To connect these results with the known visible and near ultra-violet lines of the higher spark spectra of neon and argon, it will be necessary to locate some intermediate terms, lines from which will lie in the region from λ 2200 to λ 1300. This region is inaccessible with the present spectrograph, and further study of these spectra is postponed pending the completion of a new vacuum spectrograph of greatly increased range and dispersion, which is made possible by a grant from the Carnegie Corporation through the Carnegie Institution of Washington.

We are glad to acknowledge the able assistance of our colleague, Mr. J. L. Nickerson, in making measurements and calculations.

3 Compton and Boyce, J. Franklin Inst., 205, 497, 1928.
5 See also Dorgelo and Abbink, Zeits. Phys., 41, 753, 1927; Dieke and Hopfield, Phys. Rev., 27, 638, 1926.

RELATIVE PROBABILITIES OF THE IONIZATION OF K AND L ELECTRONS OF EQUAL IONIZATION ENERGY

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Communicated June 25, 1929

1. Introduction.—Theories have been proposed by Davis,1 Rosseland,2 and Thomas3 to explain the ejection of atomic electrons by cathode-ray impact. In these theories it has been assumed that the probability of ionization depends on the energy of the cathode ray (which depends only on the applied voltage, \( V \)), the ionization energy of the electron (which is defined by \( V_0 \), the excitation voltage), and in Thomas’ theory, on the kinetic energy of the electron, which he has treated as in a circular orbit. Thomas has suggested that the probability of ionization may be different for elliptical orbits. In general, regardless of these theories, the probability of ionization may be dependent on the quantum numbers of the electron.

In order to study the effect of a quantum number by itself, we must keep \( V \) and \( V_0 \) constant (at least to a first approximation) while we compare two series involving levels which differ in that quantum number only. Since \( V_0 \) is a natural constant for each element and series we can keep it nearly constant, for this purpose, only by a proper choice of series to compare. Table 1, which shows the quantum numbers (on the basis
of wave-mechanics) of the $K$ and $L$ levels, will help us in discussing this choice.

The values of $V_0$ for the three $L$ subseries of any element are so nearly alike that they may be taken as identical for present purposes. As we go from $L_{21}$ to $L_{22}$ the azimuthal and radial numbers remain fixed while the inner number changes from 1 to 2. A comparison of the intensities of these series would then show the effect of the inner quantum number.

<table>
<thead>
<tr>
<th>LEVEL</th>
<th>AZIMUTHAL</th>
<th>RADIAL</th>
<th>INNER</th>
<th>$N_\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>49</td>
</tr>
<tr>
<td>$L_{11}$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>$L_{21}$</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>$L_{22}$</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>100</td>
</tr>
</tbody>
</table>

This effect has already been studied,\textsuperscript{4,5,6} and it has been found that the intensities are nearly in accord with Lande's sum rules. It is more difficult, however, to study the effects of the other quantum numbers. As we go from $L_{11}$ to $L_{21}$ both the azimuthal and radial numbers change; and as we go from $L_{11}$ to $L_{22}$ all three of the numbers change. A comparison of the $K$ and the $L_{11}$ series would involve a change in the radial number only, and a comparison of the $K$ and $L_{21}$ would involve the azimuthal number only; but the values of $V_0$ for a single element would differ too much to admit such comparisons.

In the experiments to be described, this difficulty was overcome by working with a target containing two elements so chosen that the values of $V_0$ for the $K$ series of one and the $L$ series of the other were as nearly alike as possible. It is essential, of course, that the mixture of these elements be homogeneous not only on a large scale but also on a scale which is small in comparison with the path length of the cathode ray in it, and that the relative proportions of the elements be known. Obviously only a compound or a solid solution satisfies these requirements. After a careful consideration of all such available combinations it was found that lead selenide (PbSe) suited the purpose best. The $V_0$ for selenium $K$ is 12.6 KV and the $V_0$'s for the lead $L$ series are $L_{11}$ 15.8, $L_{21}$ 15.2 and $L_{22}$ 13 KV. The pure lead selenide powder was placed on the target of a special Coolidge x-ray tube and the intensities of the x-ray lines of the two elements were measured. The relative probabilities of ionization were then calculated for the case of a change in either radial or azimuthal quantum number alone.

Strictly speaking, the quantities found here are not the ratios of ionization probabilities, but ratios of the products of these probabilities by corresponding efficiencies of emission as defined by Auger.\textsuperscript{7} He has
found that when atoms are ionized some of the reorganizations result in secondary photoelectrons rather than in quanta of radiation of an appropriate wave-length. The process as explained by him is this: The electron lost from an inner shell is replaced by one from an outer shell; in a certain fraction, \( \varphi \), of such replacements, a quantum of radiation of the subseries appropriate to the inner shell is emitted, while in other replacements, the energy released is used for the ejection of secondary photoelectrons from the same atom. This fraction \( \varphi \) is called the efficiency of emission. The efficiencies of emission of the \( K \) series of several elements have been studied by Martin,\(^8\) who has found a value of 60 per cent for selenium. Unfortunately, xenon and krypton are the only elements whose \( L \) series efficiencies have been studied and these only for the \( L \) series as a whole rather than by taking each subseries separately. An empirical equation found by Martin for the \( K \) series would give a value near 60 per cent if applied to the \( L \) series of lead as a whole, but this is probably unreliable. An exact evaluation of each \( L \) subseries efficiency would require experiments of a different type from the present ones, and therefore we must here avoid any definite assumptions as to the values of these efficiencies and draw definite conclusions only on the products of these efficiencies by probabilities of ionization.

There are two important sources of error in this research, which were realized before the work was commenced. The first of these is the change of the relative intensities of the lead and selenium lines due to the production of indirect rays as defined by Beatty.\(^9\) This process depends on the ejection of inner electrons by the absorption of continuous-spectrum x-rays from adjoining atoms rather than by cathode-ray impact. Theoretical calculations, based on the change of the amount of indirect radiation with atomic number, have shown in a rough way that the effect of indirect rays is not serious, but it will be considered in somewhat more

![Figure 1](image-url)
detail later. The second error results from the assumption that \( C \) and \( m \) are constants in the empirical equation\(^\text{10,6,6}\)

\[
I = C(V - V_0)^m.
\]  

(1)

Which expresses the intensity of a line as a function of the applied voltage \( V \) and the ionization voltage \( V_0 \). It is reasonable to expect these two sources of error to result in a combined error of something like 10 per cent. This is greater than the usual uncertainty of the photographic method, and therefore this method was adopted.

2. Determination of Line Intensities.—The lead selenide was made by Henry M. Leicester of the Department of Chemistry, Stanford University, who took special precautions to insure purity. Photographs of the spectra were taken by means of a spectrograph with rotating crystal. The densities of the x-ray lines were measured with a comparator-microphotometer designed by G. R. Harrison.\(^\text{11}\) This instrument had a slit width of about 10\( \mu \) and readings were taken every 50\( \mu \) across the line to be measured. Since for x-rays the intensity is proportional to the density, for small densities, the relative intensities at any two points in the spectrum could be found directly from the logarithms of microphotometer readings. This method of intensity measurement was checked by the known \( K\alpha \) doublet ratios of selenium and was found to be correct for all densities used here. In comparing \( Se \) \( K \) and \( Pb \) \( L \) lines, however, \(^*\)since the \( L \) lines were found to be somewhat wider than the \( K \), the readings were plotted on semi-log paper and the intensities were taken proportional to the areas of the peaks above the general radiation rather than the heights.

After preliminary trials, ten photographs were taken, three at 55 kv., four at 40 kv. and three at 25 kv. A typical one of these photographs taken at 55 kv. is shown in figure 1.

The change in sensitivity with wave-length was determined through a comparison of the measured lead intensities with corresponding values found from a study of the literature. No work has been reported on lead but these relative intensities were interpolated from values assigned to tungsten, platinum, thorium and uranium by Jönsson,\(^\text{5}\) Duane,\(^\text{4}\) and Allison.\(^\text{6}\) Specifically, a factor was found for each voltage used, by which the area ratio, \((\beta_1 + \beta_2)/\alpha_1\), should be multiplied, to give the intensity ratio of these lines at that voltage. The corresponding factor for the ratio of any other line to\( Pb \) \( L\alpha \) was assumed to depend linearly on wave length, and for \( Se \) \( K\alpha_1 \), this gave 0.95 at all voltages. The true intensity ratio of \( Se \) \( K\alpha_1 \) to \( Pb \) \( L\alpha \), was found to be 0.44 at 55 kv., 0.45 at 40 kv. and 0.44 at 25 kv.

3. Calculation of \( N\varphi \) Ratios.—Having obtained the relative intensities
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of the $K$ and $L$ lines, the remaining problem is to determine from these data the relative probabilities of ionization of the $K$, $L_{11}$, $L_{21}$ and $L_{22}$ states.

The general equation governing the intensity of a line produced by the rearrangements of atoms from the $r$ state of ionization to the $j$ state is given by

$$I_{rj} = \frac{N_r E_{rj} \hbar c}{\lambda_{rj}},$$

(2)

where $N_r$ represents the number of atoms put in the ionized state $r$ per unit time and $E_{rj}$ is the probability that such an atom will rearrange itself into the $j$ state of ionization with a radiation of the appropriate wave-length $\lambda_{rj}$. Adding the intensities for all the lines of the subseries, it appears that

$$N_r \sum_j E_{rj} = \frac{1}{\hbar c} \sum_j I_{rj} \lambda_{rj}.$$  

(3)

With $E_{rj}$ defined as above, $\sum_j E_{rj}$ is the efficiency, $\varphi_r$. Equation (3) then becomes

$$N_r \varphi_r = \frac{1}{\hbar c} \sum_j I_{rj} \lambda_{rj},$$

(4)

and the ratio of the numbers of atoms forced into two states of ionization $r$ and $i$ is then given by

$$\frac{N_r \varphi_r}{N_i \varphi_i} = \frac{\sum_j I_{rj} \lambda_{rj}}{\sum_j I_{ij} \lambda_{ij}}.$$  

(5)

Taking the intensity of Pb $La_1$ as a standard for all Pb lines, and calling it 100 lead units, the numerical values of $\sum_j I_{rj} \lambda_{rj}$ for the $L$ subseries of lead at high voltage, using the intensity data of Duane, Jönsson, and Allison, were found to be: $L_{11}$, 13.3; $L_{21}$, 62.2; and $L_{22}$, 163.7. In like manner, taking the intensity of Se $K\alpha_1$ as a standard for all Se lines, and calling it 100 selenium units, the numerical value for the $K$ series of selenium, based upon the intensities as given by Meyer, is 187.6. By equation (5), therefore

$$\frac{(N\varphi)_{SeK}}{(N\varphi)_{PbLa}} = \frac{187.6}{168.7} \times \frac{I_{SeK\alpha}}{I_{PbLa}}.$$  

(6)

Taking the values of the true ratio of these $\alpha_1$ lines at 25, 40 and 55 kv.
from the measurements described above, the ratios of these \((N\varphi)')s at
these voltages are 0.50, 0.515 and 0.505, respectively.

Allison\(^6\) and Jönsson\(^5\) have used the empirical equation (1) to express
the relationship between intensity and voltage, and by equation (3) it is
seen that \(N_r\) must vary in the same manner as \(I_{ij}\). Making use of this
equation, as Allison has for the different \(L\) subseries, the above ratios
give for the corresponding ratios at infinite voltage, the three values,
0.48, 0.50 and 0.50, with a mean of 0.49. For this case, therefore, where
the values of \(V_0\) differ by only 0.4 kv., the correction to infinite voltage
makes no change beyond probable errors.

For the other \(L\) subseries, the following relations are found:

\[
\frac{(N\varphi)_{PbLn}}{(N\varphi)_{PbLm}} = \frac{62.2}{163.7} = 0.38 \quad \frac{(N\varphi)_{PbLn}}{(N\varphi)_{PbLm}} = \frac{13.3}{163.7} = 0.08.
\]

In these cases, however, the excitation voltages differ by much greater
amounts, and a question arises as to how reliable the correction formula
is. Rosseland’s formula, mentioned by Allison,\(^6\) would increase each of
these by several per cent, but the known deviations from this equation
make him discard it. On the other hand, there are also known deviations
in the opposite direction, from equation (1) at high voltages. So a fair
compromise seems to be to raise these ratios by 5 per cent and express
them to the nearest unit only.

If we let \((N\varphi)_{PbLn} = 100\) units the values of the other \((N\varphi)')s may
be obtained from these ratios. They are listed in column 5 of table 1.
This shows very clearly the effect of the change of any one of the three
quantum numbers, the other two remaining constant. Comparing the
\(L_{21}\) and the \(L_{21}\) states, where the radial and the azimuthal quantum
numbers remain fixed, while the inner changes from 2 to 1, it is seen that \(N\varphi\)
changes in approximately, but not exactly, the same ratio as the inner
quantum numbers. In the case of the \(L_{21}\) and the \(K\) states, the inner
and the radial remain fixed while the azimuthal changes from 1 to 0.
Here, however, the probability of ionization changes but little, showing
that the change in azimuthal quantum number has little effect. This
conclusion is confirmed still more accurately by comparing \(L_{21}\) and \(K,\)
with due allowance for the difference in inner quantum numbers, but the
assumptions and the experimental errors discussed above must prevent
us from accepting this apparent accuracy at its full value. Comparing
the \(L_{11}\) state with \(K\), the inner and azimuthal numbers remain fixed while
the radial changes from 1 to 0. In this case \(N\varphi\) changes very noticeably,
showing that the decrease in the radial quantum number causes a very
marked increase in either the probability of ionization or the efficiency
of emission, or both.
Strictly speaking, these values of $N\phi$ should be corrected for the effect of indirect ionization mentioned above. Unfortunately, exact calculations of this effect seem to be impossible with present data, but rough estimates show that the ratios of selenium $K$ and lead $L_{21}$ to $L_{22}$ would probably change by only a few per cent. Data on absorption discontinuities indicate that the part of $N_{La}$ due to indirect ionization is almost as great (in absolute value, not relatively) as that of $N_{Ln}$. Therefore, if the $\phi$'s are somewhat alike, the ratio of $(N\phi)_{La}/(N\phi)_{Ln}$ for direct ionization only, would be even less than the value listed here. It then appears that the effect of the change in radial quantum number, on ionization caused directly by cathode ray impact, is at least as great as indicated here, although until further research is done on these efficiencies it is uncertain whether this effect is due to change in $N$ or $\phi$ or both.

4. Summary.—Data have been obtained on ratios of the values, for various subseries, of the product of two factors, the probability $N$ that a cathode ray will produce an ionization of the appropriate type, and the probability $\phi$ that the subsequent reorganization will result in radiation of some line of the subseries. Between two subseries such as $L_{21}$ and $L_{22}$, differing only in the inner quantum number, this product has been known to be practically proportional to the inner quantum number. It is found here that a difference in azimuthal quantum number only, between the $K$ and $L_{21}$, has no appreciable effect; but a difference in radial quantum number, between $K$ and $L_{11}$, has a great effect.

In conclusion I wish to thank Dr. D. L. Webster, at whose suggestion and under whose direction this work was completed, for his very generous help and advice.