to be altogether unsatisfactory. In the first place these results were not in conformity with the results obtained on the basis of chemical considerations. Those who attempted to determine the electron arrangement on the basis of the study in X-rays, thought that their results should ultimately be able to explain the chemical properties of atom.39) For example, Vegard attempted to build up a periodic system which was conformable to his results: thus the numbers of electrons on the first and the second rings for the elements in the first short period were assumed to be Li (2, 1), Be (2, 2), ... F(2, 7), Ne (3, 7).40) In order to conform Debye's conclusion to the chemical atom which had 2 electrons on the first ring, Sommerfeld proposed an interpretation that the configuration in which there are 2 electrons in the first ring and 1 electron in the second was the normal state of atom and that which has 3 electrons in the first ring was the state of supersaturation.41) Smekal also
pointed out that Kroo’s conclusion could not explain the property of Na (Z = 11) which should have a single valence electron.

The doubt against the ring arrangement of electrons was also strengthened by further attempt to determine the number, \( n_3 \), of electrons on the third ring. Smekal showed that no satisfactory expression of the frequency of \( L_\alpha \) line could be obtained whatever number might be chosen for \( n_3 \) if one, according to Kroo’s result, chose 3 and 8 for the numbers of electrons on the first and the second rings. Furthermore the lattice dynamics of ion crystals by Born and Landé revealed that their compressibility calculated on the basis of the ring atom model did not agree with the observation.

As was shown in the previous paper, according to the conclusion obtained on the basis of chemical considerations in the period considered, the atom consists of several rings or shells each of which contains a certain limited number of electrons. This number of electrons was determined, for instance for the atom of Rn (Z = 86), to be 3, 8, 18, 32, 18 and 8 from inner ring to outer. This configuration is correct as far as the rings or shells could be assumed to correspond to the quantum number 1, 2, ..., But it is not possible to deduce from the chemical consideration that each ring or shell should be characterized by different quantum numbers. However, when the presence of “multiple-quanta” rings or orbits in the ground state of atom became to be established, one could assign the quantum number 1, 2, ..., to successive rings. This was, believes the author, the contribution from the studies in X-rays to the theory of atomic structure during the period considered.

The main achievement in the study of atomic structure during the 1910’s, therefore, was the establishment of the atomic model consisting of several rings or shells each of which is characterized solely by the principal quantum number and contains certain definite number of electrons. However, the problem how to re-distribute electrons on each ring over the sub-states to be characterized by sub-quantum numbers was left unsolved. Satisfactory answer to this problem was not obtained until the 1920’s when detailed investigations on the fine structure of both optical and X-ray spectra were advanced.
Acknowledgements

The author is indebted to Prof. Tetu Hirosige for invaluable advices and discussions throughout this study. She also thanks to Mr. J. Nemoto of Japan Meteorological Agency for offering her the convenience to gain access to some literatures.

References

9) For example, P. Debye: Ref. (32) especially p. 276; S. Dashman: Ref. (8).
16) W. Kossel: Ref. (14). See the foot note 1) of p. 960.
17) N. Bohr: Ref. (11).
21) For the detailed account, the reader is referred to, for example, M. Born: The Mechanics of the Atom, Frederic Ungar, New York, 1960 (Translation of Vorlesungen uber der Atommechanik, 1925).
22) A. Sommerfeld: Ref. (18).
23) A. Sommerfeld: Ref. (18), especially p. 165.
24) W. Kossel: Ref. (14).
26) W. Kossel: Ref. (14), the foot note 1) of p. 963.
28) N. Bohr: Ref. (11).
30) W. Kossel: Ref. (19).
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38) A. Sommerfeld: Ref. (35).
39) Ref. (1), especially p. 27.
41) A. Sommerfeld: Ref. (35).
43) F. Reiche: Ibid.
44) Ref. (43).
45) Ref. (1).
46) Ref. (27).
47) In 1921 Bohr considered the quantum structure of atom for all elements of the periodic system, half theoretically and half empirically, by making use of all the evidences provided by physics and chemistry, especially of the spectral data. N. Bohr: The Theory of Spectra and Atomic Constitution, Essay III. “The Structure of the Atom and the Physical and Chemical Properties of the Elements”, Cambridge Univ. Press., London, 1924 (1st ed. 1922). For the account of this theory of Bohr, the reader is referred to S. Nisio: Ref. (1).