

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS
XXIII. ELEMENT NO. 61¹
PART ONE. CONCENTRATION AND ISOLATION IN IMPURE
STATE

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Historical

Since the time of Moseley's work, which showed definitely that an element should exist between neodymium and samarium when these elements are arranged in order of their atomic numbers, attempts have been made to isolate it. Eder² in 1917 showed that examination of the arc spectrum of samarium indicated that his material might contain traces of a new element, while five years later Hadding³ examining the X-ray spectrum of the mineral fluocerite, a basic fluoride of the cerium metals, believed he had indications of a new element in his material. Brinton and James,⁴ examining the rates of hydrolysis of the rare earth carbonates, observed that the curves connecting the volume of carbon dioxide evolved, with time, were generally uniformly spaced from praseodymium on, except after neodymium. At this point a distinct gap occurred between the curves for that element and samarium. Prandtl and Grimm⁵ in 1924 carried out exhaustive fractionation of the cerium earths as double magnesium nitrates, spreading their material over 50 fractions, but failed to obtain any indication of the presence of element No. 61. From this they concluded that this element might not be a member of the rare earth group, but could be expected to occur as a homolog of manganese along with Nos. 43, 75, 85 and possibly 93. More recently Druce and Loring⁶ have examined a concentrate from manganese material for both the K and L spectrum lines of Element 61 but without success.

Introduction

Early in 1919, the United States Bureau of Standards and the Department of Chemistry of the University of Illinois entered into an agreement for the comparative study of the arc spectra, especially in the red and infra-red regions of certain of the rarer elements, and particularly the members of the rare earth group. The results so far obtained have been pub-

¹ From a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

² Eder, *Sitzb. Akad. Wiss. Wien*, **IIA**, 125 (1917).

³ Hadding, *Z. anorg. Chem.*, **122**, 195 (1922).

⁴ Brinton and James, *THIS JOURNAL*, **43**, 1446 (1921).

⁵ Prandtl and Grimm, *Z. anorg. Chem.*, **136**, 283 (1924).

⁶ Druce and Loring, *Chem. News*, **131**, 273 (1925).

lished in a series of articles.⁷ In commenting on the results obtained with samples of neodymium and samarium Kiess remarks^{7b} "The wave-length tables contain about 1500 lines for neodymium and about the same number for samarium. A third table contains 130 lines which are common to both spectra. These lines are of unknown origin and may belong to the missing element of order No. 61, coming between neodymium and samarium. . . . Eder has published similar lists of unidentified lines which he suggests may belong to elements not yet isolated, but none of the lines of Table 3 below agree with those in his lists."

Acting on this suggestion the work was commenced in this Laboratory by L. F. Yntema.⁸ Extensive fractionation of neodymium and samarium materials was carried out using the double magnesium nitrates, the solubilities of the salts in such a series increasing with atomic number. Element 61 should, therefore, concentrate in those fractions intermediate between neodymium and samarium. X-ray analysis of the intermediate fractions, as well as of the pure neodymium and samarium, was carried out by Yntema in the Sloane Laboratory of Physics, at Yale University. While this work was in progress, fractionation was continued in this Laboratory, samples being forwarded to New Haven as desired. X-ray examination failed, however, to give any indication of the presence of Element No. 61.

In the examination of the arc spectra in a small region of the ultraviolet, it was found that the purest samples available of neodymium and samarium gave lines common to both elements, these being somewhat more intense in those fractions intermediate between the neodymium and samarium. Five of these lines were measured and corresponded to wave lengths of 3305.8 Å., 3329.1 Å., 3342.5 Å. and 3379.2 Å.

Theoretical

The problem was taken up by the present investigators in 1923 and in view of the foregoing results it was considered that the logical place to search for Element 61 would be among the rare earths. Since the most extensive researches in attempts to isolate this element had been carried out using fractional crystallization of the double magnesium nitrates as a means of separation, in which case it is natural to expect to obtain a concentration of element No. 61 in those fractions intermediate between the neodymium and samarium and, since all had resulted in failure, three reasons as to the cause presented themselves to us.

(1) Element No. 61 might be extremely scarce, perhaps the most rare of all of the rare earths, and so only infinite fractionation of tremendous amounts of material would result in separation. It is also noteworthy

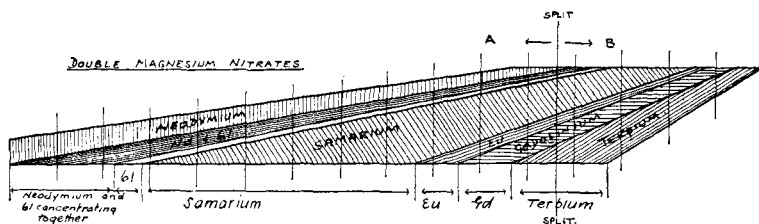
⁷ *Bur. Standards Sci. Papers* (a) 421 (1921); (b) 442 (1922); (c) 466 (1923).

⁸ Yntema, *THIS JOURNAL*, 46, 37 (1924).

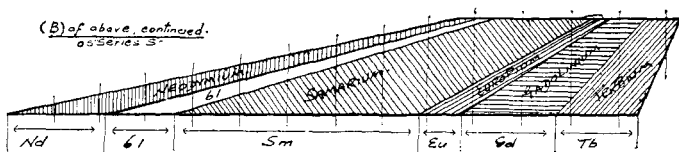
that in the rare earth group, those elements of odd atomic number are much more scarce than are those of even atomic number.

(2) Very little difference in solubility might exist between the double magnesium nitrates of either 60 and 61, or of 61 and 62, with the result that the element concentrates with one of its more plentiful neighbors, and thus reaches with difficulty the relative concentration necessary for detection by means of X-ray analysis.

(3) The solubility of the double magnesium nitrate of element No. 61 might be entirely unique in falling out of sequence with those of its congeners, and hence would not be found in fractions intermediate between neodymium and samarium in such a series.



A.—The approximate distribution of rare earths during fractionation as the double magnesium nitrates, showing the theoretical explanation for failure of previous attempts to detect element No. 61 in such a series. The sections show approximate composition of each fraction.



B.—The possibility of obtaining sufficient concentration of element No. 61 to be detected by X-ray methods, by splitting a double magnesium nitrate series as indicated above and continuing fractionation of the more soluble fractions.

Fig. 1.

The possibilities presented by (1) and (2) seemed the more probable for several reasons: first, the extremely sharp separation of neodymium from samarium when the double magnesium nitrates of these elements are subjected to fractional crystallization; second, the lack of continuity in passing from neodymium to samarium in such a study as that made by Brinton and James; and third, the presence of new lines in the arc spectra showing increased intensity in intermediate fractions.

Since, however, no new absorption bands had ever been observed in the intermediate fractions of such a series, we assumed that 61 was concentrating with the neodymium, the extensive absorption bands of which are capable of masking any other bands in those regions. In Fig. 1, we have

given a theoretical diagram of the possible concentration of No. 61 in a double magnesium nitrate series. In this we have shown the effect of fractionation if 61 should concentrate with the neodymium, the relative amounts of 61 being, of course, greatly magnified. The cross sections represent roughly approximate composition of the various fractions. From this diagram it is evident that if the rare element No. 61 concentrates with its more abundant neighbor neodymium, the ratio between these elements remains practically constant throughout most of the series. If this ratio is less than 1:1000, the detection of the new element by X-ray analysis would be impossible because this method of detection cannot be relied upon beyond this limit. Toward the soluble end of the series the ratio of 61 to neodymium becomes more favorable, but in these fractions the increasing

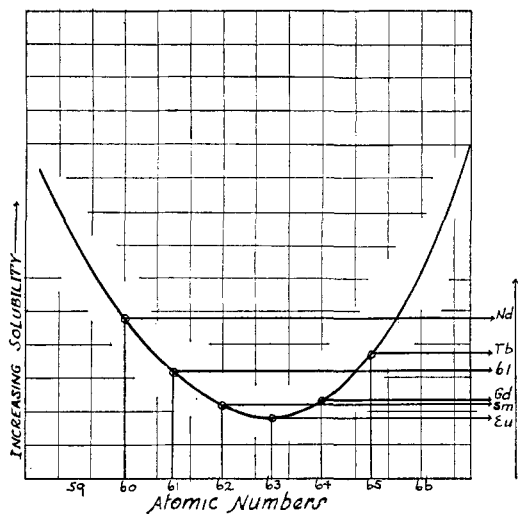


Fig. 2.—Bromates.

quantities of samarium, gadolinium and other earths reduces the effective ratio once more. It seemed probable, therefore, that if a double magnesium nitrate series were split as shown in Fig. 1, the less soluble part, A, would contain most of the neodymium and No. 61, while in the more soluble part, B, there would be a larger *proportion* of No. 61 to neodymium. Further fractionation of B should then result in the concentration of No. 61 to a degree which would make its detec-

tion by X-ray analysis possible and at the same time the samarium content would be materially reduced.

This procedure should leave the bulk of No. 61 in A, of the original series.

Now James⁹ has shown that in the case of the bromates of the rare earths, when the solubilities are plotted against atomic number, there is a gradual decrease in solubility to europium, followed by a gradual increase as shown in Fig. 2. Furthermore, experience in this Laboratory has shown that the elements arrange themselves in the approximate order of increasing solubility as follows: europium, samarium, gadolinium, No. 61, terbium and neodymium. The fractionation of the bromates should effect a separation of neodymium and No. 61 both because No. 61 occurs toward the less

⁹ James, THIS JOURNAL, 36, 2060 (1914).

soluble end of the series, thus making its separation more easily accomplished, and because terbium would be interposed between the two.

Although detection by means of X-ray analysis is sensitive only to one part in one thousand, absorption in the visible region of the spectrum is sensitive in the case of the strongest bands of neodymium to perhaps less than one part in one hundred thousand. If, then, solutions of the salts of element No. 61 show absorption, as would be expected of them, it should be possible to detect this element by this means even though it be present in amounts less than would permit of its being detected by means of X-ray methods.

In Fig. 3 we have plotted the absorption bands of pure neodymium and of pure samarium showing the broadening of the bands as concentration

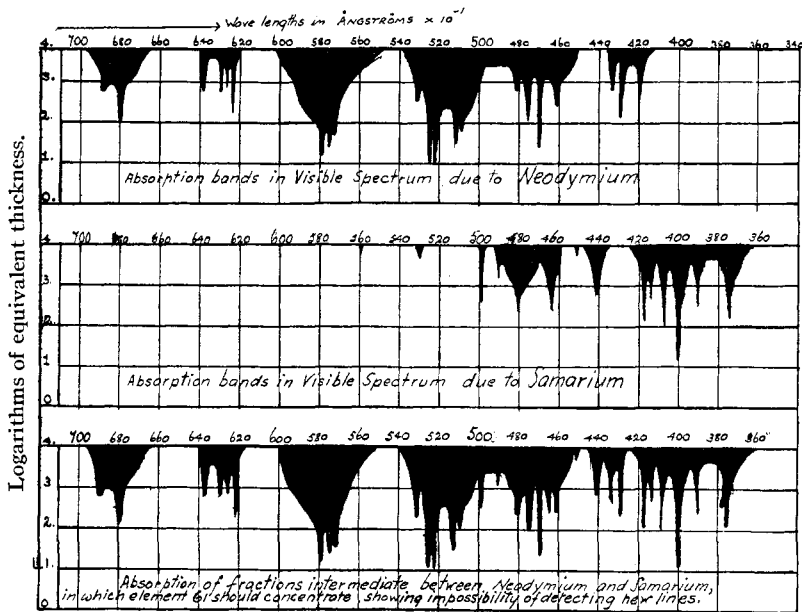


Fig. 3.

increases. The lower graph is a combination of the two upper and shows the absorption bands to be expected in intermediate fractions of a double magnesium nitrate series. It also shows the hopelessness of attempting to detect any new bands in such a mixture, because the visible portion of the spectrum is so completely filled with the broad absorption bands of neodymium and samarium.

On the other hand, if the fractionation is carried out with a bromate series as indicated in Fig. 4A, Element 61 concentrates in fractions along with terbium and gadolinium. In Fig. 5 the absorption bands for these two elements have been plotted, terbium showing but one narrow band and

gadolinium none in the visible spectrum. In the middle fractions of such a series the amounts of neodymium and samarium grow gradually less, while the proportions of terbium, gadolinium and No. 61 are increasing. The effect on the absorption spectra is seen by moving downward the dotted line in (3) of Fig. 5 until it corresponds with the solid line beneath it. In this position only the peaks of the stronger bands of neodymium and samarium are visible while the relatively narrow band of terbium is

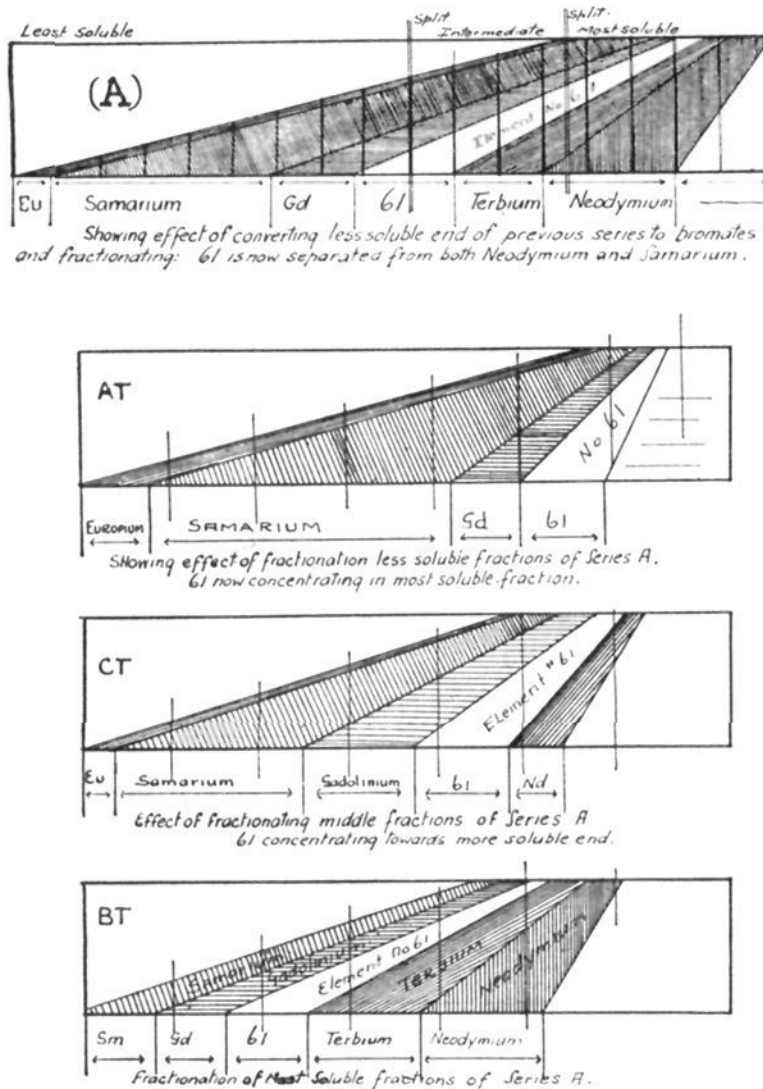


Fig. 4.—Bromates.

the only one likely to interfere with the detection of new bands. In this manner it ought to be possible to discover the presence of a new element even though it is present in amounts too small for detection by X-ray analysis.

Experimental Part

The rare earth materials in the Laboratory were carefully examined and series selected in order to test out the validity of our theory as outlined above. The series had their source in monazite residues kindly donated

by the Lindsay Light Company of Chicago. These had been extracted by F. H. Driggs of this Department and were found to contain chiefly members of the cerium group earths with small amounts of the yttrium group metals. The cerium was carefully removed by oxidation by means of potassium permanganate in a neutral solution, and the lanthanum by fractional crystallization as the double ammonium nitrates. The lanthanum-free salts were then converted to the double magnesium nitrates and subjected to exhaustive fractional crystallization. As soon as the least soluble fractions became freed from neodymium they were removed, until all remaining fractions were free from praseodymium as determined by absorption spectra. In the same way, as the neodymium fractions be-

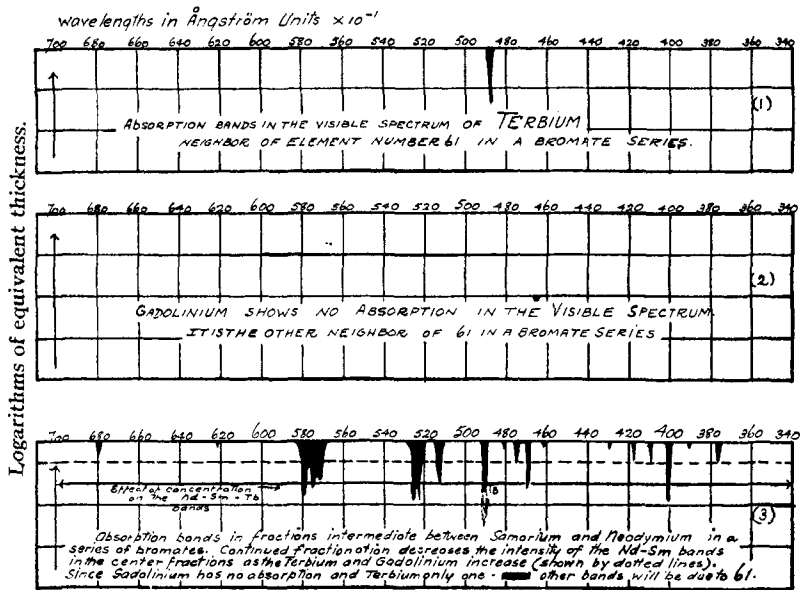


Fig. 5.

came free from samarium they were removed until the series finally consisted of fractions showing relatively small amounts of neodymium as compared with samarium together with small amounts of the yttrium group earths. Five similar series were worked over in this manner, the more soluble ends finally being combined when they showed the composition as above. These were then continued as the double magnesium nitrates until they had been spread over 15 fractions.

In the light of the foregoing theory this series was then split at a point as marked in Fig. 1 between A and B, the more soluble fractions designated by (B) in the diagram being continued as the double magnesium nitrates "Series S." This series was subjected to 103 crystallizations, the least soluble fractions being combined as they became too small to be handled.

At the end of fractionation, Fractions 1 to 6 had been combined and then constituted the least soluble fraction, consisting of about 20 g. of salt. This fraction designated as S_{1-6} was converted to the oxide for X-ray examination.

The less soluble fractions of our original series, designated by (A) in Fig. 4 were combined and converted to bromates using the James method.¹⁰ These were then subjected to fractional crystallization as "Series T."

After 65 crystallizations there was observed in Fractions 9, 10 and 11 a faint separate band at 5816 Å. which had always been regarded as due to neodymium. With the 70th fractionation it was observed that this band was becoming stronger in the intermediate fractions while at the same time the characteristic neodymium bands were becoming weaker. This seemed to indicate that the band at 5816 Å. which finally became a well-developed doublet was not due to neodymium but to some element which was concentrating in the intermediate fractions. The presence of this band in material rich in neodymium would be entirely obscured by the intense neodymium bands at 5782 Å. and 5748 Å.

In order to facilitate a study of this band, the series was split at this point in accordance with Fig. 4A. The least soluble fractions were continued as "Series AT," the most soluble as "Series BT" and the intermediate fractions as "Series CT."

If Element 61 were present as indicated by this band we should expect concentration in the most soluble fraction of AT, in the less soluble fractions of BT and nearer the soluble end in CT. Each series was subjected to about 60 further crystallizations, and in each case we obtained an increase in the intensity of the band in those fractions in which we should expect Element 61 to concentrate. The CT series shows the most intensity, with AT the least, it showing this band but faintly in the most soluble fraction only. In addition our fractions show a heavy absorption band at 5123 Å., a band which was also formerly assigned to neodymium but was extremely intense in our fractions as compared with the intensity of other neodymium bands. In Fig. 6 we have plotted the absorption spectra of the rare earths, assigning to element No. 61 bands that we have observed in our best fractions. We believe that the faint bands at 6700 Å., 5905 Å., and the stronger bands at 5830 Å., 5816 Å. and 4520 Å. are probably due to element No. 61. Bands at 4893 Å., 4411 Å. and 4177 Å., usually assigned to samarium, also appear to be stronger in our fractions than would be expected.

A study of the absorption spectra of the rare earth elements by L. F. Yntema¹¹ indicates that there is a definite relationship between the positions of the characteristic absorption bands of adjacent elements. The

¹⁰ James, *THIS JOURNAL*, 30, 182 (1908).

¹¹ Yntema, "A Theory of Color," *THIS JOURNAL*, 48, 1598 (1926).

discovery of prominent absorption bands of Element 61 in the positions 5816 Å. and 5123 Å. confirms this belief and indicates that there is a definite drift in the position of the absorption bands. This drift is toward the shorter wave lengths in Elements 59 to 64, the latter element, gadolinium, having its absorption band in the ultraviolet.

The detection of the absorption bands at 5816 Å. and 5123 Å. confirmed our belief that we were dealing with a new element and the increased intensity of these bands led us to hope that the new element had been

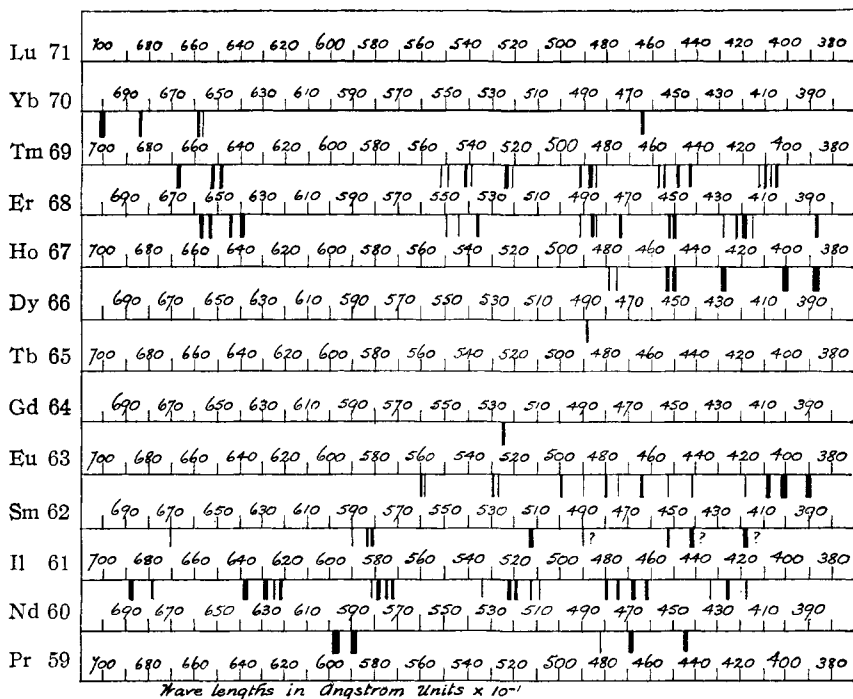


Fig. 6.

concentrated sufficiently to enable us to identify it by means of X-ray analysis.

Samples were taken from the original bromate series in which the new absorption band had first been noticed and arbitrarily designated at BT₁₄₋₁₅. (These fractions were subsequently continued as the BT series.) Samples were also taken from the fractions of CT showing the maximum amount of absorption and designated as CT₁₁. The least soluble fractions of the double magnesium nitrate series were also prepared for analysis as S₁₋₆ since, although we had not obtained any absorption bands as in the bromates, the neodymium concentration was sufficient to allow of masking of any bands due to 61 by its own absorption.

Summary

1. Fractionation of cerium group material as double magnesium nitrate concentrates element No. 61 between neodymium and samarium.
2. All fractions contain so small a proportion of No. 61 that its detection by X-ray analysis is difficult.
3. The absorption bands of Element No. 61 are masked by the broad bands of neodymium and samarium.
4. Fractionation as bromates reverses the order of solubilities, interposing gadolinium between No. 61 and samarium and terbium between No. 61 and neodymium. Under these conditions absorption bands probably due to the presence of Element No. 61 become plainly visible.

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OBSERVATIONS ON THE RARE EARTHS XXIII. ELEMENT NO. 61 PART TWO. X-RAY ANALYSIS

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In order to justify the assumption that the absorption bands obtained by the investigators, as outlined in Part I, were due to the presence of Element 61 an X-ray spectrograph of the Uhler type was constructed in this Laboratory. A tube was also constructed on which many helpful suggestions were received from Professor Manne Siegbahn who was at the University of Illinois at that time, and to whom the investigators are indeed grateful. The bulb was of the cold cathode type, the cathode being of pure aluminum and the target of copper. Both were connected to the bulb by means of ground-glass joints which permitted their ready removal at any time, and were water-cooled. The average potential applied was about 30,000 volts with an average current of from 8 to 10 ma. Its source was the 220v. power line of the University. In view of the voltage required to excite the K series and the limitations of our equipment, it was decided to photograph the L emission spectra only.

Much difficulty was encountered in keeping the rare earth oxides on the target during the bombardment with cathode rays. The oxides showed a marked tendency to fly off during the long exposures which we were compelled to make, so it was found impossible to apply the oxides in powder form. The method of fusing the oxide to the perforated surface of the target² gave better results but even this method was not entirely satis-

¹ From a thesis submitted in partial fulfillment for the requirements of the degree of Doctor of Philosophy at the University of Illinois.

² THIS JOURNAL, 46, 37 (1924).