# New Isotope Manganese-53<sup>+\*</sup>

JOSEPH R. WILKINSON AND RAYMOND K. SHELINE Department of Chemistry, Florida State University, Tallahassee, Florida (Received April 18, 1955)

Manganese-53 has been produced by the nuclear reaction  $Cr^{53}(p,n)Mn^{53}$  in the bombardment of enriched Cr<sup>53</sup> for a period of 8 hours with 9.5-Mev protons. Measurements of the decay and absorption data indicate that this nuclide is an orbital electron capturing activity without gamma rays or positrons. With the assumption that the cross section for the reactions  $Cr^{53}(p,n)Mn^{53}$  and  $Cr^{54}(p,n)Mn^{54}$  are the same, it is possible to calculate an approximate half-life of 140 years for this nuclide. These data together with those from previous measurements on the energy levels of  $Cr^{53}$  indicate that Mn<sup>53</sup> probably decays from an  $F_{5/2}$  ground state to a  $p_{3/2}$  Cr<sup>53</sup> ground state in an *l*-forbidden transition with a relatively high log ft value.

## I. INTRODUCTION

N reporting the nuclide Mn<sup>54</sup>, Livingood and Seaborg<sup>1</sup> found no trace of the nuclide Mn<sup>53</sup>. Batzel, Miller and Seaborg<sup>2</sup> observed the nuclide Mn<sup>54</sup> in the spallation of copper, but did not observe Mn<sup>53</sup>. Although nuclear systematics indicated that Mn<sup>53</sup> should be long-lived, the expenditure of the time necessary for the search for a long-lived activity did not seem justified until a careful search had been made for a short-lived activity. Accordingly, a betatron bombardment of elemental iron was undertaken at the University of Chicago betatron. The nuclear reaction expected was  $Fe^{54}(\gamma, p)Mn^{53}$ . The sample in cylindrical form was mounted directly in the beam of the betatron in such a way that the axis of the cylinder was the axis of the beam. A Geiger tube, shielded from the beam with six inches of lead, was placed parallel to the beam and two inches from the beam center. The entire apparatus has been previously described.<sup>3</sup>

If a Mn<sup>53</sup> activity in the half-life region from 0.02 second to several minutes were to be produced in this bombardment, it should have been observed. Only the half-life region in the vicinity of 9 minutes and 2 minutes is obscured by other activities. A similar type of bombardment with chemical separation of the manganese was undertaken by Marquez<sup>4</sup> to look for an activity in the intermediate half-life range. All of these results were negative.

In view of these experiments and because shell closure occurs at 28 neutrons, it seemed probable that Mn<sup>53</sup> would have a very long half-life, probably considerably longer than the half-life of Mn<sup>54</sup>. The need for a high cross section for the production of Mn<sup>53</sup> because of its probable long half-life and the necessity of keeping the contaminating Mn<sup>54</sup> activity at a minimum, seemed to

dictate low-energy proton bombardment of the enriched isotope Cr<sup>53</sup>.

### **II. EXPERIMENTAL**

A sample of  $Cr_2O_3$  containing 92.1%  $Cr^{53}$ , 5.7%  $Cr^{52}$ , 1.7% Cr<sup>54</sup>, and 0.5% Cr<sup>50</sup> was obtained from the Stable Isotopes Research and Production Division of the Oak Ridge National Laboratory. This sample was bombarded in the 60-inch cyclotron at the University of California for a period of 8 hours with 9.5-Mev protons. The total beam current for the bombardment was 29.03 microampere hours. The sample was dissolved in concentrated nitric acid to which a few drops of 30%hydrogen peroxide had been added. The solution was boiled to destroy the excess H<sub>2</sub>O<sub>2</sub> and 10 mg of manganese as  $Mn(NO_3)_2$  was added as carrier. The solution was brought to boiling and solid KClO<sub>3</sub> added to precipitate the manganese as  $MnO_2$ . The precipitate was filtered, washed with concentrated HNO<sub>3</sub>, then with distilled water and redissolved in concentrated HNO<sub>3</sub> to which a few drops of 30% H<sub>2</sub>O<sub>2</sub> had been added. The resulting solution was boiled to destroy the excess H<sub>2</sub>O<sub>2</sub> and holdback carriers of chromium, cobalt, and iron were added. The manganese was again precipitated from the boiling solution with solid KClO<sub>3</sub>. The precipitate was filtered, washed, and dissolved as before. Holdback carriers were again added and the manganese precipitated as before. This step was repeated twice more with the holdback carriers present and a final time without the holdback carriers. The final precipitate of MnO<sub>2</sub> was evaporated nearly to dryness on a hot plate and then placed in a plastic planchet and dried

TABLE I. Analysis of the long-lived components of manganese activity resulting from the proton bombardment of Cr53

Case No.	Constant amounts of activity subtracted (in counts/ minute)	Half-time of remaining straight line (in days)	Mean deviation [log_activity/day]
1	10	360	0.02341
2	20	312	0.02328
3	30	260	0.02392
4	40	210	0.02707

<sup>&</sup>lt;sup>†</sup> This work was supported in part by the U. S. Atomic Energy Commission.

This paper was taken from a portion of a thesis submitted by J. R. Wilkinson to the Graduate Faculty of Florida State University in partial fulfillment of the requirements for the Ph.D. degree.

J. J. Livingood and G. T. Seaborg, Phys. Rev. 54, 391 (1943).

 <sup>&</sup>lt;sup>2</sup> Batzel, Miller, and Seaborg, Phys. Rev. 84, 671 (1951).
<sup>3</sup> R. K. Sheline, Phys. Rev. 87, 557 (1952).

<sup>&</sup>lt;sup>4</sup> L. Marquez (private communication).

under an infrared light. The activity was then measured by means of an ordinary Geiger counter.

## III. RESULTS AND DISCUSSION

The activity of the sample was very high at first due to the presence of 5.8-day  $Mn^{52}$ . After the  $Mn^{52}$  activity had completely died away, there were at least two longer-lived activities present. These long-lived activities have now been followed for a period of 29 months.

In order to insure the purity of the sample after the observation of the long-lived activities, a second series of chemical separations similar to those already described were made. These chemical separations in no way affected the absorption characteristics or gross activity of the sample showing that the activities were manganese.

To eliminate any chance of the longer-lived activities being influenced by the relatively large amount of the 5.8-day  $Mn^{52}$  activity, that portion of the decay curve resulting from the 100 days immediately following the bombardment was discarded and only the last 26 months of the decay used in the analysis. This analysis indicates that there were only two long-lived activities present. One of these long-lived components was 310day  $Mn^{54}$  as indicated by decay and absorption characteristics. The other component was a much longer-lived manganese activity than  $Mn^{54}$ .

Simple inspection of the decay curve also indicated that this long-lived activity is present in relatively small amounts. Accordingly, small constant amounts of activity were subtracted from the over-all decay curve and the best straight line, as determined by the method of least squares, drawn through the resulting points. A plot of these straight lines gave the results shown in Table I.

As indicated in Table I, the mean deviation of the plotted points from the straight line was least for case 2 and greatest for case 4. The half-time of the remaining straight line of 312 days in case 2 agrees most closely with the half-life of Mn<sup>54</sup> of 310 days as determined by Livingood and Seaborg<sup>1</sup> and the most recent determination of the half-life of Mn<sup>54</sup> as 291 days by Backofen and Herber.<sup>5</sup> The fact that the mean deviation in case 2 was the smallest precisely when the Mn<sup>54</sup> half-life agrees most closely with previous experimental results gave some credulence to the belief that we were actually observing a new manganese activity which was very long-lived in comparison to Mn54. In particular, it would seem to be justified to assume no decay of this activity over a period of 26 months if it is formed with a cross section even remotely close to that with which Mn<sup>54</sup> is formed. However, the potential accidental coincidence between the best Mn<sup>54</sup> half-life and the mean deviation of the straight lines made it imperative







FIG. 1. Absorption curve of  $Mn^{53}$  and  $Mn^{54}$ . Curve B is an expanded plot of the dotted area in curve A.

to justify the existence of a small number of long-lived manganese counts in some independent way. In order to attain this end as well as obtain a better value of the amount of activity of the longer-lived component, the absorption curve of the sample was compared with the absorption curve of  $Mn^{54}$  which contained less than 1% Mn<sup>53</sup>.

This sample of  $Mn^{54}$  was obtained from the Oak Ridge National Laboratory and a portion of the sample chosen to give approximately the same specific activity as that of the bombarded sample. The  $Mn^{54}$  was precipitated as  $MnO_2$  in the same manner as the original sample and mounted in the same type planchet. The experimental conditions for the precipitations duplicated as closely as possible those of the precipitations of the original bombarded sample. The absorption curves of this  $Mn^{54}$  and that of the original bombarded sample were taken and compared by normalizing their gamma ray components as shown in Fig. 1. The difference between the activities of the two absorption curves when normalized is 19 counts/minute.

The close agreement of the activity of 19 counts/ minute as obtained from the comparison of the absorption curves with that calculated from the decay data justified the assignment of this amount of activity to a long-lived isotope of manganese.

The difference between the absorption curve of  $Mn^{54}$ and that of the bombarded sample is the absorption curve of  $Mn^{53}$ . This absorption curve is shown in Fig. 2.

<sup>&</sup>lt;sup>5</sup> E. W. Backofen and R. H. Herber, Phys. Rev. 97, 743 (1955).



FIG. 2. Absorption curve of Mn<sup>53</sup>.

The half-thickness from this plot was found to be 5.0 mg/cm<sup>2</sup>. This half-thickness is within the error of our experiments of the calculated value of the chromium  $K_{\alpha}$  x-ray of 4.8 mg/cm<sup>2</sup>. Not only is the half-thickness 5.0 mg/cm<sup>2</sup>, but there is a single component in the absorption plot. This indicates that there are no gamma rays present in the decay of the new long-lived manganese activity.

It is established then that we have a long-lived gammaless orbital electron capturing isotope of manganese. In view of the isotopic composition of the enriched  $Cr^{53}$  isotope used in the proton bombardment, the presence of an unassigned position in the nuclear periodic table at 25 protons and 28 neutrons, the unusual stability expected because of shell closure at 28 neutrons, and finally, the fact that this is a proton excess nucleus since it is an orbital electron capturer, the only reasonable assignment of this long-lived manganese activity is  $Mn^{53}$ .

From the Mn<sup>53</sup> activity of 19 counts/minute, the Mn<sup>54</sup> activity remaining after the gamma-ray component has been subtracted, the isotopic composition of the enriched Cr<sup>53</sup> used in the bombardment, and the cross section for the production of Mn<sup>53</sup> (assuming it is the same as that for Mn<sup>54</sup> in the reactions Cr<sup>54</sup>(p,n)Mn<sup>54</sup> and Cr<sup>53</sup>(p,n)Mn<sup>55</sup>) it is estimated that the half-life of Mn<sup>53</sup> is 140 years.



FIG. 3. A decay scheme for Mn<sup>53</sup>.

The data of McClelland et al.6 and Stelson and Preston<sup>7</sup> in studying the  $Cr^{53}(p,n)Mn^{53}$  threshold indicate that Mn<sup>53</sup> should decay with an energy of 598-kev. The ground state of  $Cr^{53}$  is known to be a  $p_{3/2}$  state, whereas the relative intensities of the Cr52 neutroncapture gamma rays<sup>8</sup> indicates that the first excited state of Cr<sup>53</sup> is probably  $p_{1/2}$ .<sup>9</sup> Therefore, Mn<sup>53</sup> should decay into the ground state of Cr<sup>53</sup> only, whether the ground state of  $Mn^{53}$  is  $F_{5/2}$  or  $f_{7/2}$ . On the other hand, other experimental indications point fairly strongly to the correct spin and parity assignment for the ground state of Mn<sup>53</sup>. If the ground state of Mn<sup>53</sup> is  $F_{5/2}$ , then a  $5/2 \rightarrow 3/2 - l$ -forbidden transition with log*ft* value from 5.0-9.0 would result in a half-life for a 598-kev orbital electron capture of 70 days to 500 years. However, the second forbidden transition  $(\log ft \text{ value} = 13.0)$ expected if the ground state of  $Mn^{53}$  is  $f_{7/2}$  would result in a half-life of  $\sim 10^6$  years. In spite of the uncertainties involved in the half-life determination of Mn<sup>53</sup> as 140 years and the assignment of  $\log ft$  values, it seems probable that the half-life is known sufficiently accurately to discriminate rather strongly against the  $f_{7/2}$ assignment as the ground state of Mn<sup>53</sup>.

On the basis of all of these considerations the decay scheme for  $Mn^{53}$  shown in Fig. 3 is proposed.

## ACKNOWLEDGMENTS

The authors wish to express their appreciation to the Stable Isotopes Research and Production Division of the Oak Ridge National Laboratory for the loan of the enriched  $Cr^{53}$  used in these experiments and to Dr. G. Bernard Rossi and the crew of the 60-inch cyclotron at the University of California for their help and cooperation in arranging the necessary bombardments.

<sup>6</sup> McClelland, Goodman, and Stelson, Phys. Rev. 86, 631 (1952).

<sup>7</sup> P. H. Stelson and W. M. Preston, Phys. Rev. 86, 807 (1952). <sup>8</sup> B. B. Kinsey and G. A. Bartholomew, Phys. Rev. 89, 375 (1953).

<sup>9</sup> R. H. Nussbaum, thesis, University of Amsterdam, December, 1954 (unpublished).