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RADIOCHEMICAL AND SPECTROMETER STUDIES OF SEVERAL NEUTRON-  
DEFICIENT ZIRCONIUM ISOTOPES AND THEIR DECAY PRODUCTS

Earl K. Hyde and Grover D. O'Kelley

December 28, 1950

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ABSTRACT

Radioactive zirconium isotopes of mass number  $< 90$  have been prepared by bombardment of niobium with 100 Mev protons. These isotopes and their decay products have been extensively studied in the beta ray spectrometer and by radiochemical methods.  $Zr^{87}$  is shown to be a  $94 \pm 6$  minute activity emitting positrons of  $2.10 \pm 0.02$  Mev energy and decaying into  $Y^{87m}$ . Accompanying its 14 hour decay into  $Y^{87}$ ,  $Y^{87m}$  has a complex gamma ray spectrum. The most prominent conversion electrons correspond to a  $0.389 \pm 0.004$  Mev gamma-ray.  $Y^{87}$  decays by orbital electron capture into  $Sr^{87m}$  which isotope decays by emission of a  $0.394 \pm 0.004$  Mev gamma-ray with a  $2.80 \pm 0.03$  hour half-life into stable  $Sr^{87}$ .  $Zr^{86}$  is a  $17 \pm 2$  hour orbital electron capturing isotope decaying into  $Y^{86}$  which in turn disintegrates into stable  $Sr^{86}$  with a half-life of  $14.6 \pm 0.2$  hours by the emission of positrons. This positron spectrum is complex, with two components of approximately equal intensity. The energies are  $1.80 \pm 0.02$  and  $1.19 \pm 0.02$  Mev. The latter appears to have a forbidden Fermi-Kurie plot corresponding to first forbidden transition with a spin change of two units and a change of parity.

The energy of the  $Zr^{89}$  positron is redetermined as  $0.910 \pm 0.010$  Mev. Conversion electrons corresponding to previously unreported gamma-rays of energy 0.027, 0.396, 0.917 and 1.27 Mev are observed. Preliminary evidence for  $Zr^{88}$  is presented which indicates that this isotope decays by the capture of orbital electrons with a half-life of the order of months into  $^{105}Y^{88}$ . Conversion electrons of 0.406 Mev gamma-ray are prominent in the decay of  $Zr^{88}$ .

#### INTRODUCTION

A number of the lighter neutron-deficient isotopes of zirconium have been prepared by bombarding high purity niobium metal with 100 Mev protons in the 184-inch synchrocyclotron. The lightest molybdenum and niobium isotopes produced by (p,xn) and (p,pxn) nuclear reactions decay quickly by orbital electron capture or positron emission to isotopes of zirconium. In addition, zirconium isotopes are produced directly by spallation reactions of the type  $Nb^{93}(p,2pxn)Zr^{93}$ . This is a convenient method of preparation of radioactive isotopes of zirconium of mass number 89 or less, free of interference from higher mass zirconium activities. The mass numbers of the stable isotopes of zirconium are 90, 91, 92, 94, and 96 so that the isotopes to be discussed all lie on the neutron deficient side of stability.

During the course of extensive radiochemical and spectrometer studies of the zirconium activities thus prepared and on their decay products, we have assembled information on the decay of  $Zr^{89}$ ,  $Zr^{88}$ ,  $Zr^{87}$ , and  $Zr^{86}$ . Much of this information is new; part of it is to be compared with the

previous work of others, with which it does not always agree. After a description of the chemical procedures employed, the detailed studies on each isotope are presented separately.

#### CHEMICAL SEPARATIONS

Thin strips of spectrographically pure niobium metal were bombarded for periods of from 5 to 20 minutes with 100 Mev protons in the 184-inch cyclotron. Such bombardments produced  $\sim 10^9$  disintegrations per minute of total zirconium activity. Numerous bombardments were carried out in the course of the research.

The niobium target foils were dissolved immediately by dropping them into a mixture of concentrated  $\text{HNO}_3$  and concentrated  $\text{HF}$ . Ten milligrams of lanthanum as lanthanum nitrate was added with stirring to precipitate  $\text{LaF}_3$ . All the zirconium activities in solution were co-precipitated with the  $\text{LaF}_3$  and cleanly separated from the niobium, a separation which has been studied by Ballou<sup>1</sup> and by Gest, Burges and Davies.<sup>2</sup> The co-separation is believed to be due to the surface adsorption of  $\text{ZrF}_6^{-2}$  ion on  $\text{LaF}_3$ . The  $\text{LaF}_3$  precipitate was contacted with strong  $\text{KOH}$  to metathesize the fluoride to the hydroxide compound.

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<sup>1</sup> N. Ballou, National Nuclear Energy Series, Plutonium Project Record, Vol. 9B, "Radiochemical Studies: The Fission Products," Paper No. 824.4 (McGraw-Hill Book Co., Inc., New York, N. Y., to be published 1951).

<sup>2</sup> H. Gest, W. H. Burges, and T. H. Davies, U. S. Atomic Energy Commission Declassified Document, AECD 2560 (April 18, 1949).

Then the hydroxide was dissolved in 2 M  $\text{HClO}_4$ . In order to scavenge out any traces of niobium which might remain, manganese dioxide was precipitated from the resulting solution by adding in turn  $\text{Mn}^{++}$  and  $\text{KMnO}_4$ .

The zirconium was extracted from the  $\text{HClO}_4$  solution by contacting it intimately for 15 minutes with an equal volume of a 0.2M solution of  $\alpha$ -thenoyltrifluoroacetone (hereinafter referred to as TTA) in benzene. Aluminum nitrate was added to the aqueous phase to complex any traces of fluoride ion which might remain from the metathesis step since fluoride ion interferes with the TTA extraction. The work of Connick and McVey<sup>3</sup> and of Huffman and Beaufait<sup>4</sup> was used as a guide in this purification step. The zirconium -TTA complex in benzene solution was thoroughly scrubbed of possible traces of extraneous activities by contact with 2M  $\text{HClO}_4$  wash solution. Then the benzene solution was diluted 10-fold and contacted with one tenth its volume of concentrated HCl to effect the return of the zirconium to an aqueous medium.

This zirconium fraction was quite pure both chemically and radioactively, but to be absolutely certain of its purity it was subjected to an additional purification step, capable in itself of effecting excellent decontamination from most other elements. The HCl solution was slowly passed through a short column (2cm x 4 mm) of Dowex -1 anion exchange resin\*

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\* Manufactured by Dow Chemical Company, Midland, Michigan; purchased from Microchemical Specialties Company, Berkeley, California

<sup>3</sup> R. E. Connick and W. H. McVey, J. Am. Chem. Soc. 71, 3182 (1949).

<sup>4</sup> E. H. Huffman and L. J. Beaufait, J. Am. Chem. Soc. 71, 3179 (1949).

which had been pre-equilibrated with concentrated HCl. Unpublished research results of this laboratory<sup>5</sup> have shown that from solutions 10M or higher in HCl concentration, negatively charged chloride complex ions of zirconium adsorb strongly on Dowex anion resin. From solutions of concentration less than 6M they do not adsorb. Niobium forms even stronger complexes but the other elements which could possibly be present are not adsorbed. Hence by passing the concentrated HCl solution through the resin column and rinsing it well with more concentrated HCl solution, the zirconium was quantitatively and cleanly adsorbed. The zirconium could be immediately desorbed by passing a 4M HCl solution through the column. In some experiments the zirconium activity was left on the column and periodically milked of its yttrium daughter activity by rinsing the column with 10-12M HCl at the proper time. The zirconium was retained quantitatively and the yttrium quantitatively removed by this step.

This isolation procedure has several advantages over some previous methods commonly used for radiochemical isolation of zirconium such as co-precipitation on barium fluozirconate. A principal one is that the zirconium is isolated in a carrier free state.

#### ZIRCONIUM 87

The decay scheme which best fits our information for  $Zr^{87}$  is presented in Fig. 1, while the detailed chemical and physical evidence on which it is based is presented below. The  $Y^{87m}$ ,  $Y^{87}$ , and  $Sr^{87m}$  isotopes were observed many years ago by DuBridge and Marshall,<sup>6</sup> who measured the

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<sup>5</sup> D. A. Orth and K. Street, Jr., preliminary report on unpublished work, University of California Radiation Laboratory Memorandum MB-IP-451 (1/27/50).

<sup>6</sup> L. A. DuBridge and J. Marshall, Phys. Rev. 58, 7 (1940).

decay constants and established the genetic relationship of  $\text{Sr}^{87\text{m}}$  to  $\text{Y}^{87}$ . They did not establish experimentally the relationship of  $\text{Y}^{87}$  to  $\text{Y}^{87\text{m}}$  but suggested it correctly. During the course of our investigation a report on  $\text{Zr}^{87}$  appeared by Robertson, Scott and Pool.<sup>7</sup> These authors prepared  $\text{Zr}^{87}$  by helium ion bombardment of separated strontium isotopes and reported it to be a  $2.0 \pm 0.1$  hour activity decaying by the emission of  $2.0 \pm 0.1$  Mev positrons and by emission of x-rays and gamma-rays.

#### Half-Life of $\text{Zr}^{87}$

The decay curve of the zirconium fraction followed through no absorber with an ordinary Geiger counter starting at a time about 1.5 hours after bombardment appears as in Fig. 2. Inspection of the curve indicates a prominent activity with a half-life of about 90 minutes but a reliable resolution of the curve is difficult because of the complexity of the mixture. The growth and decay of yttrium and strontium daughter activities is superimposed on the straight decay of 78 hour  $\text{Zr}^{89}$ , 17 hour  $\text{Zr}^{86}$ , and 94 minute  $\text{Zr}^{87}$ . The nature and energies of the radiations involved did not allow a simplification of the resolution by following the decay through properly selected absorbers. The half-life of  $\text{Zr}^{87}$  was measured by placing a sample in a high resolution beta ray spectrometer and following the decay of positrons of a specific energy in the high energy region.\* Other positron

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\*We wish to thank C. I. Browne, Jr. for assistance in this experiment.

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<sup>7</sup> B. E. Robertson, W. E. Scott, and M. L. Pool, Phys. Rev. 76, 1649 (1949).

activity was present (principally 0.910 Mev  $Zr^{89}$ ) but by choosing an energy beyond the  $Zr^{89}$  positron endpoint, the interference from it and from other causes was reduced to a minimum. A typical decay curve is shown in Fig. 3. The points shown have been corrected for the normal counter background of 38 counts per minute. As the result of several determinations we obtain a value of  $94 \pm 6$  minutes for the half-life. Our value is somewhat shorter than the  $120 \pm 6$  minute value found by Robertson et al.<sup>7</sup>

#### Energy of $Zr^{87}$ Positron

The positron spectrum of the zirconium fraction was run within a few hours after bombardment at a time when  $Zr^{87}$  was the predominant positron activity, the ratio of  $Zr^{87}$  to  $Zr^{89}$  being 4 to 1. A carrier-free sample was mounted on a thin tygon film ( $\approx 30 \mu\text{g}/\text{cm}^2$ ) onto which an extremely thin film of gold had been evaporated in vacuo. It was then possible to ground the source to the frame of the spectrometer by means of the aluminum holder and avoid source charging effects.

The 25cm radius of curvature beta ray spectrometer used in these investigations is of the double-focusing type proposed by Svartholm and Siegbahn<sup>8</sup> and by Shull and Dennison.<sup>9</sup> The focusing angle is  $\pi\sqrt{2}$  or approximately 255 degrees, and the inhomogeneous field varies approximately as  $1/\sqrt{r}$ . For a resolution of 1.3 percent, the theoretical transmission is about 1 percent; in practice the machine is usually baffled down, which reduces the transmission considerably.

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<sup>8</sup> N. Svartholm and K. Siegbahn, Arkiv. Mat. Astron. Fysik. 33A, No. 21 (1946); see also A. Hedgram, K. Siegbahn, and N. Svartholm, Proc. Phys. Soc. 63A, 960 (1950).

<sup>9</sup> F. Shull and D. Dennison, Phys. Rev. 71, 681 (1947) and 72, 256 (1947).

The spectrometer was calibrated with the conversion line<sup>10</sup> of Cs<sup>137</sup> and the calibration was checked by determining the energy of the P<sup>32</sup> beta particle. A value of  $1.685 \pm 0.01$  Mev was obtained in excellent agreement with recent values of others.<sup>11</sup> Our resolution was usually 1.5 percent with resolution defined for a monoenergetic electron as the full half-width of the electron line in momentum units divided by the momentum of the line and expressed in percent. Our electron detector was a Geiger tube filled to a regulated pressure of 8.8 cm with a 10 percent ethylene, 90 percent argon mixture. The tube window was a grid-supported formvar film of approximately 30  $\mu\text{g}$  per  $\text{cm}^2$  thickness. The magnet power supply was electronically regulated to better than 0.1 percent.

The Fermi-Kurie plot of the Zr<sup>87</sup>-Zr<sup>89</sup> mixture was resolvable into the  $2.10 \pm 0.02$  Mev component of Zr<sup>87</sup> and the  $0.910 \pm 0.010$  Mev component of Zr<sup>89</sup> and no others. The portion of the plot beyond the Zr<sup>89</sup> end point is shown in Fig. 4. Our value agrees with the value obtained by Robertson et al.<sup>7</sup> by aluminum absorption measurements within their experimental error.

An examination of the electron spectrum showed no prominent conversion electrons which could be assigned to Zr<sup>87</sup>, nor could evidence be found for Zr<sup>87</sup> gamma-radiation by lead absorption measurements on the freshly purified zirconium, but we are not able to set very low limits on the possible presence of unconverted gamma radiation. Robertson et al.<sup>7</sup> found

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<sup>10</sup> L. M. Langer and R. D. Moffatt, Phys. Rev. 78, 74 (1950).

<sup>11</sup> L. M. Langer and H. C. Price, Jr., Phys. Rev. 76, 641 (1949).

gamma-rays of 0.35 and 0.65 Mev energy and x-radiation accompanying the decay of  $Zr^{87}$ .

Identification of Decay Products of  $Zr^{87}$

If an yttrium fraction is milked from the purified zirconium by the HCl-anion exchange method outlined above within two or three hours after the bombardment, the yttrium fraction is nearly 100 percent  $Y^{87m}$  with a nearly undetectable trace of  $Y^{86}$  and  $Y^{88}$ . If the decay of this activity is followed with a thin window Geiger tube using no absorber, the resulting decay curve is as shown by the experimental points in Fig. 5. What is represented by this curve is principally the decay of 14 hour  $Y^{87m}$  and the growth and decay of the conversion electrons of the 2.80 hour  $Sr^{87m}$  granddaughter. The contribution to the counting rate of the gamma-radiation of  $Y^{87m}$  and  $Sr^{87m}$  and of the x-radiation of 80 hour  $Y^{87}$  is relatively small. Shown on Fig. 5 is a theoretical curve drawn for the case of a 14 hour parent decaying to an 80 hour daughter with undetectable radiation and a 2.80 hour granddaughter whose radiation is detected with the same efficiency as that of its grandparent. It is seen that the experimental points follow the theoretical curve except for a leveling off on a line 18 percent below the theoretical curve. This difference may be attributed to a difference in the conversion coefficients of the 0.389 Mev gamma-ray of  $Y^{87m}$  and the 0.394 Mev gamma-ray of  $Sr^{87m}$ , the latter being slightly lower.

Convincing auxiliary proof that the decay chain is as represented by Fig. 1 was obtained by establishing that the growth and decay of the  $Sr^{87m}$  nuclide occurred quantitatively as indicated. A pure sample of  $Y^{87m}$

was prepared as described in the last experiment and at intervals of many hours the  $\text{Sr}^{87\text{m}}$ , which was in transient equilibrium with it, was isolated and measured with a Geiger counter.

The chemical procedure was the following. One milligram of yttrium and of strontium were added to the  $\text{Y}^{87\text{m}}$  solution in 1 ml of dilute HCl. Then 0.5 ml of a solution of 8-hydroxy quinoline (660 mg dissolved in 50 ml acetone and diluted to 200 ml with water) was added. Yttrium 8-hydroxy quinolate was precipitated by adding concentrated  $\text{NH}_4\text{OH}$  dropwise until the precipitate just failed to redissolve. After the precipitate was heated in boiling water five minutes, centrifuged and separated, it was redissolved in dilute HCl and set aside until the time of the next milking. To the original supernate four drops of saturated sodium oxalate solution were added, followed by one drop of dilute ammonia to precipitate strontium oxalate. This precipitate was evaporated on a platinum disc and counted. In several cases the decay of the strontium sample activity was followed to establish the identity of the activity. All counts were taken on the same counter using identical conditions and the counts were extrapolated back to the time of separation from yttrium. This chemical procedure is based on one given by DuBridge and Marshall.<sup>6</sup>

Ten milkings were carried out on three separate samples. The results for one sample are shown in Fig. 6. The crosses are the experimental points. The line is the theoretical growth and decay curve for a 2.80 hour granddaughter of an initially pure 14 hour parent when the daughter half-life is 80 hours. It is concluded that the genetic relationships are correctly stated in Fig. 1.

### Half-Life of Sr<sup>87m</sup>

In one of the strontium separations discussed in the last section an active sample was carefully repurified from any trace of yttrium activity and its decay followed down to background in a chlorine filled Geiger tube. From the resulting curve shown in Fig. 7, a half-life of  $2.80 \pm 0.03$  is determined in excellent agreement with the recent results of Mann and Axel.<sup>12</sup>

### Parent Daughter Relationships of Zr<sup>87</sup> - Y<sup>87m</sup>

This relationship was established in an experiment which also served to measure the half-life of Zr<sup>86</sup>. Three hours after bombardment a purified zirconium fraction was adsorbed on a short Dowex-1 resin column from concentrated HCl solution. A constant slow flow of pure concentrated HCl was maintained through the column. Under the conditions used no detectable amount of zirconium activity stripped off the column while the yttrium daughter activity appeared in the elutriant solution as soon as it was formed. The amount of yttrium activity appearing in a definite period of time was determined at frequent intervals by counting the activity under standardized conditions. The samples were counted within a half-hour of the time the yttrium was formed. In the early samples the predominant activity was 14 hour Y<sup>87m</sup> identified by the conversion electron of the 0.389 Mev gamma ray and by its half-life, but as its 94 minute parent Zr<sup>87</sup> disappeared, the percentage of 14.6 hour Y<sup>86</sup>, identified by its positron radiation, steadily rose. This gave rise to the two component curve seen in Fig. 8 where the initial counts of yttrium activity collected in a standardized time interval are plotted against time. This curve

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<sup>12</sup> L. G. Mann and P. Axel, Phys. Rev. 80, 759 (1950).

may be resolved into a 16.8 hour component representing  $Zr^{86}$ , which we round off to  $17 \pm 2$  hours, and an 85 minute component representing  $Zr^{87}$  within the rather large error of the experiment.

The Radiations of  $Y^{87m}$ ,  $Y^{87}$  and  $Sr^{87m}$

Weightless samples of  $Y^{87m}$  freshly isolated from the  $Zr^{87}$  parent were mounted on thin tygon films ( $< 30 \mu\text{g}/\text{cm}^2$ ) and examined in the spectrometer. The most prominent radiations were the conversion electrons (See Fig. 9) of the 0.389 Mev gamma ray. The energy was determined by extrapolating the leading edge of the line. The K/L ratio was  $8.3 \pm 0.5$ . Both the K/L ratio and the half-life suggest electric  $2^5$  pole radiation.

Mann and Axel<sup>12</sup> report the much lower value of 0.374 Mev for this gamma ray. Furthermore, they state that in only 50 percent of its disintegrations does  $Y^{87m}$  decay by isomeric transition to  $Y^{87}$ , while in half the disintegrations,  $Y^{87m}$  decays to  $Sr^{87m}$  directly. They place their 0.374 Mev gamma-ray in this latter transition. We find it difficult to fit our experimental results to this decay scheme.

Robertson et al.<sup>13</sup> report that 14 hour  $Y^{87m}$  decays by positron emission and not by isomeric transition to  $Y^{87}$  and state that  $Y^{87m}$  and  $Y^{87}$  decay independently to  $Sr^{87m}$ . From the evidence given in the present paper this clearly cannot be the case. Possibly what Robertson and co-workers were measuring was the 14.6 hour yttrium activity which we have assigned to  $Y^{86}$  (see below), which in their bombardments would have appeared through the  $Sr^{84}(\alpha, pn)Y^{86}$  reaction.

As the  $Y^{87m}$  conversion electrons decay out, the conversion electrons of the  $Sr^{87m}$  granddaughter grow in as shown by the plots in Fig. 10.

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<sup>13</sup> B. E. Robertson, W. E. Scott, and M. L. Pool, Phys. Rev. 78, 318 (1950).

Figs. 9 and 10 represent the same sample examined approximately 3 hours, 28 hours, and 45 hours after preparation of a pure  $Y^{87m}$  sample. The  $Sr^{87m}$  gamma-ray energy is  $0.394 \pm 0.004$  Mev. The K/L ratio is 7.2 which, within our experimental error, is in agreement with Mann and Axel's<sup>12</sup> value, 6.9. The K-line of the  $Sr^{87m}$  gamma-ray falls between the K and L lines of the  $Y^{87m}$  gamma-ray.

Our value for the  $Sr^{87m}$  gamma-ray energy may be compared to Helmholtz's<sup>14</sup> 1941 value of 0.386 and to Mann and Axel's<sup>12</sup> recent value of 0.390 Mev.

Within experimental error, the area under the  $Y^{87m}$  K-line peak decayed with the proper 14 hour half-life while the sum of the areas under all four peaks decayed in a manner similar to the experimental points of Fig. 5 thus indicating that the observed conversion lines are correctly assigned.

In addition to these prominent lines, an examination of the electron spectrum of freshly prepared  $Y^{87m}$  showed six conversion electron lines in the region above 1 Mev.

No detailed study has yet been made of these electrons but they decayed with a 14 hour half-life. Auger electrons were observed but not studied. No negative beta particles were observed, and the total number of positrons was  $< 0.001$  times the number of conversion electrons. No conversion electrons beyond the Auger region were observed for the 80 hour  $Y^{87}$  or the  $Sr^{87m}$  except the  $Sr^{87m}$  lines already discussed.

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<sup>14</sup>A. C. Helmholtz, Phys. Rev. 60, 422 (1941).

Lead absorption curves were determined on these isotopes to obtain evidence supplementary to the spectrometer results. A lead absorption curve on a sample of  $Y^{87m}$  is shown in Fig. 11. Another curve for a sample of  $Y^{87}$  in equilibrium with its daughter  $Sr^{87m}$  but nearly free of  $Y^{87m}$  is shown in the same figure. Figure 11 shows that considerable hard gamma-radiation of energy  $>1.0$  Mev accompanies the decay of  $Y^{87m}$ , but is not present in the decay of  $Y^{87}$  of  $Sr^{87m}$  which supports the assignment of the group of energetic conversion electrons mentioned above to  $Y^{87m}$ . The gamma ray component of the lower curve is believed to represent the 0.394 Mev gamma ray of  $Sr^{87m}$ . Robertson et al.<sup>13</sup> report conversion electrons of a 0.5 Mev gamma-ray of  $Sr^{87m}$  and Mann and Axel report that the K-capture decay of 80 hour  $Y^{87}$  is immediately followed by emission of a 0.485 Mev gamma ray. We failed to see these conversion electrons in our spectrometer studies, but the conversion coefficient measured by these authors is small enough that we could have overlooked them. If this 0.485 Mev gamma-ray is correctly assigned, the absorption curve of Fig. 11 represents a 1/1 mixture of a 0.485 and a 0.394 Mev gamma ray.

#### YTTRIUM 86

When a purified zirconium fraction was allowed to decay for 24 hours after bombardment and then stripped of its yttrium daughters, no more of the mass 87 chain daughters were formed. If a fresh yttrium fraction was then separated after a few hours or a day or two, considerable positron activity was found. The activity decayed as shown in Fig. 12 with a half-life

of  $14.6 \pm 0.2$  hours. The small amount of long-lived activity amounting to  $< 0.1$  percent of the initial counting rate is  $Y^{88}$ . A lead absorption curve was determined, and it was found that a 1.4 Mev gamma ray accompanies the decay as shown in Fig. 13. This yttrium activity was identical to an yttrium isotope discovered by S. V. Castner<sup>15</sup> in bombardments of strontium isotopes and assigned by him to mass number 86. Castner found through relative yields of this nuclide from bombardments of strontium isotopes of different isotopic enrichments with proton beams of differing energies that the most probable mass assignment was 86, but this is not certain.

A carrier-free sample of this activity was studied in the spectrometer with interesting results. A Fermi-Kurie plot of the positron spectrum corrected for instrumental distortion according to Owen and Primakoff<sup>16</sup> is shown in Fig. 14. Two components are present in about equal intensity, with maximum energies of  $1.80 \pm 0.02$  Mev and  $1.19 \pm 0.02$  Mev. There are not sufficient data on the high energy component to establish any deviation from linearity, but the low energy group appears to be forbidden. The comparative half-life of the low energy positron ( $ft \sim 10^6$ ) indicates a first forbidden transition, while the spectral shape suggests a spin change of two units and a change of parity. According to the theory of forbidden spectra<sup>17,18</sup> dividing the ordinates of the plot of the low energy component in Fig. 14 by  $a^{1/2}$  should

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<sup>15</sup> S. V. Castner, unpublished results.

<sup>16</sup> G. E. Owen and H. Primakoff, Phys. Rev. 74, 1406 (1948).

<sup>17</sup> E. J. Konopinski and G. E. Uhlenbeck, Phys. Rev. 60, 308 (1941).

<sup>18</sup> E. J. Konopinski, Rev. Mod. Phys. 15, 209 (1943).

yield a straight line if the transition is of this type. The factor  $a = (\epsilon^2 - 1) + (\epsilon_0 - \epsilon)^2$ , with  $\epsilon$  the energy in units of  $m_0c^2$ , arises from the unique energy dependence of this transition. Fig. 14 shows such a corrected plot, and it is seen that a straight line does indeed result.

The factor  $C = (\epsilon^2 - 1)^2 + (10/3)(\epsilon^2 - 1)(\epsilon_0 - \epsilon)^2 + (\epsilon_0 - \epsilon)^4$  gave a poor fit. Conformity to this factor would have indicated a second forbidden transition with a spin change of 3 units and no change in parity.

Internal conversion lines were sought, but none were seen. However, the samples were of comparatively low intensity, and the presence of gamma radiation other than the hard 1.4 Mev gamma ray cannot be ruled out.

#### ZIRCONIUM 89

The previously reported<sup>6,19</sup> 78-80 hour nuclide,  $Zr^{89}$ , was the prominent activity in our zirconium fractions when repurified several days after bombardment. By this time the other zirconium activities had decayed out with the exception of  $Zr^{88}$ , discussed below, which because of its long half-life and inefficiently counted x-radiation contributed only a few percent to the total radiation at this time. A decay curve for such a zirconium sample counted in a chlorine filled Geiger tube through no absorber is shown in Fig. 15. The long-lived component is  $Zr^{88}$ ; the 77 hour component is  $Zr^{89}$ .

Carrier-free samples of this activity mounted on thin tygon films were examined in the spectrometer. The  $Zr^{89}$  positron energy redetermined by a Fermi-Kurie plot of our data gave a value of  $0.910 \pm 0.010$  Mev. Our new value is somewhat lower than the value of 1.07 Mev determined by

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<sup>19</sup> R. Overstreet, L. J. Jacobson, and J. G. Hamilton, as reported in Manhattan Project Metallurgical Laboratory Report CH-498 (February 15, 1943).

Overstreet, Jacobson and Hamilton<sup>16</sup> by aluminum absorption.

The original communication<sup>6</sup> on Zr<sup>89</sup> stated that no gamma radiation accompanied its decay; however, we observed four groups of conversion electrons. The high energy groups corresponding to <sup>gamma</sup>energies of  $0.396 \pm 0.004$ ,  $0.917 \pm 0.005$  and  $1.27 \pm 0.01$  Mev are shown in Fig. 19. It was established that they decayed at the proper rate to be assigned to Zr<sup>89</sup>. In addition K and L conversion electrons corresponding to a gamma-ray of  $0.027 \pm 0.001$  Mev and Auger electrons were observed. It is apparent that the decay scheme of Zr<sup>89</sup> is complex. A lead absorption curve shown in Fig. 17 corroborated the presence of hard gamma radiation and the decay of this radiation through 5.8 grams per cm<sup>2</sup> lead absorber plotted on Fig. 15 followed the Zr<sup>89</sup> half-life.

#### ZIRCONIUM 86

The parent of the 14.6 hour Y<sup>86</sup> was looked for but no clear cut direct evidence for its radiations could be found. This in itself is good evidence that Zr<sup>86</sup> is an orbital electron capturing nuclide. Positron activity would have contributed a prominent component to the gross decay shown in Fig. 2 and in particular would have been seen in the many zirconium samples studied in the spectrometer during the course of this work. It seems clear then that this isotope decays predominantly by orbital electron capture and that its inefficiently counted x-rays are unobserved in the presence of interfering Zr<sup>89</sup> and Zr<sup>87</sup> activity. Its half-life was determined indirectly in the manner discussed above and presented in Fig. 8, namely, by determining the amount of Y<sup>86</sup> formed in the zirconium fraction as a function of time.

## ZIRCONIUM 88

Zirconium fractions repurified months after bombardment still retained considerable radioactivity. This activity was found to consist of x-radiation, gamma-radiation, and conversion electrons. The x-rays were identified as yttrium x-rays by analyzing them with a proportional counter coupled to a multi-channel differential pulse analyzer, a technique described by Hanna, Kirkwood, and Pontecorvo.<sup>20</sup> The conversion electrons were measured in our spectrometer and the gamma ray energy was determined to be  $0.406 \pm .004$  Mev. The mass assignment of 88 is made on the basis of the isolation of the  $Y^{88}$  daughter identified by its 105 day half-life and by its x- and gamma-radiation. The half-life of  $Zr^{88}$  is of the order of a month. These results on  $Zr^{88}$  are only preliminary.

## ACKNOWLEDGMENTS

The authors wish to express their thanks to James T. Vale, Lloyd Houser and members of the 184-inch cyclotron crew for carrying out the numerous bombardments. This work was carried out under the auspices of the Atomic Energy Commission.

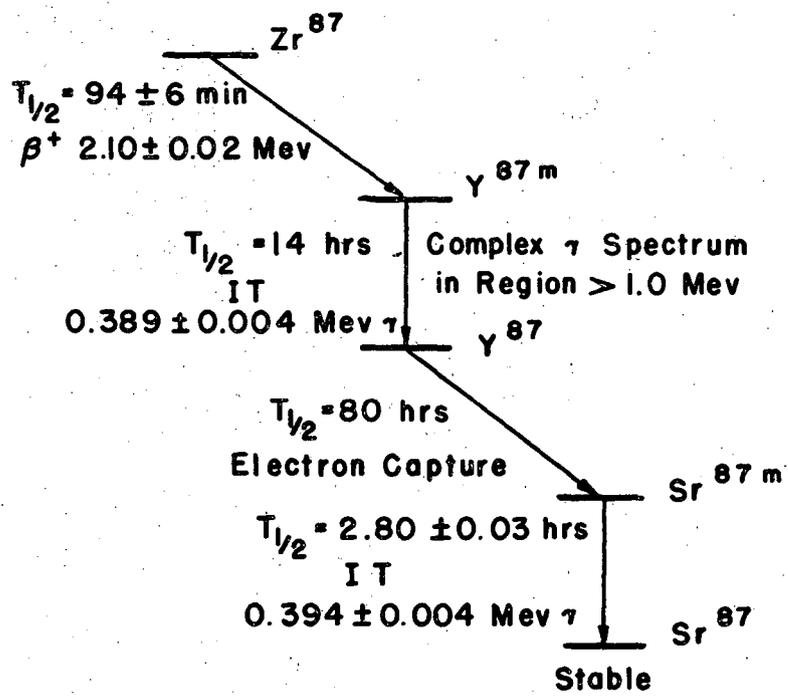
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<sup>20</sup> G. C. Hanna, D. H. W. Kirkwood, and B. Pontecorvo, Phys. Rev. 75, 985 (1950).

## FIGURE CAPTIONS

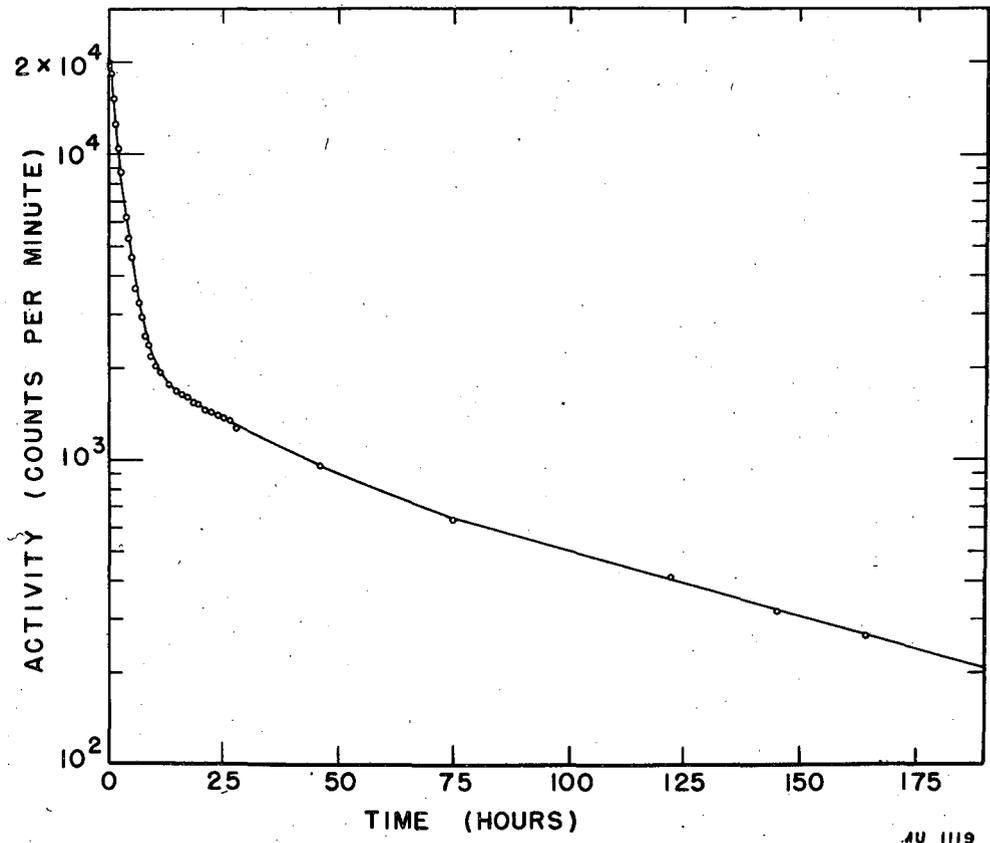
- Fig. 1 Decay Scheme of  $Zr^{87}$
- Fig. 2 Gross no-absorber decay of radioactivity in zirconium fraction starting 1.5 hours after bombardment
- Fig. 3 Half-life of  $Zr^{87}$  determined by measuring decay of monoenergetic positrons of 1.47 Mev in spectrometer
- Fig. 4 Fermi-Kurie plot of high energy part of  $Zr^{87}$  positron spectrum
- Fig. 5 Decay of an initially pure  $Y^{87m}$  sample. Points and dotted line are experimental. Solid curve is the theoretical decay of an initially pure 14 hour activity decaying to an 80 hour daughter and a 2.8 hour granddaughter when the parent and granddaughter activities are assumed to count with equal efficiencies and the radiation of the daughter is undetected.
- Fig. 6 Growth and decay of  $Sr^{87m}$  is an initially pure sample of  $Y^{87m}$ . Points are experimental. Line is theoretical curve for growth of 2.8 hour granddaughter of an initially pure 14 hour activity and its 80 hour daughter.
- Fig. 7 Half-life of  $Sr^{87m}$
- Fig. 8 The rate of formation of yttrium daughter activity in the zirconium fraction as a function of time, starting three hours after bombardment. Resolution of shorter-lived component plotted on expanded time scale in insert. Resolved components represent half-lives of  $Zr^{86}$  and  $Zr^{87}$ .
- Fig. 9 The conversion electrons of the 0.389 Mev gamma-ray of  $Y^{87m}$
- Fig. 10 The conversion electron spectrum 28 hours and 46 hours after preparation of pure  $Y^{87m}$  sample showing growth of conversion electrons of 0.394 Mev gamma-ray of  $Sr^{87m}$ .
- Fig. 11 Lead absorption curve on  $Y^{87m}$  (no  $Y^{87}$  or  $Sr^{87m}$  present) and on an equilibrium mixture of  $Y^{87}$  and  $Sr^{87m}$  (no  $Y^{87m}$  present). Samples mounted on platinum 3.6 cm from the window of commercial chlorine filled amperex Geiger tube, housed in aluminum-lined lead shield. 0.94 gms per  $cm^2$  beryllium absorber immediately below window. Lead absorbers immediately below beryllium.
- Fig. 12 Half-life of  $Y^{86}$
- Fig. 13 Lead absorption curve on  $Y^{86}$ . Conditions equivalent to Fig. 11.

- Fig. 14 Fermi-Kurie plot of positron spectrum of  $Y^{86}$ . The plot having ordinates  $(M/I^2F)^{1/2}$  is the unresolved curve after a small instrumental distortion correction. The plot of  $(M-M'/I^2F)^{1/2}$  is the resolved low energy group, and the curve with ordinates  $(M-M'/aI^2F)^{1/2}$  has been corrected as explained in the text.
- Fig. 15 Decay of  $Zr^{89}$  is a sample repurified one week after bombardment through no absorber and through 5.8 grams per  $cm^2$  lead absorber. Long-lived background is  $Zr^{88}$ .
- Fig. 16 Conversion electrons of  $Zr^{89}$
- Fig. 17 Lead absorption curve for  $Zr^{89}$ . Sample mounted on platinum was 5.2 cm away from end window Geiger tube filled with argon-alcohol mixture. 1.9 grams beryllium absorber immediately below counter window. Lead absorbers immediately above sample. One half-inch lead around tube. Tube and sample unboxed.



MU 1184

Fig. 1



AU 1119

Fig. 2

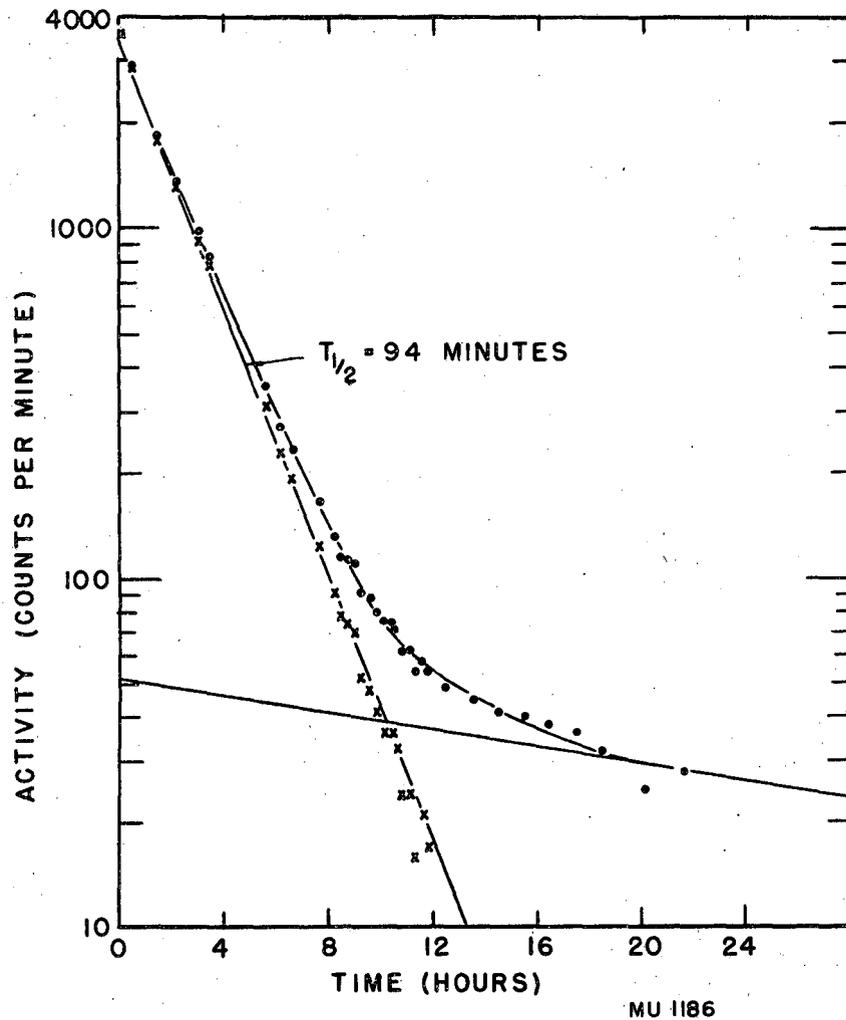


Fig. 3

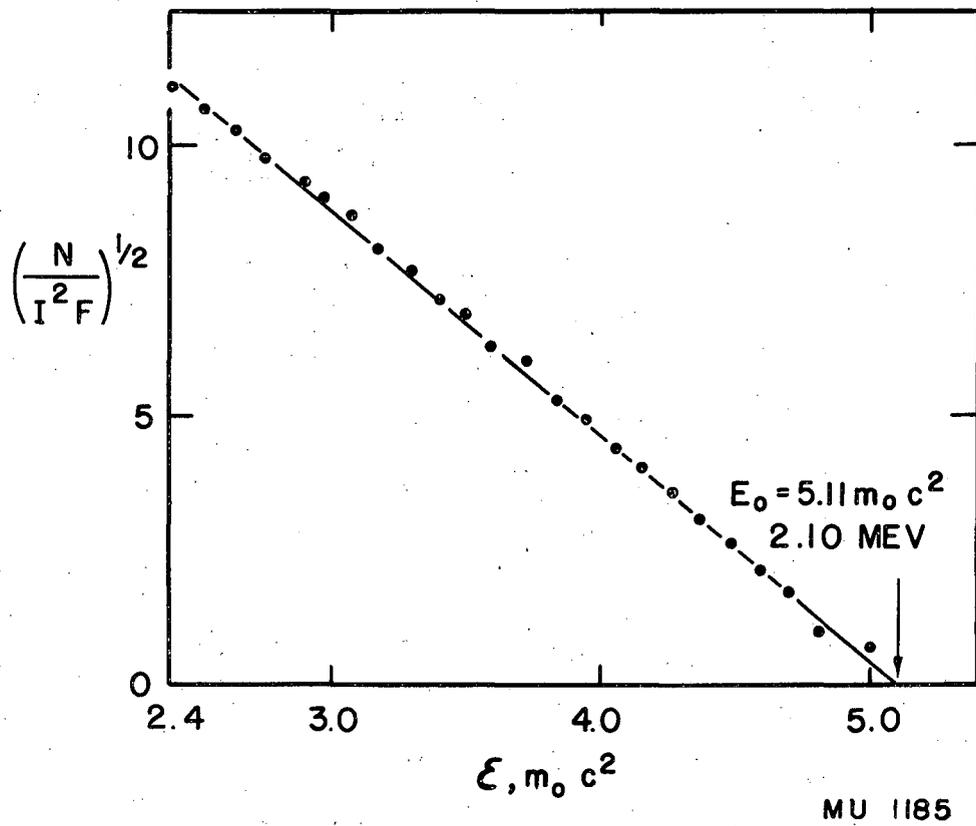
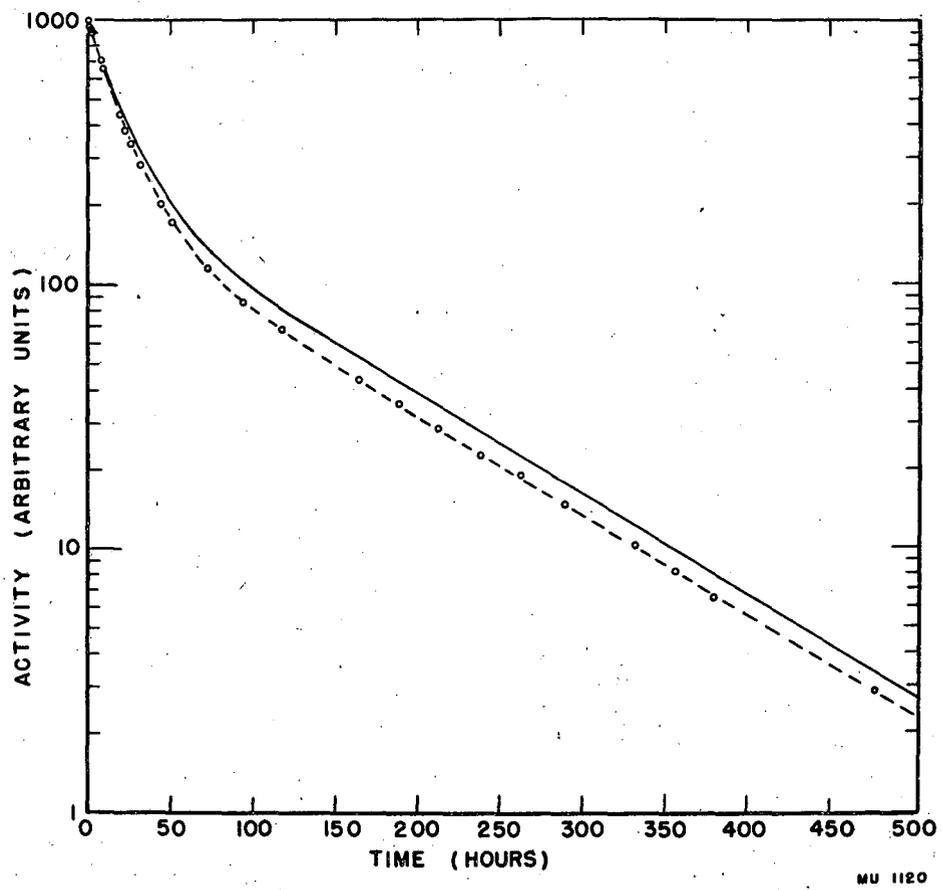


Fig. 4



MU 1120

Fig. 5

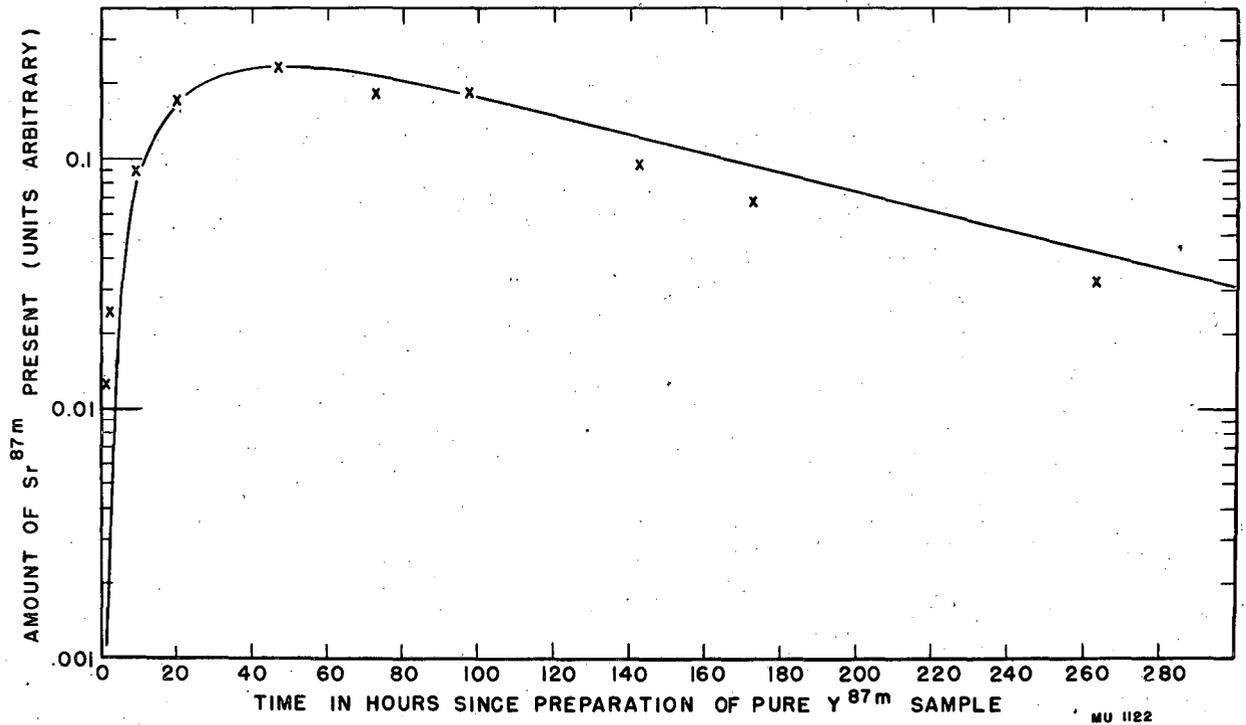


Fig. 6

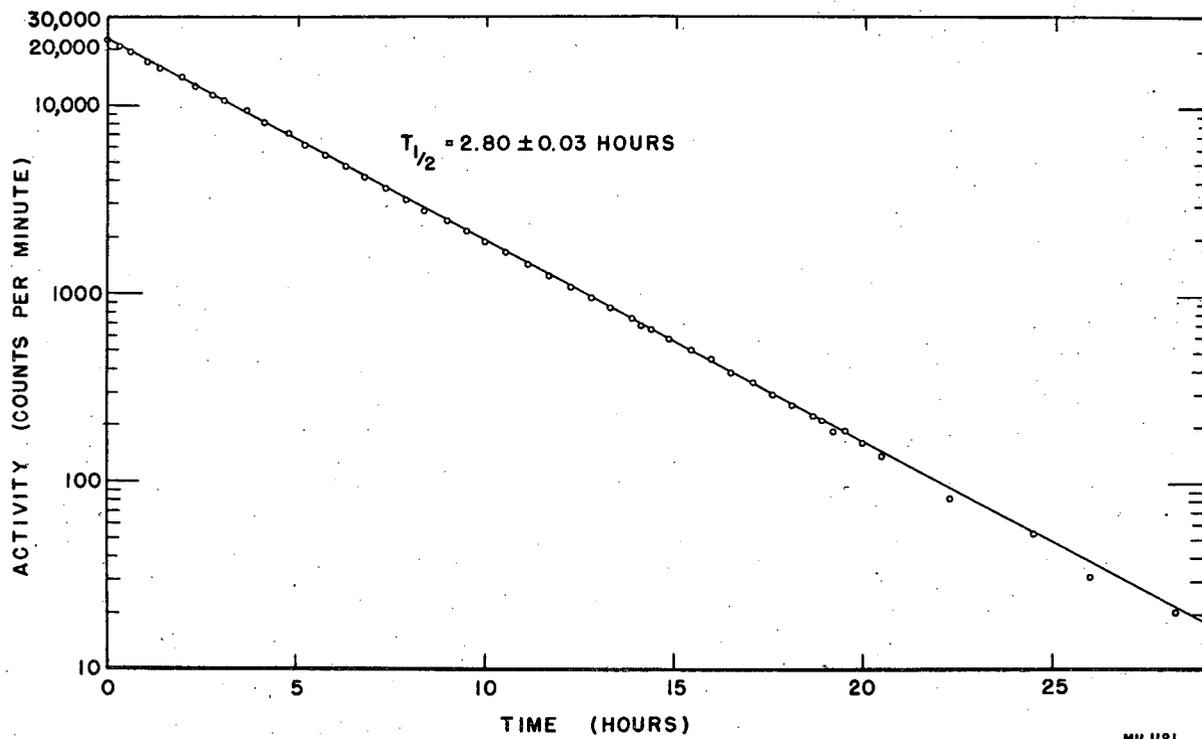


Fig. 7

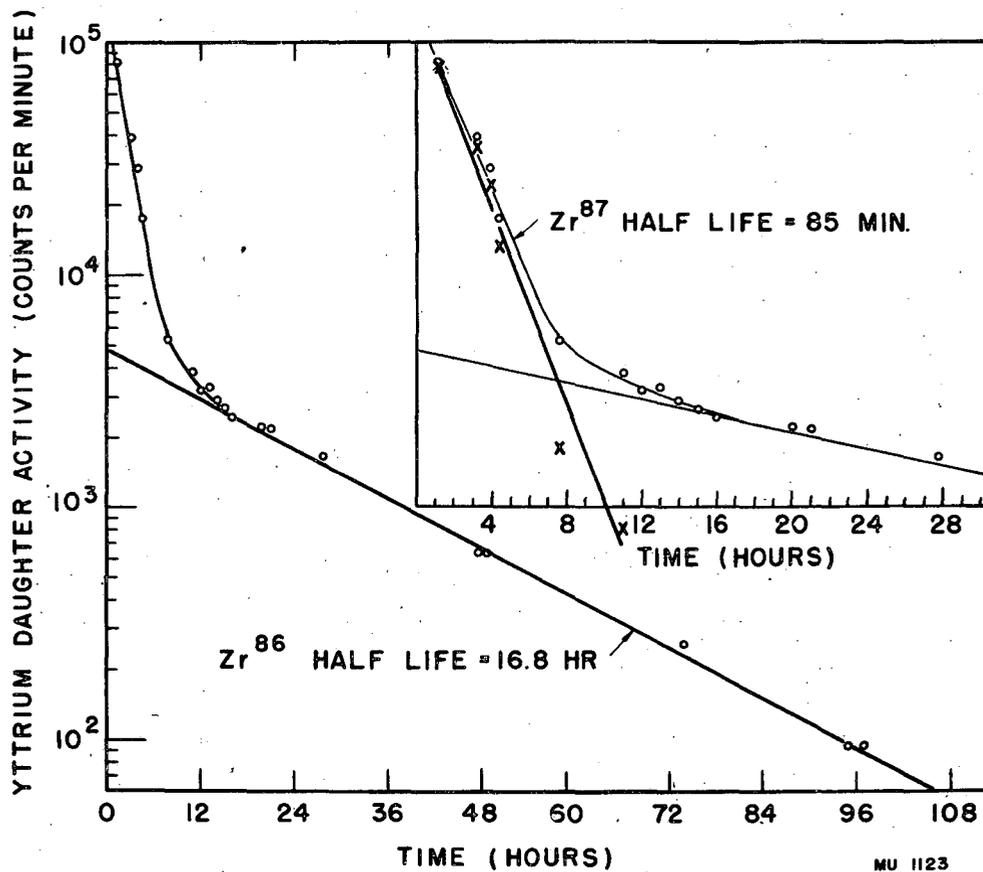


Fig. 8

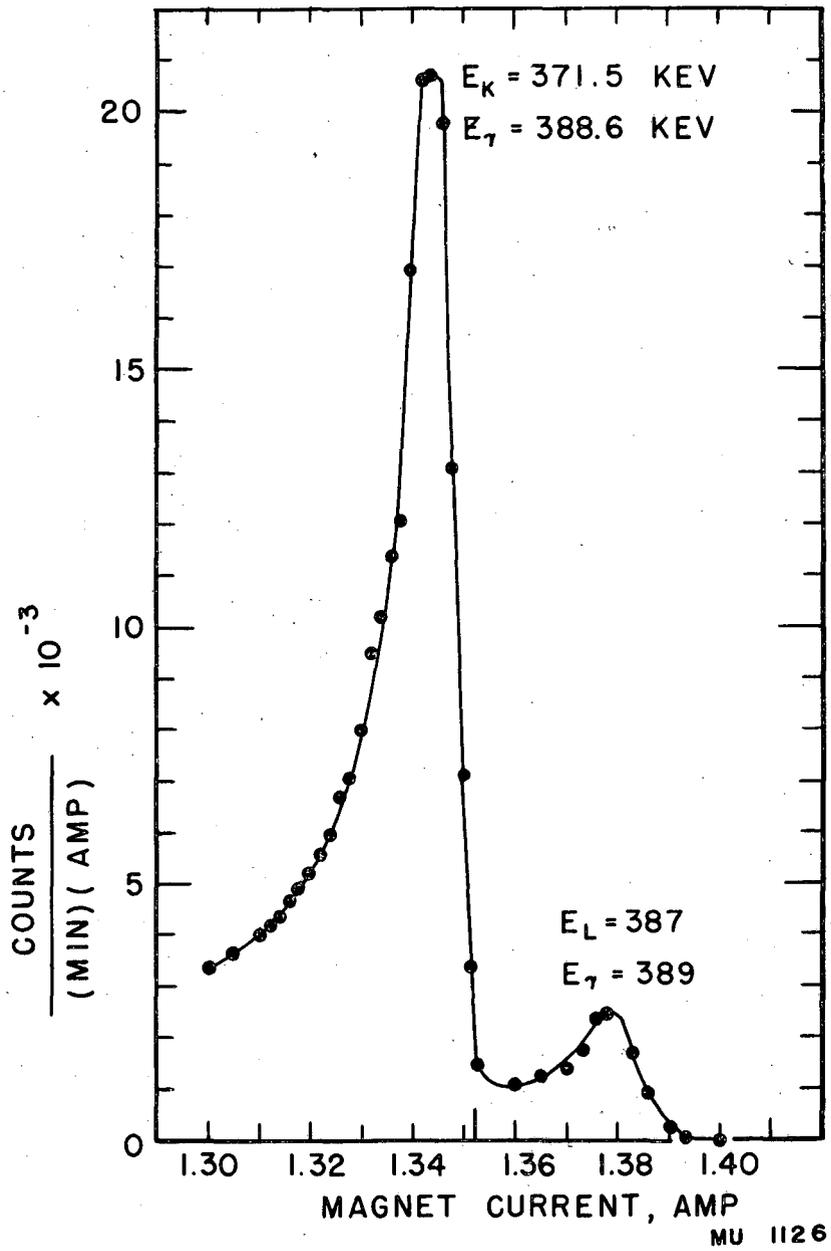


Fig. 9

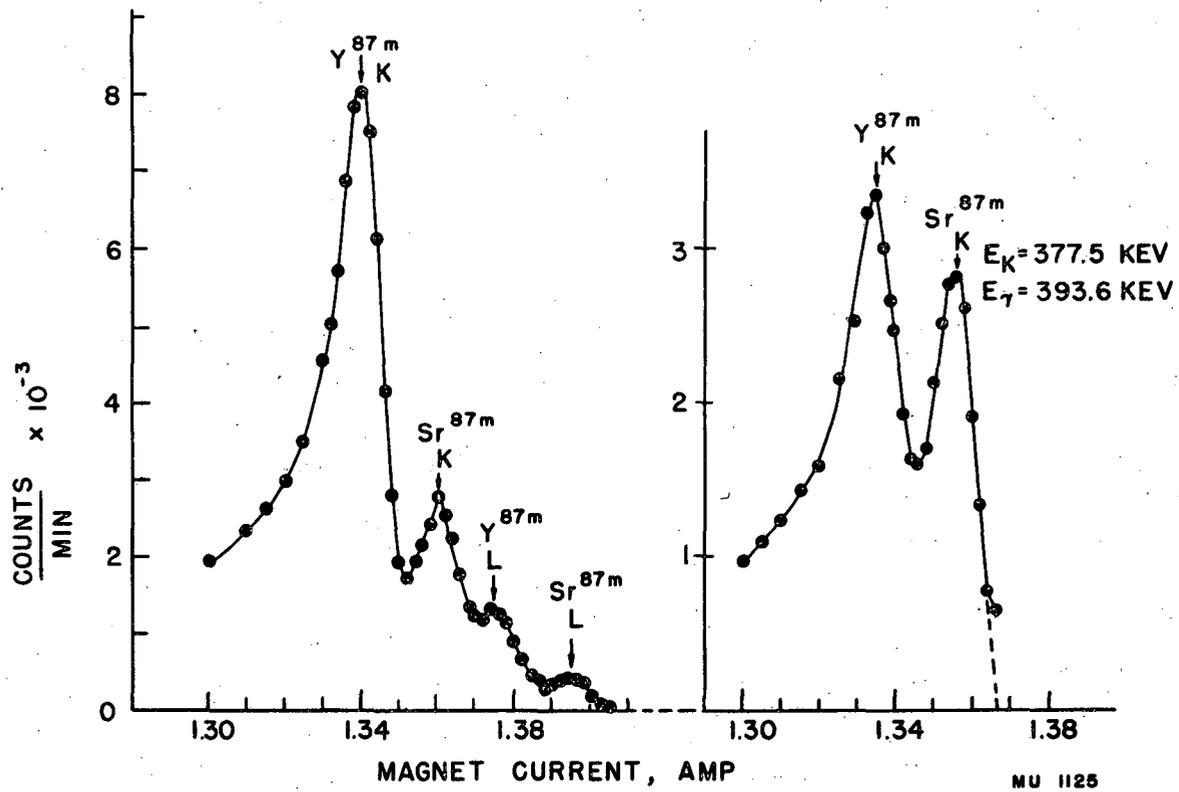
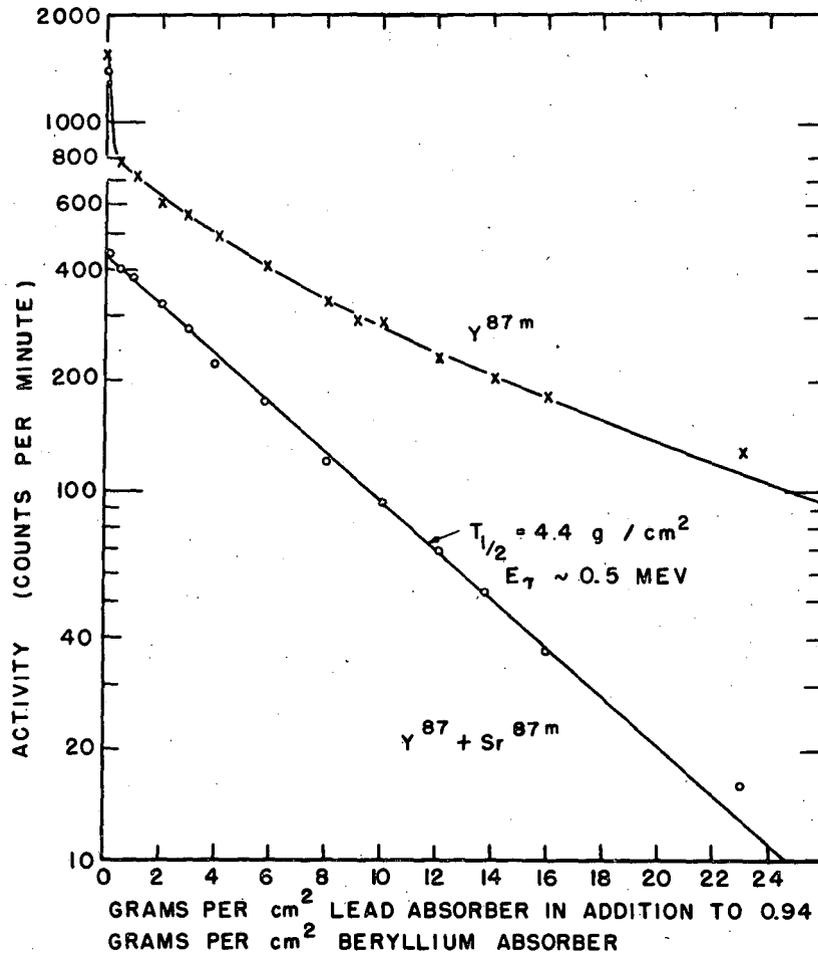


Fig. 10



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Fig. 11

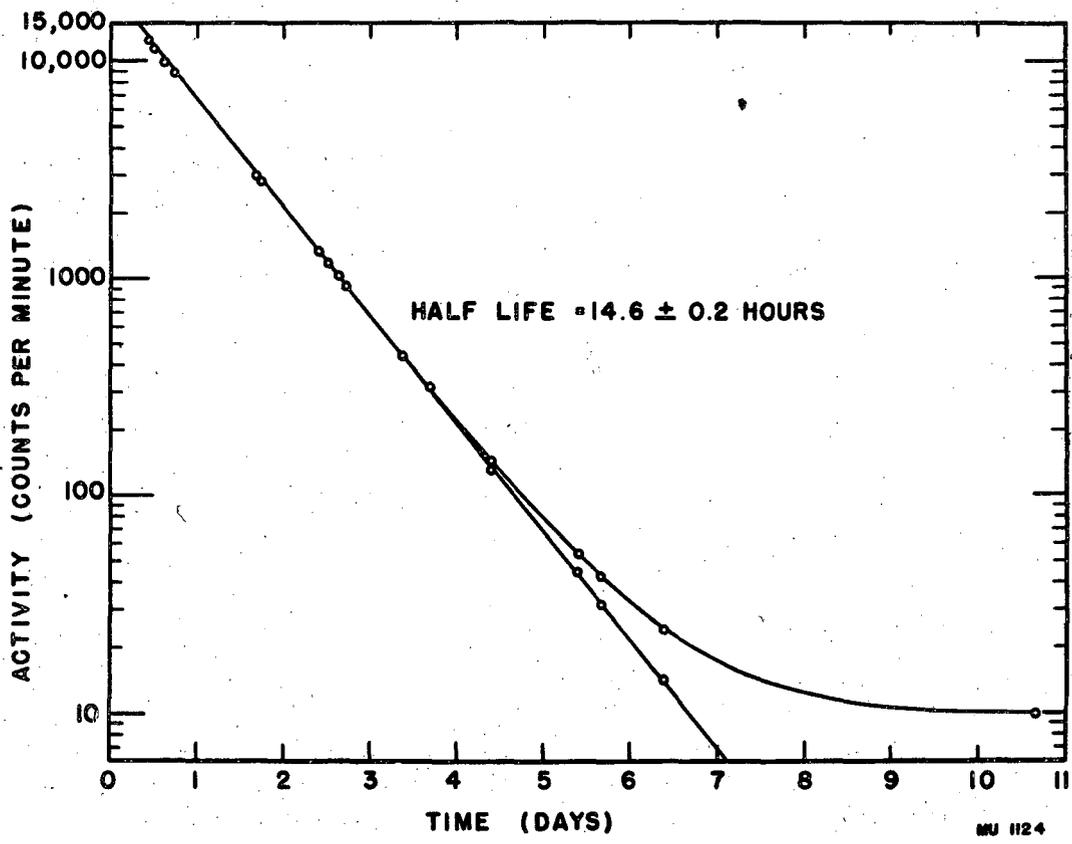


Fig. 12

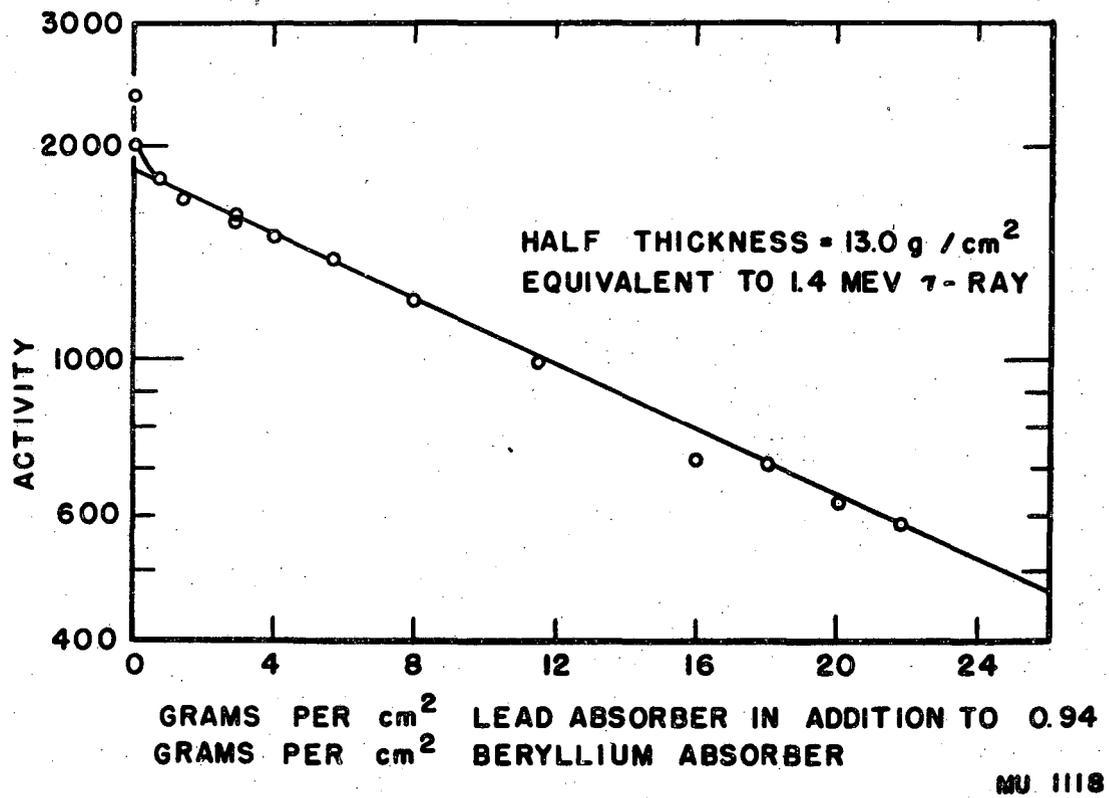


Fig. 13

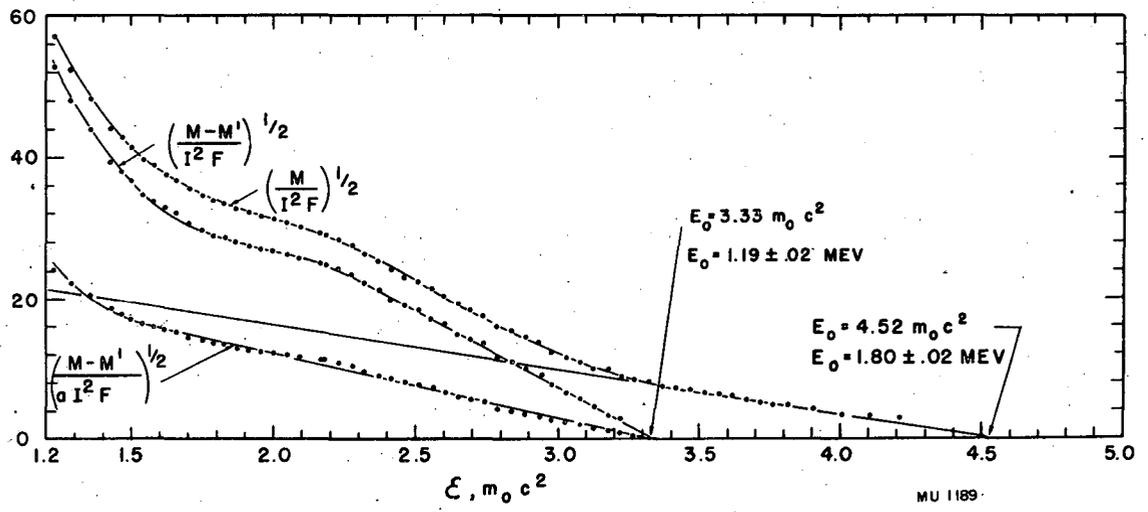


Fig. 14

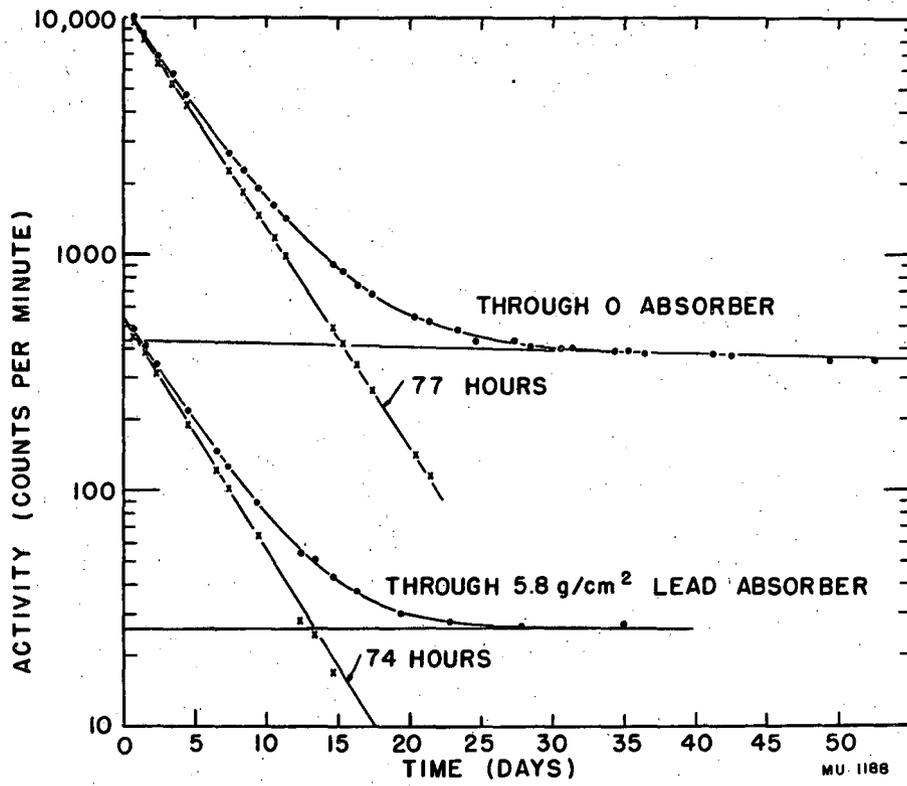


Fig. 15

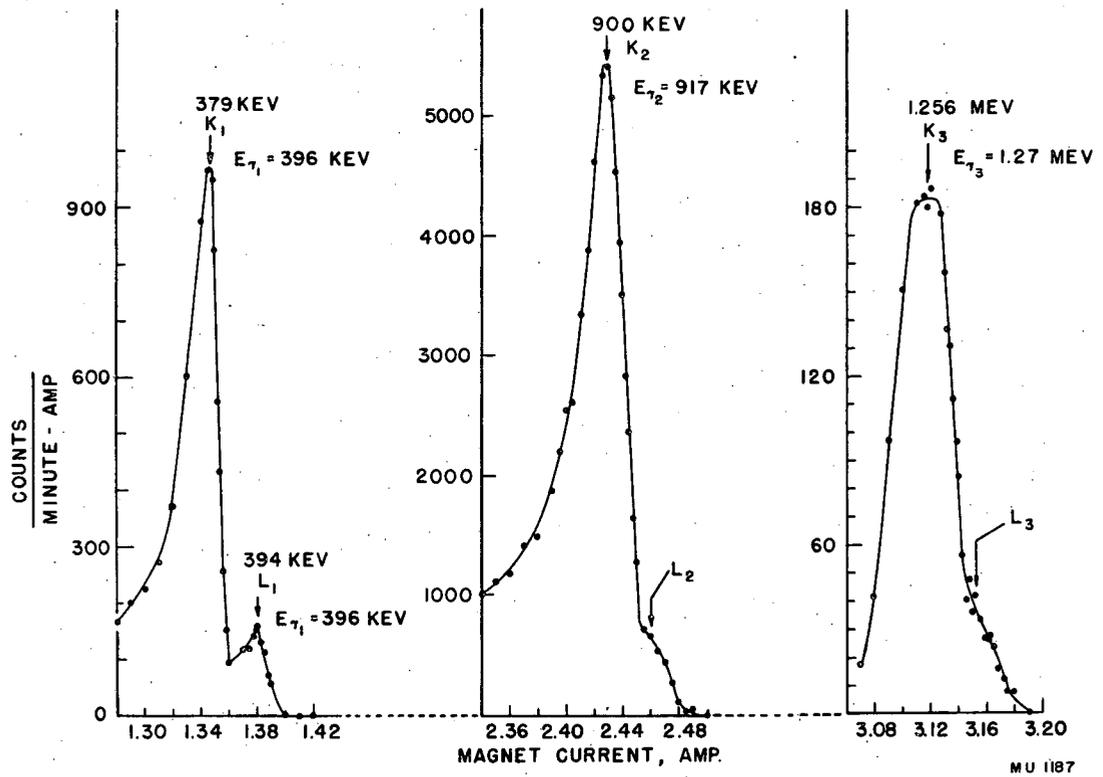


Fig. 16

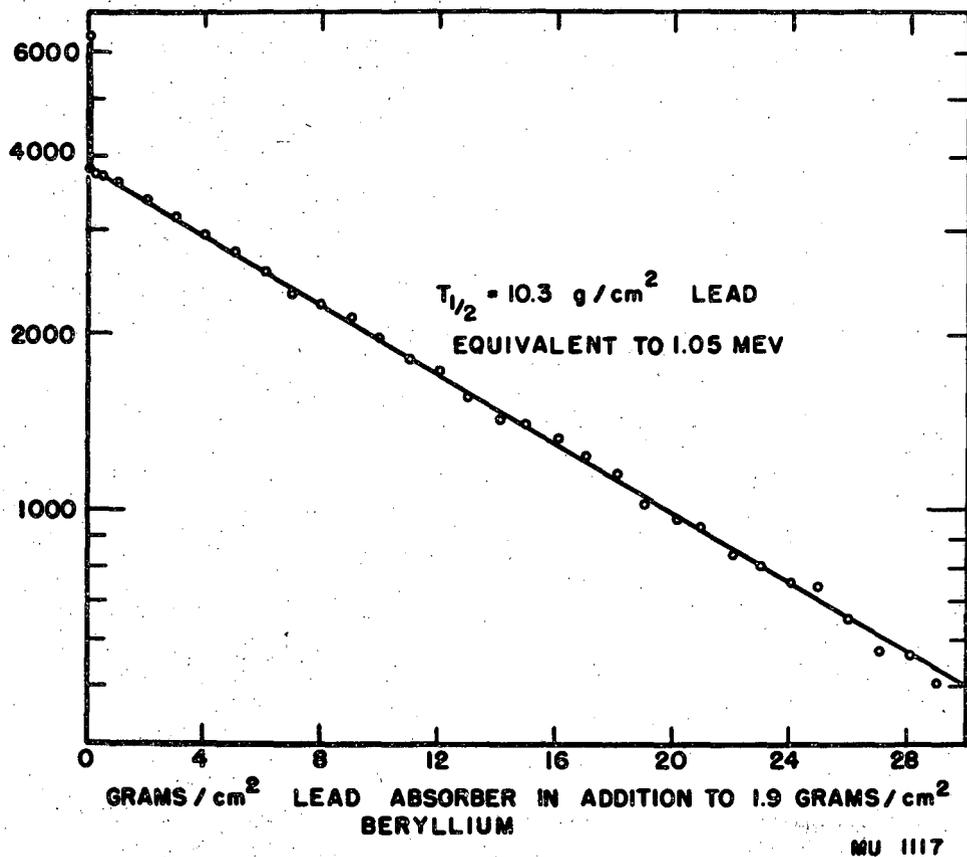


Fig. 17