

with the result that

$$\mu = 1/(x_2 - x_1) \{ \ln(I_1/I_2) - \ln(1+s_1)/(1+s_2) \}.$$

The values for s_1 and s_2 are calculated using the method described in reference 1 and 4. These scattered intensities include the coherent and Compton-scattered radiation and depend on the maximum angle of scatter in the absorber of a photon which can reach the detector. Values of $\ln(1+s_1)/(1+s_2)$ are given in Table I. These corrections were minimized experimentally by placing the absorber in the position which gave the largest effective absorption coefficient.

DISCUSSION

The results of this experiment using differential energy selection indicate very good agreement with theory when the absorption coefficient is maximized by appropriate positioning of the absorber.

As a result it seems likely that the present theoretical expression¹² for the photoelectric cross section is reliable near 1 Mev for heavy elements through $Z=74$ (wolfram).

The authors desire to thank Mr. R. A. Taylor for invaluable help with regard to electronic problems.

¹² Hulme, McDougall, Buckingham, and Fowler, Proc. Roy. Soc. (London) **A149**, 131 (1935).

New Isotopes of Niobium: Nb^{89} and $\text{Nb}^{89m}\dagger$

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(Received April 1, 1954)

A new 1.9 ± 0.3 -hour activity was found in niobium fractions isolated from proton irradiated niobium and zirconium metal foils. By identification of the 78-hour daughter activity, the mass assignment has been made to Nb^{89} . Evidence indicates that the decay is a simple positron emission of 2.9 ± 0.4 Mev maximum energy. Evidence was also obtained for the existence of the $\frac{1}{2}$ - isomeric state in Nb^{89} which decays with a 0.8 ± 0.3 -hour half-life by positron emission to the similar 4.4-minute state in Zr^{89} .

OBSERVATION of the niobium fraction obtained from ~ 60 -Mev proton bombardment of niobium metal in the internal beam of the Harvard synchrocyclotron indicated the presence of a new activity of approximately two-hour half-life. In order to identify and characterize this activity, niobium metal foils were irradiated for periods of 45–60 minutes with protons of maximum energy varying from ~ 50 Mev (roughly the threshold for the reaction) to ~ 75 Mev, and zirconium metal foils were bombarded for similar periods with protons of 40–45 Mev maximum energy.

After irradiation, the niobium target foils were dissolved in a mixture of nitric and hydrofluoric acids containing molybdenum, zirconium, and yttrium carriers. Zirconium was then separated from the solution as barium fluozirconate by the addition of barium ion, and this precipitation was repeated once or twice more. Upon dilution with water, yttrium fluoride also precipitated from the supernatant. After centrifugation, the niobium was precipitated with ammonia, washed, and dissolved in concentrated hydrochloric acid. This solution was made approximately $3M$ in HCl by first saturating with HCl gas and then diluting with the appropriate amount of water. Two extractions with tributyl phosphate removed the molybdenum, and the aqueous phase was again saturated with HCl gas. Niobium was then separated from residual zirconium

and yttrium by extraction from the HCl solution with diisopropyl ketone. The zirconium target foils were treated in a somewhat similar manner except that they were dissolved in hydrofluoric acid alone, the barium fluozirconate precipitation was done at least three times, and there was no necessity for the molybdenum extraction with tributyl phosphate.

Samples of the niobium fractions so obtained were followed on an end-window (3.5 mg/cm^2) Geiger counter, and resolution of the decay curves indicated a two-hour activity plus the known 14.7-hour Nb^{90} and longer activities. An aluminum absorption curve taken immediately after the chemical separation showed that the major particulate radiation seemed to consist of positrons of 2.9 ± 0.4 -Mev maximum energy. Counting samples of the niobium fraction through 620 or 571 mg/cm^2 of aluminum cut down the fraction of interfering activities (mainly Nb^{90}) and showed that these high energy positrons had a 1.9 ± 0.3 -hour decay. There was also a suggestion of a small amount of a shorter-lived activity. The decay of samples followed with a scintillation counter employing a well-type NaI(Tl) crystal gave a similar value for the half-life and indicated more strongly the possible presence of an additional gamma activity of just under one-hour half-life. An example of the decay curves obtained is shown in Fig. 1. Crude gamma integral pulse-height curves taken with the scintillation counter indicated a greater percentage of annihilation radiation associated

[†] This work was supported by the U. S. Atomic Energy Commission.

with the two-hour activity than with that of Nb⁹⁰, in fact, annihilation radiation seems to be the principal type of gamma associated with the former activity.

To determine the mass assignment of the new niobium activity and to confirm the value of the half-life, an effort was made to separate quantitatively the daughter activity at timed intervals, and then to follow the decay for identification. The parent-daughter separation was attempted at first by either precipitation of zirconium as the barium fluozirconate or extraction of the niobium into diisopropyl ketone. Neither of these methods is very satisfactory quantitatively, but both showed that there was an ~80-hour daughter activity and that the parent had a half-life between 1½ and 3½ hours. A much better separation technique makes use of the difference in behavior of hydrochloric acid solutions of niobium and zirconium on strong base anion resins; the former ions stick much more strongly than the latter.¹ Aliquots of the chemically purified niobium fractions were placed on Dowex-2 anion exchange resin columns and washed free of their zirconium and yttrium daughters with 7M HCl. At periodic intervals the daughters that have grown back into the parent fraction were separated by further elutions with small amounts of 7M HCl. Eight such sets of five to nine separations per set were done on samples from several bombardments, the time intervals used in a set varying from 30 minutes to two hours, and the yields of the daughter activities were followed in

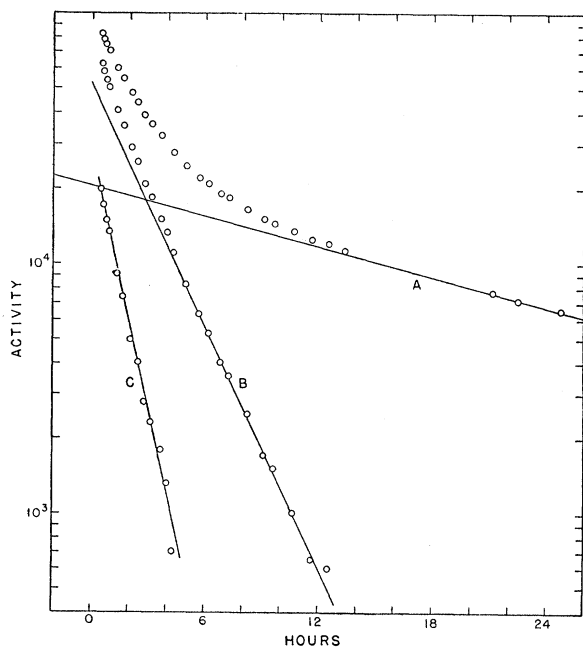


FIG. 1. Decay of niobium sample followed with a scintillation counter using a NaI(Tl) crystal. Curve A, resolution of 14.7-hour Nb⁹⁰. Curve B, resolution of 1.9-hour Nb⁸⁹. Curve C, resolution of 0.8-hour Nb⁸⁹.

¹ Huffman, Iddings, and Lilly, J. Am. Chem. Soc. **73**, 4474 (1951).

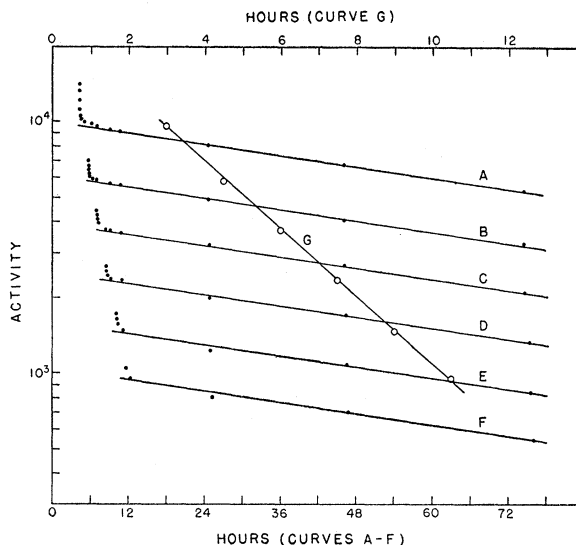


FIG. 2. Yield of Zr⁸⁹ and Zr^{89m} daughters at successive 1½-hour separations from niobium parent, curves A to F. Curve G is a plot of the yields of Zr⁸⁹ extrapolated to the times of separation, giving 2.2 hours for the half-life of Nb⁸⁹.

the scintillation counter. The result of a typical set of data is shown in Fig. 2 where the activity of the daughters is plotted against time. These curves are extrapolated back to the time of the parent-daughter separation, and the slope of a straight line drawn through these extrapolated points gives in the eight sets of data values for the half-life of the parent ranging between 1.8 and 2.4 hours. This is in good agreement with the value 1.9 ± 0.3 hours obtained from observation of the direct decay of the niobium fraction.

It was observed that after a small amount of short-lived activity died out, the daughter activities decayed with an ~80-hour half-life. This would have to be 78-hour Zr⁸⁹, or possibly 80-hour Y⁸⁷ formed through the chain Zr⁸⁷ $\xrightarrow{1.6 \text{ hr}}$ Y^{87m} $\xrightarrow{14 \text{ hr}}$ Y⁸⁷.² However, integral gamma pulse-height curves taken with the scintillation counter showed that the gamma radiation consisted of two groups of about one-half and somewhat less than one Mev energy which correspond to the annihilation radiation of Zr⁸⁹ and the 913-kev gamma of the 14-second Y^{89m} in equilibrium with it and not to the 485- and 390-kev gammas of Y⁸⁷ and Sr^{87m}.² This was confirmed by chemical separation of niobium, zirconium, and yttrium from samples of the daughter; the activity followed the zirconium fraction. Therefore, the parent nuclide must be Nb⁸⁹.³

² Hollander, Perlman, and Seaborg, Revs. Modern Phys. **25**, 469 (1953).

³ E. K. Hyde (private communication). Kofstad, Mathur, and Hyde have identified Zr⁸⁷ and Zr⁸⁹ by scintillation spectrometry in the zirconium milkings of niobium fractions isolated from high energy proton and helium ion bombardments of silver, zirconium, and yttrium targets. Independently of the present investigation and, in fact, previously, Levine and Hyde have observed an ~2 hour positron emitter of 3.0–3.2 Mev maximum energy in the niobium fraction from zirconium irradiated with 40–60 Mev protons.

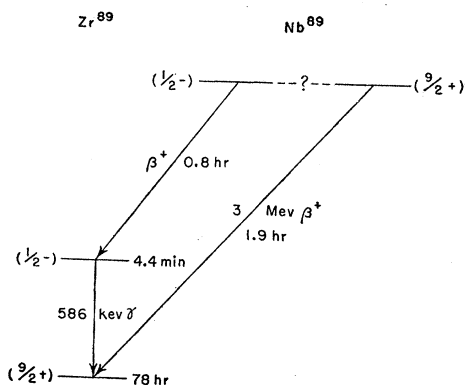


FIG. 3. Proposed decay scheme for Nb^{89} . It is not known which level in Nb^{89} is the excited state and what percent of its decay goes to the ground state.

There is a 4.4-minute isomeric state of Zr^{89} which might also be involved in the decay, and if it could be observed would certainly confirm the mass assignment to 89. As was mentioned above, a small amount of short-lived activity was indeed observed in the daughter activities, and by getting samples from the resin columns to the scintillation counter within 5–10 minutes of the start of the separation, the characteristic 4.4-minute decay of Zr^{89m} was easily resolvable from the 78-hour Zr^{89} .⁴ Investigation of the quantitative relationships between these decays however showed some anomalies. Making reasonable assumptions for the relative counting efficiencies of the 586-keV gamma of Zr^{89m} and of the radiations of Zr^{89} and the Y^{89m} in equilibrium with it showed that the amount of Zr^{89m} was too small by a factor of the order of 25 to account for all of the Zr^{89} . What is of greater significance is that this factor varied with the time since bombardment, becoming larger the longer the period of time. Analyses of six sets of 5–9 milkings apiece showed that the 4.4-minute Zr^{89m} was coming from a parent decaying with a 0.8 ± 0.3 -hour half-life, and hence independently of the two-hour Nb^{89} .

From consideration of the single-particle shell model of the nucleus,⁵ Nb^{89} would be expected to have either a $9/2+$ or a $1/2-$ ground state with the other spin level as a low-lying isomeric state. As has been pointed out by Goldhaber and Hill,⁶ the odd-mass niobium isotopes show a regular behavior in the pattern of these isomeric

states. The spacing between the $1/2-$ excited state and $9/2+$ ground state decreases with decreasing neutron number from 750 keV at Nb^{97} to a minimum of -105 keV (the $1/2-$ level actually lies the lower and is the ground state) at Nb^{91} which has a closed shell of 50 neutrons. Thereafter, the $1/2-$ level is expected to rise again so that at Nb^{89} the levels should be close and with either one possible as the ground state. The existence of this pair of isomeric states in Nb^{89} explains the observation of parents with differing half-lives decaying into Zr^{89} and Zr^{89m} . Furthermore, since these last nuclides are also a $9/2+$, $1/2-$ isomeric pair, one would not expect either of the niobium isomers to decay directly to both levels in zirconium, but only to the corresponding one, that is the $9/2+$ state in niobium to the $9/2+$ state in zirconium and the $1/2-$ state to the $1/2-$ state. The experimental results described above then indicate that the $9/2+$ to $9/2+$ transition to Zr^{89} has a 1.9-hour half-life and that the $1/2-$ to $1/2-$ decay to Zr^{89m} has a 0.8-hour period. The direct transition by positron emission from one of the isomeric states in niobium to the corresponding one in zirconium is an allowed transition with the transforming nucleon remaining in the same shell. Calculation of the $\log ft$ value for the 2.9-MeV positron of the predominant 1.9-hour transition gives 6.1,⁷ which is at the upper limit for an allowed transition but agrees with the value 6.0 for the similar $9/2+$ to $9/2+$ transition of Zr^{89} to Y^{89m} . Support for the idea of such direct transitions is furnished by the observation that the major gamma radiation associated with the decays seems to be annihilation radiation and by a calculation of the ground state to ground state disintegration energy.⁸ The result, 4 MeV, agrees with the observed 2.9 ± 0.4 MeV maximum energy of the positrons, suggesting the possibility of only low-energy gammas, which, however, are most unlikely considering the allowed nature of the positron transition.

A probable decay scheme is suggested in Fig. 3. With the equipment available, it was not possible to observe directly the decay of Nb^{89m} to Nb^{89} nor to determine the amount of this branching. Reasonable assumptions, though, indicate that the amount of decay by this path should be less than that by positron emission, so that although observation in the niobium fraction of a low-energy gamma or its conversion electrons decaying with either an hour or a two-hour half-life would help settle the decay scheme, it is probably a somewhat difficult problem.

It is a pleasure to acknowledge helpful discussions with Dr. E. K. Hyde.

⁴ E. K. Hyde (private communication). Mathur and Hyde have confirmed by scintillation spectrometry the presence of Zr^{89m} in the zirconium milkings of niobium fractions isolated from proton bombardment of niobium.

⁵ M. G. Mayer, Phys. Rev. **78**, 16 (1950).

⁶ M. Goldhaber and P. D. Hill, Revs. Modern Phys. **24**, 179 (1952).

⁷ S. A. Moszkowski, Phys. Rev. **82**, 35 (1951).

⁸ C. D. Coryell, Ann. Rev. Nuclear Sci. **2**, 305 (1953).