Behavior of Zirconium-95 and Niobium-95 in Dilute Hydrochloric Acid toward Cation Exchange Resin

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(Received February 26, 1958)

Zirconium and niobium nuclides contained in fission products are ^{95}Zr—^{95}Nb and ^{97}Zr—^{97}Nb. The abundance of short-lived ^{97}Zr—^{97}Nb becomes negligibly small in a cooling period of about 10 days, while that of comparatively long-lived ^{95}Zr—^{95}Nb increases to the maximum after a longer period of about 200 days. Even after a few years, its abundance is still remarkable[1].

Zirconium-95 and niobium-95 in a mineral acid solution are present as radiocolloids[2] and the chemical behavior of these colloids is very complicated. Although many investigations[3] have been made regarding the chemical separation of ^{95}Nb from ^{95}Zr, the behavior of these nuclides toward the

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[1] H. F. Hunter and N. E. Ballow, *Nucleonics*, **9**, No. 11, C-2(1951).

[2] J. Schubert and E. E. Cohn, ibid., **4**, No. 6, 2 (1949); J. Schubert and J. W. Richter, *J. Colloid Sci.*, **5**, 376 (1949).

[3] K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **73**, 2900 (1951); **73**, 9 (1951); R. E. Wacker and W. H. Baldwin, AEC report, *ORNL*, 637 (1950).

cation exchange resin has not been thoroughly investigated. The author has made a study of the difference in the adsorbability of ^{95}Zr and ^{95}Nb to the cation exchange resin and also the effects of conditions of preparing solutions on the adsorbability.

Experimental

Material.—Zirconium-95 was obtained as oxalate complex from U.S.A.E.C.. Since it has been allowed to stand for about one year, ^{95}Zr and its daughter, ^{95}Nb, must be in transient equilibrium. The activity of this material was about 100 μC. To this, 10 ml. of concentrated sulfuric acid was added and heated slowly to almost dryness. After repeating this step twice more, the residue was heated with 200 ml. of 0.2 N hydrochloric acid to be dissolved. An aliquot of this solution, having an activity of about 1 μC, was used as a sample. The aliquot contained about 10^{-13} mole each of ^{95}Zr and ^{95}Nb, thus corresponding to about 5×10^{-11} mol./l., respectively.

Procedures.—After slurring the cation exchange resin Dowex 50-X8 (100 to 200 mesh) was placed in a glass tube, the resin was washed with 3 N hydrochloric acid to convert it into the hydrogen form and further washed completely with demineralized water. After complete washing, the interstitial water was replaced by 0.2 N hydrochloric acid. The resin bed was 0.7 cm. in diameter, 6.5 cm. in length and its volume was 2.5 ml.. A 2 ml. aliquot of the 0.2 N hydrochloric acid solution of ^{95}Zr—^{95}Nb mixture was diluted to 20 ml. with 0.2 N hydrochloric acid and poured into the column. Then 70 ml. of 0.2 N hydrochloric acid, 20 ml. of demineralized water, and 40 ml. of 0.5% oxalic acid solution or 3 N hydrochloric acid were poured successively. The flow rate was 0.5 ml. per minute. The 2 ml. fractions of the effluent were poured successively into the glass dishes which were 2.5 cm. in diameter and 0.6 cm. in height, and then heated with an infrared lamp to dryness. The activity in the dishes was measured by a G.M. counter whose window was 2.5 mg./cm^2 in thickness. The distance between the test sample and the window was 1.5 cm. and about 8% of the total activily was counted.

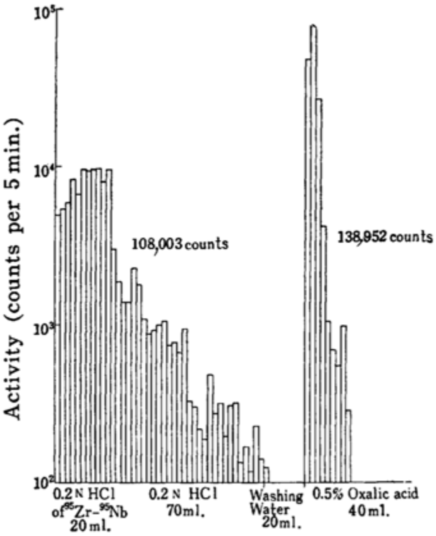

Fig. 1. Elution of a ^{95}Zr—^{95}Nb mixture. effluent fraction: 2 ml.

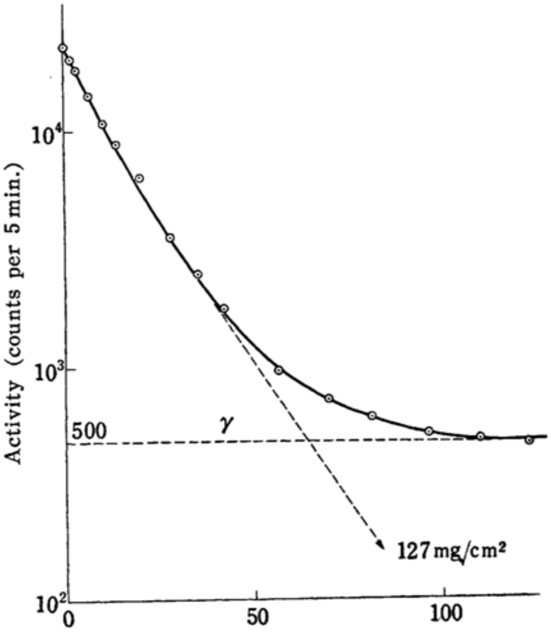

Fig. 2. Aluminum absorption curve of 0.5% oxalic acid fraction.

Results

Difference in Adsorbability of ^{95}Zr and ^{95}Nb.—The results obtained by the above mentioned procedures are shown in Fig. 1. It will be seen that ^{95}Zr—^{95}Nb mixture could be separated into two fractions; the one eluted by 0.2 N hydrochloric acid and the other by 0.5% oxalic acid. To identify ^{95}Zr and ^{95}Nb in these fractions, the maximum β-energy of the fraction activity was determined using a set of aluminum abosorbers. Instead of measuring the maximum β-energy of activities on all dishes, suitable aliquots of two fractions of 0.2 N hydrochloric acid and 0.5% oxalic acid were evaporated to dryness and the β-energy was measured. The results are shown in Figs. 2 and 3. The values of maximum range in Figs. 2 and 3, converted into MeV., agree with those for ^{95}Zr—β and ^{95}Nb—β in Table I. As shown

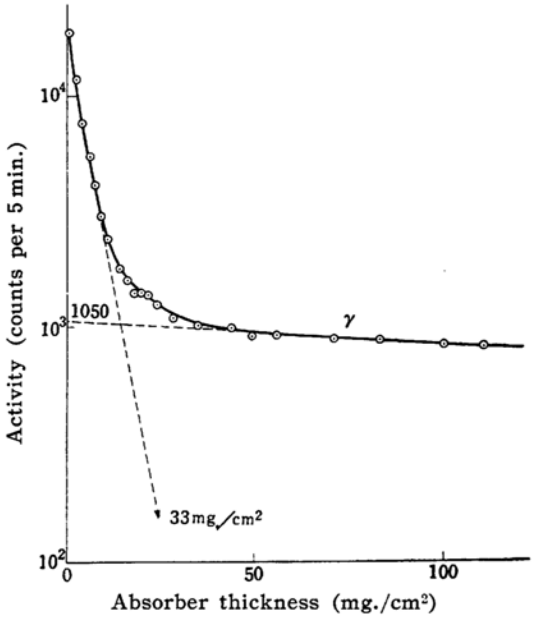

Fig. 3. Aluminum absorption curve of 0.2 N HCl fraction.

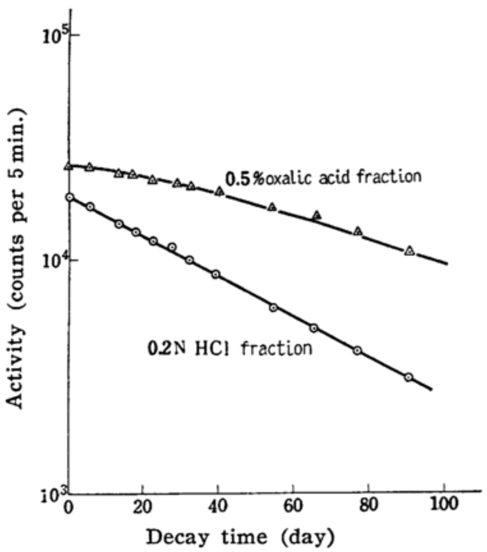

Fig. 4. Decay curves of two fractions.

TABLE I.

Nuclide	Half-life (day)	λ(day^{-1})	β(MeV)	γ(MeV)
^{95}Zr	65	0.01066	0.364	0.754
^{95}Nb	35	0.0198	0.165	0.76

in Fig. 4, the decay curve of the 0.5% oxalic acid fraction shows the production of ^{95}Nb from ^{95}Zr. After 26 days, the curve shows a half-life of 65 days. On the other hand, the activity of the 0.2 N hydrochloric acid fraction decayed with a half-life of 35 days. These half-life values coincide with those of ^{95}Zr and ^{95}Nb shown in Table I.

From the measurement of the maximum β-energy and the half-life, it was found that the 0.2 N hydrochloric-acid fraction contained mainly ^{95}Nb and the 0.5% oxalic-acid fraction mainly ^{95}Zr.

Relation between Time of Preserving the Solution of ^{95}Zr—^{95}Nb and the Adsorbability of ^{95}Zr.—Since ^{95}Zr and ^{95}Nb in a mineral acid solution are present as radiocolloids, it was thought probable that there might be an appreciable difference in adsorbability toward a cation exchanger between a fresh solution and an aged solution of ^{95}Zr—^{95}Nb.

After storage of the fresh sample solutions which were prepared as described before for 3, 7, 10 and 15 days, the experiments were carried out similarly. The results are shown in Fig. 5. It is obvious that the amount of ^{95}Zr retained on the resinbed decreases as time passes. when thesolution is 10 days old, ^{95}Nb and a considerable amount of ^{95}Zr are eluted in the same fraction. This phenomenon may be related to the characteristics of ^{95}Zr, the pH, other ions and dust in the solution, the wall of the vessel, etc., but can not be defined quantitatively.

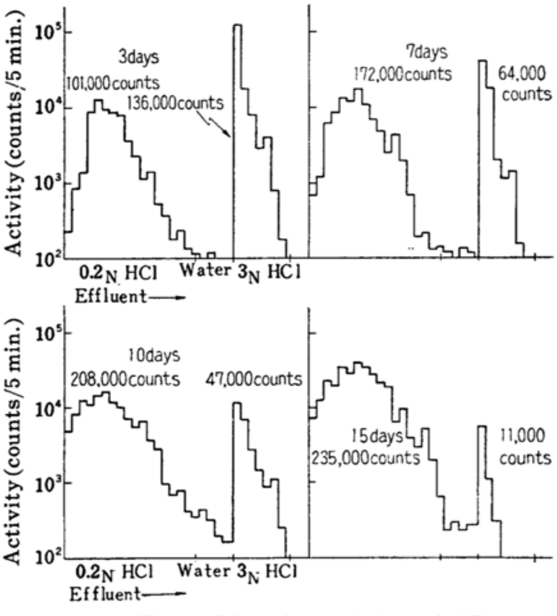

Fig. 5. Time of keeping solution of ^{95}Zr and ^{95}Nb and adsorbability of ^{95}Zr.

Variation in Adsorbability of ^{95}Zr and ^{95}Nb with the Concentration of Hydrochloric Acid.—Two fractions of ^{95}Zr and

^{95}Nb were obtained by the procedure described above, and each fraction was converted into 0.2 N hydrochloric acid solution. To 0.1 ml. aliquots of these solutions 25 ml. of hydrochloric acid having the following concentrations was added respectively: 0.01, 0.02, 0.04, 0.06, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 1.0, 1.9, 2.85 and 3.8 N. The addition of the small volumes of ^{95}Zr or ^{95}Nb solution did not appreciably change the hydrochloric acid concentrations of the resultant solutions. The activities of ^{95}Zr or ^{95}Nb in these solutions were about 0.5 μC corresponding to 10^{-13} mole (5×10^{-12} mol./l.).

These solutions were transferred to glass-stoppered flasks containing one gram each of air-dried Dowex 50—X8 (100 to 200 mesh) which had been treated with hydrochloric acid, and were agitated for five hours, at 25°C. Five-hour agitation was sufficient to give constant adsorption values. After the resin had settled the aliquots of the supernatant solution were transferred to glass dishes, evaporated to dryness, and their activities were measured. Also the entire procedure was run without the addition of the resin. Fig. 6 shows the relation between the adsorbability (%) of ^{95}Zr and ^{95}Nb and the concentration of hydrochloric acid. The adsorbability is defined by the ratio of the difference in activity between the aliquot obtained without resin and that with resin to the activity of the aliquot obtained without resin.

Fig. 6 indicates that about 0.2 N hydrochloric acid is suitable for the separation of ^{95}Zr from ^{95}Nb. As mentioned already, the adsorption of neither nuclide is due to the ion exchange. Consequently the complete separation of ^{95}Zr from ^{95}Nb is difficult even though there is a difference in adsorbability of both nuclides. Nevertheless by repeating the procedures a complete separation will be possible. It is also indicated that 3 N hydrochloric acid may be used as an eluent for ^{95}Zr instead of 0.5% oxalic acid. This was later confirmed experimentally.

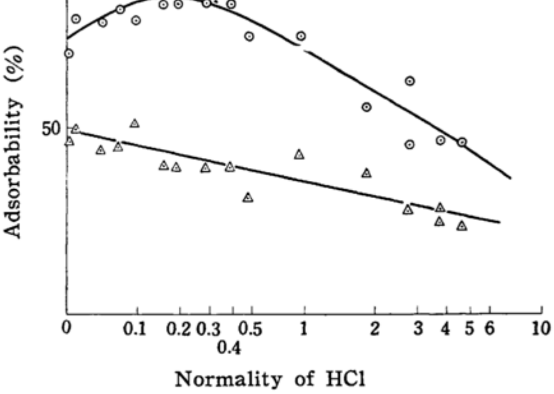

Fig. 6. Effect of hydrochloric-acid concentration on the absorbability of ^{95}Zr and ^{95}Nb.

Effect of Concentrations of Zr and Nb.—It was thought desirable to investigate the separation of larger amounts of ^{95}Zr and ^{95}Nb than 0.5 μC. Because of the limited amounts of these nuclides, nonactive isotopes were used as carriers. For this purpose a solution of reagent grade zirconium oxychloride ($ZrOCl_2\cdot8H_2O$) and an oxalic acid solution of niobium pentoxide previously fused with potassium bisulfate were prepared. From these solutions, four solutions containing 10^{-9}, 10^{-8}, 10^{-7}, and 10^{-6} mol./l. each of zirconium and niobium were prepared, and 10^{-13} mol./l. each of ^{95}Zr and ^{95}Nb was added as tracers. These four solutions were then treated with concentrated sulfuric acid, and processed as mentioned above. As a result, in all the cases tested, the degree of separation of ^{95}Nb from ^{95}Zr was the same as that with 0.5×10^{-11} mol./l. It may be concluded that the separation of ^{95}Nb from ^{95}Zr is possible under the conditions described in the experimental part, in the concentration range 10^{-12} to 10^{-6} mol./l.

Effect of Strontium.—Schubert[2)] reported that the state of tracer amounts of ^{95}Zr and ^{95}Nb in dilute mineral acid was radiocolloid and the adsorbability of these nuclides to a cation exchanger increased with the concentration of other cations. In the group-separation of fission products with a cation exchange resin, it is often the case that the complicated behavior of ^{95}Zr—^{95}Nb makes their complete separation impossible[4,5)]. As a large amount of strontium is found in fission products, the effect of this ion on the adsorbability of ^{95}Zr and ^{95}Nb was investigated to solve this problem. The sample solution contained about 2 μC of ^{95}Zr—^{95}Nb (about 10^{-12} mol.) in a volume

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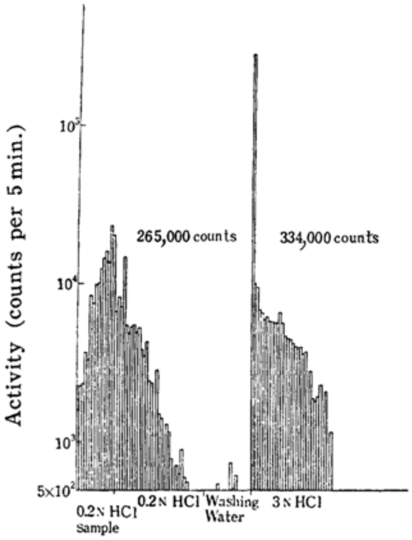
4) E. R. Tompkins, J. X. Khym and W. E. Chon, *J. Am. Chem. Soc.*, **69**, 2769 (1947); W. E. Cohn, G. W. Parker and E. R. Tompkins; *Nucleonics*, **3**, No. 5, 22 (1948).

5) T. Shiokawa, T. Ozaki, T. Kambara and M. Yagi, *The 1st Atomic Energy Symposium*. (1957), Tokyo, Japan, Section: Material and Chemistry, B-33.

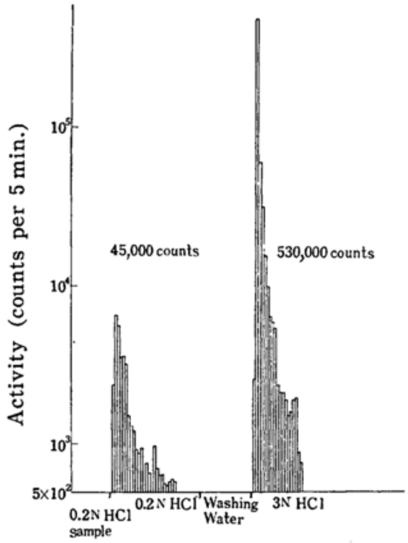
of 20 ml. of 0.2 N hydrochloric acid. To a series of this solution, 1 mg. (0.571×10^{-3} mol./l.), 2 mg. (1.141×10^{-3} mol./l.), 3 mg. (1.712×10^{-3} mol./l.), and 4 mg. (2.282×10^{-3} mol./l.) of strontium (as chloride) were added respectively. After passing 20 ml. of the sample solution through the same resin column as described before, elution was done successively with 50 ml. of 0.2 N hydrochloric acid, 30 ml. of washing water, and 50 ml. of 3 N hydrochloric acid. The results are shown in Figs. 7, 8, 9 and 10. It is pointed out that, when the strontium concentration is 2.282×10^{-3} mol./l., ^{95}Nb is eluted with difficulty with 0.2 N hydrochloric acid (Fig. 10). In other words, separation of ^{95}Nb from ^{95}Zr becomes impossible under such a condition.

In the group separation of ^{95}Zr and ^{95}Nb from fission products using a cation exchange resin, a good recovery may be obtained when 0.2 N hydrochloric acid



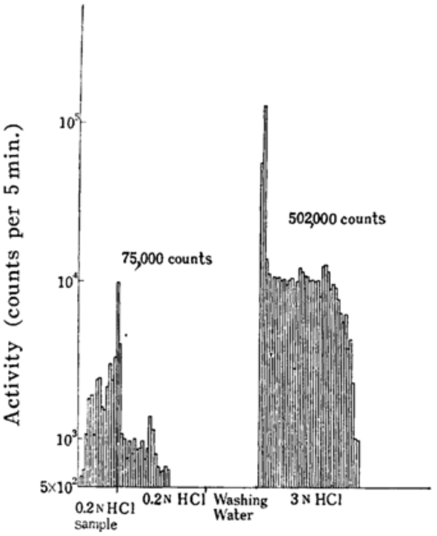
Effluent fraction: 1.5 ml.

Fig. 7. Effect of 1 mg. Sr^{2+}. Sample solution: 20 ml.



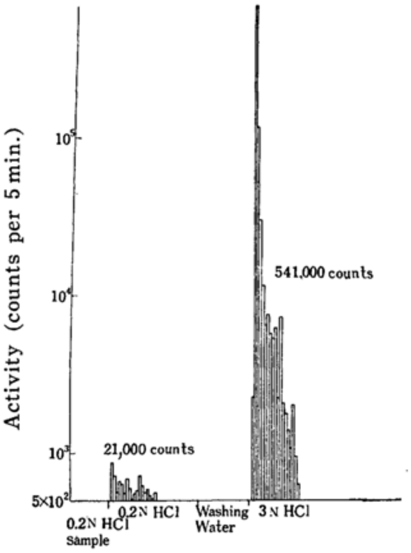
Effluent fraction: 1.5 ml.

Fig. 9. Effect of 3 mg. Sr^{2+}. Sample solution: 20 ml.



Effluent fraction: 1.5 ml.

Fig. 8. Effect of 2 mg. Sr^{2+}. Sample solution: 20 ml.



Effluent fraction: 1.5 ml.

Fig. 10. Effect of 4 mg. Sr^{2+}. Sample solution: 20 ml.

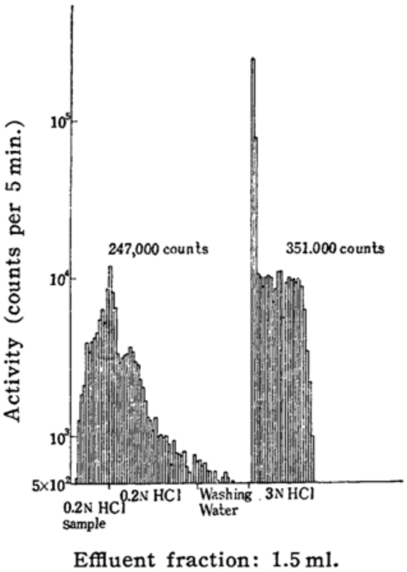


Fig. 11. Effect of 2 mg. Sr^{2+} previously adsorbed.

solution of ^{95}Zr and ^{95}Nb containing a large amount of strontium is passed through the resin and the elution of two nuclides is made with 0.5% oxalic acid.

When 2 mg. of strontium was first adsorbed to the resin column and then a solution of ^{95}Zr—^{95}Nb was poured into the column, the result shown in Fig. 11 was obtained. By comparing Fig. 8 with Fig. 11, it is seen that the activity of ^{95}Nb in the effluent is greater in the latter. It is believed that this is due to the change in the state of ^{95}Nb rather than to the variation of the resin surface. The effect of the cations other than the strontium ion will be studied in future.

Separation of ^{95}Zr and ^{95}Nb Using Other Cation Exchangers.—According to Schallert⁶⁾, ^{95}Zr and ^{95}Nb were strongly adsorbed by Amberlite IR-1 and IR-100. As these resins were no more available, experiments were carried out with Amberlite IR-120 and Diaion SK. The results were the same as those with Dowex 50-X8.

Adsorption of ^{95}Zr and ^{95}Nb to a Glass Vessel.—It is said that the tracer amounts of ^{95}Zr and ^{95}Nb in dilute mineral acid were adsorbed on a glass vessel⁷⁾. In the present work, a solution of ^{95}Zr that had been kept in a soft-glass bottle for 30 days did not show any appreciable loss due to the adsorption. On the other hand, about 0.5% of ^{95}Nb activity was lost when 0.2 N hydrochloric acid solution of ^{95}Nb had been kept in a glass bottle for 3 days, and considerable activity was lost when this solution had been kept for 30 days.

Summary

By passing 0.2 N hydrochloric acid solution of tracer amounts of ^{95}Zr and ^{95}Nb (about 10^{-11} mol./l., 10^{-13} mol., or 1 μC, with respect to each nuclide) through a cation exchange resin column (Dowex 50—X8, Amberlite IR-120, or Diaion SK) and eluting with 0.2 N hydrochloric acid, a fraction containing mainly ^{95}Nb was obtained. A fraction containing mainly ^{95}Zr was then obtained by eluting with 0.5% oxalic acid or 3 N hydrochloric acid. With higher concentrations of non-active zirconium and niobium (about 10^{-6} mol./l. each), similar results were also obtained.

As the 0.2 N hydrochloric acid solution of ^{95}Zr—^{95}Nb became aged, the adsorbability of ^{95}Zr decreased. Effect of hydrochloric acid concentration on the adsorbability of ^{95}Zr and ^{95}Nb was studied and the concentration range 0.1 to 0.3 N was found to be suitable for separation.

The adsorbability of ^{95}Nb increased with an increase in the concentration of strontium ion.

This work has been done in the laboratories of the Government Chemical Industrial Research Institute, Tokyo. The author wishes to express his thanks to Dr. Toshio Nakai for helpful suggestions and guidance in the course of this work. Thanks are also due to Dr. Kenjiro Kimura for his advice and encouragement. The helpful suggestions of Mr. Hiroshi Onishi in the preparation of this manuscript are also acknowledged.

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6) P. O. Schallert, AEC report, *ORNL*-1144, (1952).

7) A. G. Maddock and W. Pugh, *J. Inorganic and Nuclear Chem.*, **2**, 144 (1956).