Radioactive Isotopes of Lutetium and Hafnium*

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A study has been made of neutron-deficient radioactive isotopes of lutetium and hafnium produced by bombardments of thulium and ytterbium with alpha-particles of various energies; of ytterbium with 10-Mev protons, and of lutetium with protons of energies from 10 to 70 Mev. Seven radioactive isotopes of lutetium and four of hafnium, all previously unreported, are described.

I. INTRODUCTION

IN continuation of the investigations[1] on neutron-deficient radioactive isotopes of the rare earth elements, a study has been made of radioactive isotopes of lutetium. Since the interpretation of the data has depended upon the characterization of lutetium daughters of hafnium parent activities, radioactive isotopes of hafnium have also been studied.

The techniques of bombardments of rare earth oxides, chemical separations of the rare earth elements, the measurement of radioactivities, etc., have been described previously.[1a]

Using the 60-in. Crocker Laboratory cyclotron, bombardments were made of thulium with various energies of alpha-particles and of ytterbium with both alpha-particles and 10-Mev protons. Lutetium was bombarded with protons from 15- to 32-Mev energy using the linear accelerator and with protons of 40- to 75-Mev energy using the 184-in. cyclotron. Lutetium activities were also produced in spallation reactions of tantalum with 190-Mev deuterons.

After bombardment, the rare earth oxides were dissolved in hot perchloric acid, hafnium carrier was added, and the hafnium then precipitated from $3N$ acid solution as the phosphate. After metathesis to the hydroxide and solution in nitric acid, scavenging separations of rare earth fluorides were made and the hafnium was finally precipitated as barium hafnium fluoride. Hafnium was also separated by extraction with benzene solutions of thenoyltrifluoroacetone (TTA).

The rare earths were recovered after removal of hafnium by precipitation first of the hydroxide and subsequently of the fluoride and oxalate. The chemical identity of the rare earth activities was shown by separation using the ion-exchange resin column procedure. Chemical separation of lutetium daughter activities grown in hafnium samples was made by initial separation of the hafnium as phosphate, then repeated precipitation of the lutetium as fluoride and oxalate using lanthanum as a carrier.

The radiation characteristics of the radioactive isotopes were obtained from aluminum and lead absorption measurements; the contribution of soft quantum radiation was obtained by aluminum absorption after removal of electrons by beryllium foils of suitable thickness—a correction for absorption of the soft quantum radiation in this foil was made before resolution of the aluminum absorption curves. Electron radiations were also studied on a simple magnetic spectrometer. The approximate ratios of the various components of the complex radiations found in species studied decaying by orbital electron capture were obtained from the various measurements; activities were corrected for absorption of radiations in counter windows and air gap, fluorescence yields of L and K x-rays were taken as 0.5 and 0.8, respectively, and the counting efficiencies of L and K x-radiation of ytterbium and lutetium in the mica window argon-alcohol tubes used were taken as 4 percent and 0.5 percent, respectively. The decay of the lutetium and hafnium isotopes is accompanied by L and K x-radiation, the average half-thicknesses being 14 to 15 mg/cm^2 aluminum and 100 to 105 mg/cm^2 lead, respectively.

The data on lutetium and hafnium isotopes are summarized in Table I.

II. LUTETIUM ISOTOPES

Study of lutetium produced in the bombardment of thulium with alpha-particles of various energies from 15 to 38 Mev has led to the characterization of five radioactive isotopes of lutetium of half-lives 1.7-days, 8.5-days, ~600-days, 6.7-days and 4.0-hours; these have been allocated to masses 170, 171, 171, 172, and 172, respectively. From short bombardments at 38 Mev, the 1.7-day and 8.5-day activities were resolved; the disappearance of the 1.7-day activity below a bombarding energy of 30 Mev furnished identification of this activity as mass 170 produced by the $(\alpha, 3n)$ reaction. The 4.0-hour and 6.7-day activities were obtained at low energies by the (α, n) reaction and thus both have mass 172. At intermediate energies the decay and absorption curves were impossible to resolve by simple absorption methods in view of the similarities of the 6.7-day and 8.5-day activities. The ~600-day activity, considered to be Lu^{171}, was found at all bombarding energies.

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[1] G. Wilkinson and H. G. Hicks, (a) Phys. Rev. **75**, 1370 (1949); (b) **75**, 1687 (1949); (c) **79**, 815 (1950).

In the bombardment of lutetium with 19-Mev deuterons, 10-Mev protons, and fast neutrons, a 165-day activity was produced; this can surely be allocated to mass 174 corresponding to $(d, p2n)$, (p, pn), and $(n, 2n)$ reactions.

The resolution of decay and absorption curves of lutetium activities produced in the proton and alpha-particle bombardments of ytterbium has proved difficult. The 4.0-hour Lu^{172} activity was recognized only through its positron emission, as the 3.7-hour Lu^{176} activity[2] is also formed in high yield, while the longer-lived activities form a very complex mixture.

A second very long-lived lutetium activity of half-life ~500 days was found in 30- to 50-Mev proton bombardments of lutetium, and was shown to be the daughter of the 23.6-hour Hf^{173} discussed below.

Lutetium isotopes have also been separated following growth from hafnium activities produced in alpha-particle bombardment of ytterbium and in proton bombardments of lutetium. The 1.7-day, 8.5-day, 6.7-day, and ~600-day activities have been resolved. The measurement of the radiation characteristics of these activities was more easily accomplished than was the resolution of decay and absorption data obtained from lutetium isotopes produced in $Tm+\alpha$ and $Yb+p$ bombardments.

The 1.7-day, 8.5-day and long-lived (probably both the ~500 and ~600 day), lutetium isotopes have also been found in the ion-exchange column-separated lutetium fraction of rare earth activities produced in bombardment of tantalum with 190-Mev deuterons.

The existence of other, short-lived, activities of lutetium and also of hafnium is possible as species with a half-life less than about fifteen minutes, except for lutetium daughters of longer-lived hafnium parent activities, could not be studied in this work.

165±5-day Lu^{174}.—This activity was found in the lutetium fraction from bombardments of lutetium with fast neutrons, 10-Mev protons, and 19-Mev deuterons; it has also been found together with the well known[2] 6.7-day Lu^{177} in the bombardment of hafnium with 19-Mev deuterons. Allocation to mass 174 can be made with certainty on the basis of formation by $(n, 2n)$, (p, pn), and $(d, p2n)$ reactions in lutetium and the (d, α) reaction in hafnium. The value $\sim 5\times 10^{-4}$ barns for the cross section for the $(d, p2n)$ reaction of the 19-Mev deuterons in lutetium was calculated from the ratios of the beta-particle activity of the 6.7-day Lu^{177} formed by Lu^{176}-d-p reaction and the activity of the 165-day Lu^{174}.[3] The decay of 165-day Lu^{174} has been followed through four half-lives. From the type of absorption curve obtained and from a study on a simple magnetic spectrometer, hard electrons observed in the radiations appear to be negative beta-particles. The x-radiation present is too abundant to be accounted for by isomeric transition. The isotope probably decays both by beta-emission and by orbital electron capture. The approximate ratios of the various radiations corrected for counting efficiencies are 0.16-Mev e^-: 0.6-Mev β^-: L x-ray: K x-ray: γ-ray$=\sim 0.7$: ~ 0.2: ~ 1.5: 1: ~ 0.1. Allowing for L an K x-rays arising from conversion, the decay by beta-particle emission is about 20 percent of the total disintegrations.

TABLE I. Data on Lu and Hf isotopes.

Isotope	Type of radiation	Half-life	Energy of radiation in Mev: Particles	Energy of radiation in Mev: γ-rays	Produced by
Lu^{170}	K,e^-,γ	1.7±0.1 days	0.1	~2.5	Tm-α-3n, Ta-d-3z13a, Hf^{170} K decay
Lu^{171m}	K,e^-,γ	8.5±0.2 days	0.17, ~0.5 (weak)	~1.2	Yb-p-n Tm-α-2n Hf^{171} K decay Ta-d-3z12a
Lu^{171}	K,e^-,γ	~600 days	~0.1	~1	Tm-α-2n
Lu^{172}	K,e^-,γ	6.70±0.05 days	0.13, ~0.6 (weak)	1.2	Tm-α-n Hf^{172} K decay Yb-p-n
Lu^{172m}	β^+,K?	4.0±0.1 hours	1.2	—	Tm-α-n Yb-p-n Lu-p-p3n
Lu^{173}	K,e^-,γ	~500 days	~0.1, ~0.18	~0.22 0.8	Lu-p-p2n Hf^{173} K decay Yb-p-n
Lu^{174}	K,e^-,γ β^- (~20%)	165±5 days	0.16 e^- 0.6 β^-	~1	Lu-n-2n Hf-d-α Lu-d-p2n Lu-p-pn
Hf^{170}	β^+,K?	112±2 minutes	2.6	—	Lu-p-6n
Hf^{171}	K,e^-,γ	16.0±0.5 hours	0.15	1.4	Lu-p-5n Yb-α-3n
Hf^{172}	K,e^-,γ	~5 years	0.23	~0.28 0.8	Lu-p-4n Yb-α-2n,3n Ta-d-2z11a
Hf^{173}	K,e^-,γ	23.6±0.1 hours	~0.1, 0.22	~1	Lu-p-3n Yb-α-n,2n,3n

~500-day Lu^{173}.—This activity has been found in bombardments of lutetium with 30- to 40-Mev protons, and has been separated at regular time intervals during the decay from the 23.6-hour hafnium activity formed in alpha-particle bombardments of ytterbium.

The quantity of residual lutetium activity formed in decay of a sample of pure 23.6-hour Hf^{173} made by the $(p, 3n)$ reaction in the bombardment of lutetium with 25-Mev protons in the linear accelerator, together with the estimated counting efficiencies, gives a half-life of 400 to 600 days for this isotope. The direct decay has been followed only through two years as yet, yielding a value ~500 days. The radiation characteristics are very similar to those of the ~600-day lutetium formed in alpha-particle bombardments of thulium, but the methods of production indicate the occurrence of two distinct species. The ratios of the various radiations obtained from samples of the activity produced by decay of the 23.6-hour Hf^{173} and directly in the proton bombardment of lutetium are 0.1-Mev e^-: ~0.18-

[2] A. Flammersfeld and J. Mattauch, Naturwiss. 31, 66 (1943). J. Mattauch and A. Flammersfeld, Isotopic Report, Z. Naturforsch., Tubingen (1949).

[3] From the measurement of the beta-particle activities of the 3.7-hour Lu^{176} and 6.7-day Lu^{177} activities, the isotopic cross sections for (d, p) reactions of 19-Mev deuterons in Lu^{175} and Lu^{176} were estimated to be $3.4\pm 0.3\times 10^{-2}$ and $5.9\pm 0.4\times 10^{-2}$ barns, respectively. The higher value for the cross section of Lu^{176} may be due to the neutron binding energy of about 1 Mev higher for the odd neutron nucleus over the even neutron nucleus.

Mev e^-: L x-ray: K x-ray: ~0.22-Mev γ-ray: 0.8-Mev γ-ray = 0.3: ~0.01: ~0.8: 1: ~0.07: ~0.02.

4.0±0.1-hour Lu^{172}.—This activity was produced in all alpha-particle bombardments of thulium, but in highest yield at the lower bombarding energies indicating production of the (α, n) reaction. The hard particle radiation found in the aluminum absorption was shown to be a positron of maximum energy 1.2 Mev; sufficient activity was not available for good measurement of lead absorption, but the ratio of positrons to gamma-rays is about 1:2. The activity was also found in alpha-particle and proton bombardments of ytterium.

6.70±0.05 day Lu^{172}.—The decays of column-separated lutetium fractions from 10-Mev bombardments of ytterbium and low energy alpha-particle bombardments of thulium showed a half-life of about seven days, noticeably less than the half-life of the 8.5-day activity produced in 38-Mev alpha-particle bombardments of thulium. The hafnium activity of about five years half-life allocated to mass 172 has been found to have a lutetium daughter, the decay of which has been followed through over ten half-lives. The radiation characteristics agree well with those obtained for the activity produced in low energy alpha-particle bombardments of thulium, and it is fairly certain that the activities are due to the same isotope. The ratios of the various radiations of the 6.7-day activity are 0.13-Mev e^-: ~0.6-Mev e^-: L x-ray: K x-ray: 1.2-Mev γ-ray = ~0.2: ~0.01: ~0.5: 1: ~0.5.

8.5±0.2-day Lu^{171}.—In the 38-Mev alpha-particle bombardments this activity was observed through seven half-lives; in the lower energy bombardments, the half-life obtained was decidedly lower, undoubtedly due to the presence of the 6.7 day activity allocated to mass 173 and produced in the (α, n) reaction in thulium. While allocation to mass 171 is not certain only on the basis of yields in alpha-particle reactions in thulium, the isotope has been found to be produced by decay of a 16-hour Hf^{171} formed in proton bombardment of lutetium in highest yields at 50–60 Mev. Growth of the 1.7 day-Lu^{170} together with growth of the 8.5-day species was observed only in hafnium activities produced by 60 to 75-Mev protons on lutetium and hence, in view of the production of both isotopes in alpha-particle bombardments of thulium, allocation of the 8.5-day activity is made to mass 171. The aluminum absorptions of the radiations of the activities from Tm+α bombardments and from hafnium decays are identical. The ratios of the various radiations of the 8.5-day Lu^{171} are 0.17-Mev e^-: ~0.5-Mev e^-: L x-ray: K x-ray: 1.2-Mev γ-ray = ~0.05: ~0.005: ~0.5: 1: ~0.2.

~600-day Lu^{171}.—In all bombardments of thulium with alpha-particles, the column separated lutetium fractions contained a species decaying with a half-life of about 600 days. The decay has been followed as yet through only three years. The activities available, except those from a special long bombardment made to determine the radiation characteristics, were low, and the determination of yields was difficult. The yield of the 600-day activity in 38-Mev bombardments was about 0.2 that of the 8.5-day activity and appeared also to follow roughly the variation with bombarding energy to be expected for production by an $(\alpha, 2n)$ reaction. Provisional allocation is made to mass 171, making the 600-day activity isomeric with the 8.5-day Lu^{171}.

The radiation characteristics are very similar to those of the long-lived (~500-day) activity produced by decay of the 23.6-hour hafnium isotope which must be allocated to mass 173 from its method of production. The long-lived activity found in the lutetium fraction from spallation reactions in tantalum may be a mixture of long-lived isotopes (~500 day and ~600 day). The ratios of the various radiations of the ~600-day activity obtained from alpha-particle bombardments of thulium are ~0.1-Mev e^-: L x-ray: K x-ray: ~1-Mev γ-ray = ~0.2: ~0.8: 1: ~0.01.

1.7±0.1-day Lu^{170}.—This activity was observed in bombardments of thulium with alpha-particles of energy greater than about 30 Mev. It was also found in the decay of a short-lived hafnium parent (112-min Hf^{170}). Allocation to mass 170 thus seems fairly certain. The approximate ratios of the various radiations are ~0.1-Mev e^-: L x-ray: K x-ray: ~2.5-Mev γ-ray = ~0.3: ~0.5: 1: ~0.5. While the allocation of the 1.7-day activity to Lu^{170} is fairly certain, the yield of this isotope in the 38-Mev bombardment of thulium is only about 0.01 barn, a value much lower than that obtained for the $(\alpha, 3n)$ reaction in holmium.[1a] It is therefore possible that there exists a short-lived activity which is isomeric with the 1.7-day Lu^{170}.

III. HAFNIUM ISOTOPES

In addition to the 70 day Hf^{175} activity described previously,[4] the bombardments of ytterbium with 38- and 20-Mev alpha-particles and of lutetium with protons of 15- to 75-Mev energy have led to the recognition of four additional activities.

23.6±0.1 hour Hf^{173}.—In the bombardments of ytterbium with 20-Mev alpha-particles and of lutetium with 18- to 32-Mev protons from the linear accelerator, an activity of 23.6 hours half-life was obtained; the radiation characteristics were identical in both cases. In bombardments of ytterbium with 38-Mev alpha-particles the half-life obtained was somewhat shorter, which is undoubtedly due to the formation of the 16 hour Hf^{171} activity produced by $(\alpha, 3n)$ reactions in Yb^{170}; this shorter-lived activity would not be formed in the lower energy alpha-particle bombardments. The decay of 23.6 hour Hf^{173} has been followed through eight half-lives and the ratios of the radiations are: ~0.12 Mev e^-: ~0.22 Mev e^-: L x-ray: K x-ray: ~1 Mev γ-ray = ~0.3: ~0.02: ~0.3: 1: ~0.1. A search

[4] G. Wilkinson and H. G. Hicks, Phys. Rev. 75, 696 (1949).

for a short-lived lutetium daughter of this activity led to the conclusion that no Lu^{173} (isomeric with the $\sim$500 day Lu^{173} produced in the decay), is found with half-life between 1 minute and the $\sim$500 day Lu^{173}. Successive chemical separations of lutetium from hafnium activities produced in a long 30-Mev alpha-particle bombardment of ytterbium showed that the $\sim$500 day lutetium activity was formed as the daughter of the 23.6 hour hafnium.

$\sim$5 year Hf^{171}.—This activity has been found in the hafnium fractions from bombardments of ytterbium with alpha-particles, of lutetium with protons, and of tantalum with 190-Mev deuterons, after decay of the 70-day Hf^{174}. The decay has been followed for over two years, and the half-life appears to be about five years. The activity is the parent of a 6.70-day lutetium daughter; both the decay of the separated daughter and its growth in purified hafnium have been studied. No other daughter activities with half-lives greater than one minute have been observed. The $\sim$5-year activity decays predominantly by emission of x-radiation, only weak intensities of electrons and γ-rays being found; electron energies from a simple magnetic spectrometer correspond to the conversion of a 0.28-Mev γ-ray observed in lead absorption measurements. The ratios of the various radiations corrected for counting efficiencies, etc., are $\sim$0.23-Mev e^-: L x-ray: K x-ray: $\sim$0.28-Mev γ-ray: 0.8-Mev γ-ray $= \sim$0.05: $\sim$1:1: $\sim$0.06: $\sim$0.06. The x-ray intensities of the $\sim$5-year hafnium and the 6.70 day lutetium in secular equilibrium are in agreement with the assumption that the K x-radiation, corrected for contribution of x-rays arising from conversion, represents disintegration by orbital electron capture.

16.0±0.5-hour Hf^{171}.—In 38-Mev alpha-particle bombardments of ytterbium, a hafnium activity of $\sim$22-hours half-life was obtained and ascribed to a mixture of the 16.0-hour Hf^{171} and the 23.6-hour Hf^{173}. The apparent half-life was observed to be greater at lower bombarding energies. In bombardments of lutetium with protons of energy 40- to 70-Mev, chemical separation showed that a 16.0±0.5 hour hafnium activity was produced in maximum yield at about 50 Mev. Successive chemical separations of lutetium showed that the decay of the 16-hour activity formed the 8.5-day Lu^{171}. No lutetium activities of half-lives greater than about one minute, other than the 8.5-day Lu^{171}, could be detected; the decay of the 8.5-day daughter activity was followed through over eight half-lives. The ratios of the radiations of the 16-hour activity obtained from absorption measurements on a sample from 50-Mev proton bombardment of lutetium are 0.15-Mev e^-: L x-ray: K x-ray: 1.5-Mev γ-ray $= \sim$0.2: $\sim$1.5: 1: $\sim$0.3. The radiations are different from the 23.6-hour hafnium, but some contamination due to the latter is probable. In tantalum the yield of the $(p, 3n)$ reaction at 50 to 60 Mev was less than 0.1, that of the $(p, 5n)$ reaction and the situation for lutetium is probably similar.

112±2-min Hf^{170}.—The 112-min activity was found in bombardments of lutetium with protons of energy greater than about 60 Mev. The activity decays with emission of positrons of maximum energy 2.4 Mev which were studied through six half-lives on a simple magnetic spectrometer. No appreciable amount of electromagnetic radiation, other than annihilation radiation, was observed to decay with this half-life. The isotope most likely decays by positron emission without appreciable electron capture. The 16-hour hafnium activity was also formed in the bombardments up to the maximum of 75 Mev studied, and the chemically separated lutetium daughter activities showed the presence of the 8.5-day Lu^{171}. However, the initial daughter separations showed that about 90 percent of the gross lutetium activity was caused by the 1.7-day Lu^{170} and that the yield of this activity fell roughly corresponding to the decay of the 112-min hafnium. In view of the comparatively weak activities available, the parent-daughter relationship of the 112-min hafnium and the 1.7-day lutetium activities was not studied in greater detail.

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