

The Element of Atomic Number 61; Illinium.

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AN important result of the development of Moseley's atomic number rule has been the impetus it has given to the search for missing elements. It is true that later arrangements of the Periodic Table indicated that eka-caesium, eka- and dwi-manganese, and eka-iodine were missing, but there were no theoretical grounds for supposing that eka-neodymium might exist until Moseley's rule showed that element number 61 was still to be identified. Moseley's work was of inestimable value to one engaged in completing the list of chemical elements for several reasons—first, it gave definite information as to the existence and location of gaps in the Periodic Table; secondly, it gave a basis for the calculation, prior to its discovery, of the X-ray spectrum of an element and indicated a technique by which lines in that spectrum might be identified; and, finally, it originated a method of examination so searching that a mixture of two elements, so closely similar in chemical properties as to be almost inseparable, could be definitely analysed. Were it not for the work of Coster and Hevesy on the X-ray examination of zirconiferous minerals, the presence in them of element number 72 would probably be still unsuspected and hafnium (or celtium) would still be listed among the rare earths. Chemical tests made on zirconium ores had frequently indicated the non-homogeneity of zirconium, but they could not give the definite proof afforded by an X-ray analysis.

The proof that a rare earth element was missing, the atomic number of which would place it between neodymium and samarium, explained the sharp break in the sequence of properties that comes in the rare earth group between those two elements. The differences in solubilities of the double salts formed by rare earth nitrates with magnesium nitrate appear to be quite uniform, excepting in the case of neodymium and samarium, since fractional recrystallisation of that double salt will accomplish a strikingly sharp separation of those two elements. There is the same break in the sequence of solubilities of other salts, in basicity, as indicated by the rate of hydrolysis, etc. It also appears that the absorption spectra show the same general variation, and, as will be shown later, the absorption bands of element number 61 seem to fit into the regular sequence.

Because element number 61 might be expected to share the striking similarity in properties and the common occurrence in minerals of the other members in the rare earth group, it seemed logical to institute a search for it in monazite sands, a mineral in which the first members of that family, the so-called cerium earths, predominate. Since that mineral is rich in neodymium, 60, and in samarium, 62, it would be surprising to learn of the absence of 61 there and its presence in a mineral containing little or none of 60 and 62.

The original material used in the investigation was the rare earth residue remaining from monazite sands after the extraction of thorium and part of the cerium for use in the manufacture of Welsbach mantles. It was given to this laboratory by the Lindsay Light Company of Chicago. After the remaining cerium

was removed by the usual methods, the other rare earths were fractionally recrystallised as double magnesium nitrates. Very pure neodymium and samarium, the latter subjected to further purification by other methods, were sent to the Bureau of Standards at Washington for use in an extensive investigation being pursued on the infra-red arc spectra of the rare earths. It was found that a number of identical new lines were present in both samples, and the suggestion was made that they might be due to the presence of a small amount of a new element. Eder had noted the same phenomenon. Later, when the ultra-violet arc spectra of neodymium, samarium, and of intermediate fractions containing both were examined, lines common to all three were found. However, X-ray analysis of those same samples showed no indication of the presence of an element with atomic number 61. Prandtl and Grimm had subjected rare earth material to separation by the same method and then to a fractional precipitation with ammonia, and could find no evidence of the missing element by X-ray analysis.

It seemed that the solubility of the double magnesium salt of element number 61 is very similar to that of neodymium, and its separation by recrystallisation of that salt offered little hope of success. The order of solubility of the bromates of the cerium group earths is the reverse of the order obtaining with the double magnesium nitrates, and that suggested a means of separating neodymium and thus concentrating element number 61. It is easier to separate a small amount of one element from a larger amount of a second if the former is in the less soluble end of the series of recrystallisations. Accordingly the neodymium-rich material thought to contain element number 61 was converted to bromate and again recrystallised.

A marked change in the absorption spectra of the solutions that began to appear after repeated recrystallisation indicated the probable concentration of the missing element. Two bands, one at 5816 Å.U. and another at 5123 Å.U., that had shown very faintly in supposedly pure neodymium, became stronger in some fractions as the other neodymium bands disappeared. Because these two bands, if assigned to element number 61, find their places in a more or less regular sequence shown by bands of neighbouring elements, it was thought they might belong to that element.

X-ray analysis confirmed the theory and showed the presence of element number 61 in those fractions. A mean value of five determinations of 2.2781 Å.U. was found for the $L\alpha_1$ line and one determination of 2.0770 Å.U. for the $L\beta_1$ line. A faint indication of the $L\beta_3$ line was also noted. It is assumed that these results prove the presence of element number 61.

The name assigned to the element is Illinium (II).

There are several reasons that may be advanced to explain why the element escaped detection by means other than X-ray analysis. It must be extremely rare. Its solubility in a series of fractional recrystallisation is next to that of the very abundant neodymium, which tends to spread into the illinium-rich members of a series. The large number of absorption bands exhibited by both neodymium and samarium would tend to mask

its absorption spectrum. Finally, the solubility of its double magnesium nitrate, which salt is commonly used for the separation of closely related elements, is close to that of neodymium. Evidence supporting this latter is found in the fact that the absorption bands at 5816 Å.U. and 5123 Å.U. found in supposedly pure neodymium purified by that method are shown to belong to illinium.

The identification of illinium as the missing rare earth completes the list of rare earth elements. Work has been instituted involving the extraction of several hundred pounds of the crude material with the purpose in view of obtaining enough of the element in pure enough state to study its properties, its relationship to other members of the group, and its atomic weight.

The Periodic System, Chemical Bonds, and Crystal Structure.¹

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A GREAT advance was made in the Bohr theory of the Periodic System by the discovery of Stoner and of Main Smith that the numbers of electrons in the different subdivisions of the *L*, *M*, *N*, . . . shells are not equal, as Bohr originally assumed, but unequal. The details of the new scheme are given in the following table, which shows the sub-groups of the shells, with the numbers of electrons in each :

TABLE OF X-RAY LEVELS.

	n_{11}	n_{21}	n_{22}	n_{32}	n_{33}	n_{43}	n_{44}
<i>K</i>	2
<i>L</i>	2	2	4
<i>M</i>	2	2	4	4	6
<i>N</i>	2	2	4	4	6	6	8
	n_1	n_2		n_3		n_4	

It will be noticed that the *K*-shell is single, the *L*-shell triple, the *M*-shell fivefold, and so on, in agreement with X-ray data (three *L* absorption edges, etc.). For the principal quantum numbers we still have of course $n=1$ in the *K* levels, 2 in the *L* levels, and so on.

At the top of the table is the quantum number notation which we find necessary for classifying X-ray spectra. There are, besides the principal quantum number n , two subordinate ones which we write as suffixes. They are denoted either by k_1 and k_2 , or by k and j , and it is understood that while $k_1=k$, $k_2=j+\frac{1}{2}$; j is the so-called inner quantum number, and is, according to our scheme (developed in a previous lecture), half-integral, in the same way as in the alkali spectra. The two types of spectra are analogous, as is emphasised especially by Landé. We increase the magnitude of j , merely for typographical reasons, by $\frac{1}{2}$, so as to obtain a whole number k_2 , in agreement with our practice in the case of the alkalis.

The numbers in the body of the table are now throughout equal to $2k_2=2j+1$. But $2j+1$ is the quantum weight, or number of orientations of the angular momentum j in a magnetic field, so that Main Smith and Stoner make the number of electrons in a given energy level equal to the quantum weight, $2j+1$, of that level.

At the foot of the table the numbers n_k describing the orbital types are given. We must direct special attention to the fact that any two shells that form a 'relativity doublet' in the X-ray spectra belong to the same orbital type n_k , which is in complete opposition

to the original view from which the relativity formula was derived.

In replacing n_k by n_{kj} , we are introducing the same problem as has arisen in the case of the visible spectra. The characteristics of the orbit of a single electron ought to be fully determined by two quantum numbers, n and k , together with a third, m , to give the orientation of the orbit in space; that is to say, corresponding to the three degrees of freedom of the rotating electron, we should have altogether three quantum numbers. But we have already seen (in the earlier lectures) that even with hydrogen we require a j in addition to n and k , or three quantum numbers merely for the characteristics of the orbit, which is thus not fully described without four numbers. We need not be surprised then when the same problem arises with X-ray spectra, so that here also a single orbit must be described not as an n_k orbit but as an n_{kj} orbit. May we hope that the solution of the difficulty will be found along the lines of the new quantum mechanics introduced by Heisenberg and developed, for example, by Dirac? It is true we are confident that this will dispose of the old difficulties as to half-quantum numbers, and so on, that arise especially in the anomalous Zeeman effect; but it seems unlikely that it will succeed in providing a new degree of freedom for the orbital electron. Most probably we shall be compelled to make a new hypothesis that will introduce this into the Hamiltonian function of the system. In this connexion we may recall the striking suggestion of S. Goudsmit of the 'spinning electron' (proposed, in some respects, by Porson previously, though Porson gave no definite relations to quantum numbers); it may be that here we shall find the explanation of the missing degree of freedom.²

The j of the individual electron must not be confused with the j of the whole atom, the outermost shell of which is composed, in general, of several orbits of the type in question. This latter j we will distinguish by a bar, so that \bar{j} refers to the atom as a whole; moreover, it refers to the atom in its fundamental or unexcited state. In other words, \bar{j} is the inner quantum number of the fundamental term. In 1925 I enunciated two theorems in the *Physikalische Zeitschrift*, about this \bar{j} of the fundamental term and its relation to the position of the element in the periodic table :

1. Every completed sub-group is distinguished by $\bar{j}=0$.

² Indeed, from a paper of Heisenberg and Jordan, now in print in the *Zeits. f. Phys.*, it appears that both new mechanics and 'spinning electron' are needed in order to account for the relativity doublet arising between two levels that differ by j and not, as in the original theory, by k .

¹ From a series of University of London lectures on "Atomistic Physics," delivered at the Royal College of Science during March 1926.