The Nuclide P^{33} and the P^{32} Spectrum*

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(Received May 21, 1951)

P^{33} has been produced by the bombardment of sulfur, sodium sulfide, and lithium chloride with the 48-Mev gamma-ray spectrum of the University of Chicago betatron. The reactions involved are $S^{34}(\gamma,p)P^{33}$, $Cl^{35}(\gamma,2p)P^{33}$, and $Cl^{37}(\gamma,\alpha)P^{33}$. The P^{33} activity has a 25 ± 2 day half-life with a 0.27 ± 0.02-Mev negative beta-ray. There is less than one (0.5-Mev) gamma for every fifteen betas. The activity was observed in the presence of P^{32}, and its ratio to the P^{32} activity did not change with chemical purification. Beta-ray spectra of the weak component observed in Oak Ridge carrier-free P^{32} indicate that this weak activity is P^{33} produced by the reaction $S^{33}(n,p)P^{33}$. The cross section for pile neutrons for this reaction is approximately 0.029 barn. The Fermi plot of the beta-ray spectrum is straight with a log ft value of 5.2. A decay scheme for P^{33} is proposed.

I. INTRODUCTION

IN looking at a table of isotopes in the vicinity of P^{33} one finds that P^{33} is largely surrounded by stable and known radioactive isotopes, yet itself is unknown. Often when such a circumstance arises it is because the nuclide in question has either a very short half-life, a very long half-life and a weak radiation, or because it has the same half-life as a known activity. In each of these cases its detection is difficult. P^{33} in particular would be expected to have a long half-life and a weak radiation, for it is an odd-even isotope like the stable P^{31} to which just one excess neutron pair has been added. Thus, in the case of chlorine, which has an additional proton pair, the stable Cl^{35} corresponds to stable P^{31}, whereas Cl^{37}, which corresponds to P^{33}, is now stable. Indeed, if one calculates the decay energy for P^{33} by calculating the masses of S^{33} and P^{33} from the Fermi-Weizsäcker equation, one obtains 0.23 Mev. Assuming this energy and that the transition $P^{33}\rightarrow S^{33}+\beta^-+\nu$ is allowed ($ft=10^5$), the half-life is about 70 days. In some preliminary experiments in which phosphorus fractions were separated from chlorine irradiated at the betatron, the separated activity showed a half-life longer than 14 days when counted with a thin window counter. This evidence indicated that P^{33} might indeed be longer lived than P^{32}. In experiments at the Chalk River Pile, however, Yaffe and Brown[1] found a 22-sec activity which they assigned to P^{33}.

Since one should be able to make P^{33} from sulfur by the $S^{34}(\gamma,p)P^{33}$ reaction, and also from chlorine by the $Cl^{37}(\gamma,\alpha)P^{33}$ and $Cl^{35}(\gamma,2p)P^{33}$ reactions, it seemed advisable to look for P^{33} in the irradiation of sulfur and chlorine with 48-Mev gamma-rays from the University of Chicago betatron.

II. SEARCH FOR SHORT-LIVED P^{33}

In order to look for very short-lived activities a sample was counted in place, without chemistry, immediately after turning off the betatron beam. The sample of sulfur was a pressed pill cylinder, 8 inches in length, and $\frac{3}{4}$-inch in diameter. It was mounted directly in the beam in such a way that the axis of the cylinder was the axis of the beam. A Geiger tube was placed parallel to it and about 2 inches off the beam center. The counter was shielded from the beam by 6 inches of lead. The betatron and the Geiger tube were controlled by a motor-driven timing switch which executed a duty cycle: betatron—on 3 sec, off 5 sec, on 3 sec, etc., synchronous with counter—off 3 sec, on 5 sec, off 3 sec, etc. The scaler pulse was fed directly to one pen of a two-channel Brush recorder. The other pen was fed 60 cycle ac to act as a timer. In this way it was possible to irradiate samples for 3 sec and then to count them within milliseconds after the beam was turned off for a period of 5 sec. This apparatus was used to look for a new activity of half-life from 0.2 second to 2 minutes where no chemical separation was effected. No indication of a new short-lived activity was found within the experimental error of the measurement, which was very small.

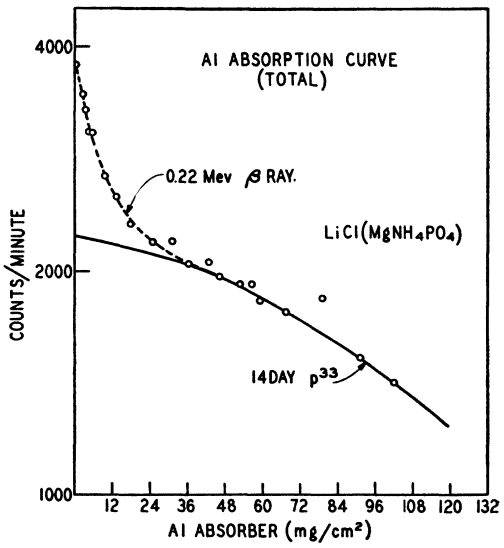

FIG. 1. Absorption curve on the phosphorus fraction from the gamma-ray irradiation of lithium chloride.

* Part of this work was reported at the Washington, D. C., meeting of the American Physical Society, April, 1951. Phys. Rev. **83**, 215 (A) (1951).

[1] L. Yaffe and F. Brown, Phys. Rev. **82**, 322 (1951).

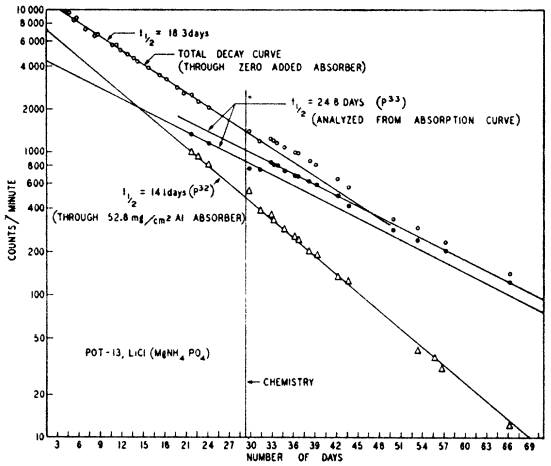

FIG. 2. Decay of the phosphorus fraction analyzed for strong and weak beta-ray components.

Using, then, a "rabbit" to transport the sample quickly after irradiation, and the traditional end-window Geiger tube and counting setup, we irradiated chlorine and sulfur with gamma-rays. In each case the phosphorus was separated as the ammonium phosphomolybdate.[2] No indication of a new activity of half-life from 2 minutes to 14 days was found. Thus, no new activity was found in the half-life region from 0.2 second to 14 days with the exception of the 1 to 3 second and 1 to 3 minute regions, which would be obscured by the strong activities of S^{31} (2.6 sec) and P^{30} (2.55 min), respectively. Accordingly, it seemed advisable to look for a longer lived activity.

III. 25-DAY PHOSPHORUS NEGATIVE BETA-EMITTER

Samples of sulfur and lithium chloride were irradiated by the gamma-rays of the University of Chicago betatron, the sulfur for 225 hours over a period of $1\frac{1}{2}$ months and the lithium chloride for 244 hours over a slightly longer time than the sulfur. After irradiation the sulfur was melted in boiling concentrated nitric acid in the presence of phosphate carrier, and the phosphate was precipitated twice as ammonium phosphomolybdate in 1N nitric acid. The lithium chloride was dissolved in hot concentrated nitric acid and after the reaction had stopped the solution was diluted to 1N nitric acid. Phosphate carrier and sodium sulfate holdback carrier were added. Ammonium phosphomolybdate was precipitated and washed with ammonium molybdate solution. The precipitate was dissolved in dilute ammonia and ammonium sulfide was added to hold back sulfide and sulfur. The phosphate was then precipitated twice as the magnesium ammonium phosphate.

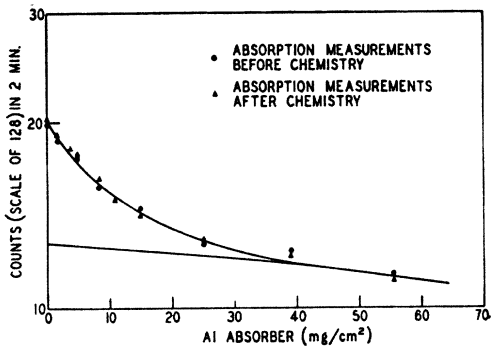

FIG. 3. Absorption curve on the phosphorus fraction from the gamma-ray irradiation of sulfur before and after chemistry.

Absorption curves were taken on these samples (Fig. 1). A 0.22-Mev beta-ray component was observed. Decay curves were also taken on these samples, utilizing appropriate absorbers to diminish the counting rate of the weak beta-ray component. In this way, the gross decay curve (Fig. 2) was broken into two components, one the 14-day P^{32} and the other a new 25-day activity. The thin window counter used to take the decay curves of Fig. 2 was replaced after the 60th day. The new tube had a thinner window, so that the weak beta-ray component was counted more efficiently and consequently the decay curve deviated discontinuously. It may be noticed that the total decay curve deviated also, but the decay of the hard beta-ray component is constant.

If this activity were an impurity, it would most probably be S^{35} (0.167 Mev β^-, half-life 87 days), Ca^{45} (0.25 Mev β^-, half-life 152 days), or Pa^{233} (0.23 Mev β^-, half-life 27.4 days).[3] Since protoactinium has several gamma-rays and conversion electrons associated with its decay, and no indication of these was found, it was eliminated from consideration.

A chemical purification of phosphorus was made in the presence of sulfur and calcium carriers. The sulfur was in the form of sulfate, sulfite, and sulfide, and the calcium was in the Ca^{++} state.

The chemistry consisted of dissolving the samples in 6N HCl, adding calcium, sulfate, and sulfite carriers and then adding concentrated nitric acid to oxidize the sulfite to sulfate and precipitating the sulfate with barium. After centrifuging to remove the barium sulfate, the phosphate was precipitated as ammonium phosphomolybdate to separate it from calcium. As before the phosphomolybdate was washed and dissolved in ammonium hydroxide, and ammonium sulfide was added to hold back sulfide and sulfur. Two precipitations as the magnesium ammonium phosphate were done before counting. This rather extensive chemistry in no way affected the relative amount of P^{32} to the new low energy component. The absorption curves before and after chemistry are shown in Fig. 3. Therefore, this new activity is certainly a phosphorus activity. Magnetic deflection experiments show the activity to be a

[2] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* (John Wiley and Sons, Inc., New York, 1929), pp. 38, 581.

[3] Way, Fano, Scott, and Thew, *Nuclear Data* (Circular of the Natl. Bur. of Standards 499, 1950), pp. 28, 38, 264.

negative beta-emitter. Therefore, the activity is a 25-day negative-beta-emitting phosphorus of approximately 0.22 Mev.

IV. THE BETA-SPECTRA OF P^{32} AND THE 25-DAY PHOSPHORUS ACTIVITY

Earlier work by Agnew[4] in this laboratory on the beta-spectrum of P^{32} revealed the presence of an anomaly in the low energy region. This anomaly becomes pronounced below 250 kev and was not observed with certainty before.[5] Agnew's result was subsequently confirmed by Warshaw *et al.*,[6] whose spectrum shows an even more pronounced "bump" in the momentum plot at low energies. The interpretation that the anomaly was due to a complex beta-spectrum seemed improbable, since P^{32} is known not to emit gamma-rays.[7] The work reported here, along with that of Jensen and Nichols,[8] shows that the anomaly is due to the presence of a hitherto unknown beta-emitter, having just the half-life and energy to account for all the observations.

The beta-spectrum of various samples of radioactive phosphorus were studied with the same double lens

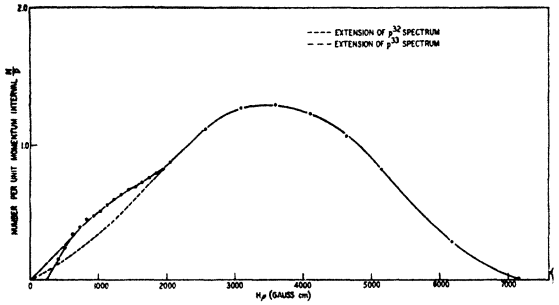

FIG. 4. The beta-spectrum of 27-day-old carrier-free phosphorus from Oak Ridge.

beta-ray spectrometer as was used by Agnew.[9] The samples studied were carrier-free P^{32} obtained from the Isotopes Division at Oak Ridge and measured (a) 27 days after end of irradiation, (b) 242 days after end of irradiation, and (c) 308 days after the end of the irradiation; and also phosphorus purified radiochemically from (d) sulfur and (e) chlorine, which had been irradiated with gamma-rays up to 48 Mev from the University of Chicago betatron.

The spectrometer was used with 9 percent resolution and 4 percent transmission. Samples (*a*) and (*b*) were measured by using a Nylon window counter of window thickness approximately 80 $\mu g/cm^2$ which cuts off electrons below 3 kev. This window is supported on a grid

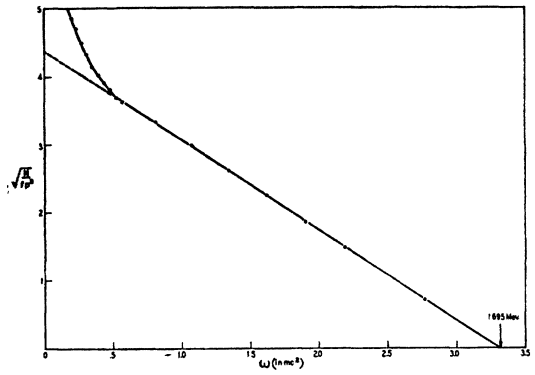

FIG. 5. Fermi plot of the beta-spectrum of 27 day old carrier-free phosphorus from Oak Ridge. $E_{max}=1.695\pm0.005$ Mev.

which reduces the transmission by a factor of 3. Due to the weakness of samples (*c*), (*d*) and (*e*) a counter was used without a grid but with a mica window with a window thickness of 0.96 mg/cm^2. The mica window cuts off electrons below about 12 kev. The cut-off energies of the beta-rays were determined from the beta-ray spectra. The sources were deposited on 15 $\mu g/cm^2$ Nylon foil made conducting by evaporating aluminum of thickness approximately 5 $\mu g/cm^2$. The internal conversion line of Cs^{137} was used to check the energy calibration and resolution of the instrument at each setting used.

Figure 4 shows the beta-spectrum of the 27-day-old carrier-free phosphorus from the Isotopes Division at Oak Ridge. This curve is quite similar to the one obtained by Agnew and Warshaw and shows the anomalous "bump" at low energy. The conventional Fermi plot is shown in Fig. 5. It is straight from 1.7 Mev to about 300 kev and then rises abruptly at low energy.

Figure 6 shows the momentum plot of samples of the 308-day-old phosphorus, curve *I*; the 242-day-old phosphorus, curve *IV*; and the gamma-irradiated samples of chlorine, curve *II*; and of sulfur, curve *III*. Curves *II* and *III* were taken about 27 days after the end of the irradiation. The source thicknesses were about 5 mg/cm^2 for the 242-day-old phosphorus, 20 mg/cm^2 for the 308-day-old phosphorus, and 15 mg/cm^2 for both bombardment samples. All these samples

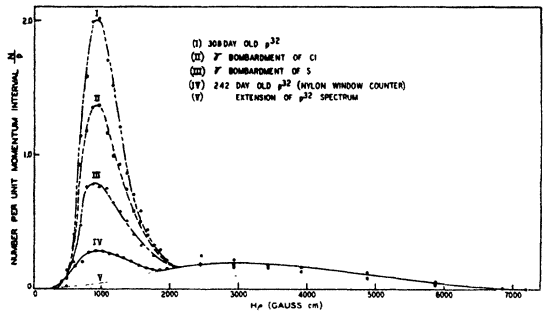

FIG. 6. The beta-spectra of various phosphorus fractions in which the P^{32} component has been normalized.

[4] H. M. Agnew, Phys. Rev. **77**, 655 (1950).
[5] E. M. Lyman, Phys. Rev. **51**, 1 (1937); J. L. Lawson, Phys. Rev. **56**, 131 (1939); K. Siegbahn, Phys. Rev. **70**, 127 (1946); E. J. Scott, Phys. Rev. **74**, 1240 (1948); L. M. Langer and H.C. Price, Phys. Rev. **76**, 641 (1949).
[6] Warshaw, Chen, and Appleton, Phys. Rev. **80**, 288 (1950).
[7] Kurie, Richardson, and Paxton, Phys. Rev. **49**, 368 (1936).
[8] E. N. Jensen and R. T. Nichols, Phys. Rev. **83**, 215(A) (1951).
[9] H. M. Agnew and H. L. Andersen, Rev. Sci. Instr. **20**, 869 (1949).

suffer from thick-source distortion. The ordinates have been adjusted to make the high energy part of the spectra coincide. Examination of these curves makes it clear that the anomaly is due to some other activity which has a longer half-life than that of P^{32} (14.1 days). By comparing the total amounts of the new activity uncer curve *I* and curve *IV*, the half-life can be estimated and is about twice that of P^{32}.

Table I shows the increase of the low energy component of Oak Ridge carrier-free phosphorus as a function of time. This phosphorus is obtained from the irradiation of sulfur in the pile. Since both Agnew[4] and Warshaw *et al.*[6] observed their P^{32} samples over only 5 and 3 half-lives respectively, it is easy to understand from this table why they observed no change in the low energy "bump."

A determination of the end point energy of the new activity from these spectra is $E_{max}=0.27\pm0.02$ Mev, as shown in Fig. 7.†

V. ASSIGNMENT, DECAY SCHEME, AND MASS

Using an end-window counter and an appropriate absorber to cut out all betas, an upper limit for the number of gamma-rays was determined. There is less than one 0.5-Mev gamma to every fifteen low energy component betas.

TABLE I. Variation of percentage of low energy component in Oak Ridge carrier-free phosphorus.

No. of half-lives of P^{32} ($T_{\frac{1}{2}}=14.1$ days)	Percent of low energy component ($T_{\frac{1}{2}}=25$ days)
0	1.9
1	2.5
2	3.4
3	4.7
4	5.9
5	8.6
10	38.8

A run was done in which a sample of sulfur and a sample of lithium chloride were irradiated in the betatron for 21 hours over a period of three days. The ratios of the yields of the weak beta-ray component to the strong beta-ray component, correcting for half-life and absorption are, from sulfur,

$$A_{weak}/A_{strong}=0.79$$

and, from lithium chloride,

$$A_{weak}/A_{strong}=1.02,$$

where A_{weak} and A_{strong} are the saturation activities at the end of the irradiation of the weak and strong (P^{32}) components, respectively, corrected for the window thickness of the counter.

These two pieces of data suggest a mass assignment. The various possible mass assignments are P^{32}, P^{33}, P^{34} or P^{35}. In the irradiation of sulfur, P^{34} and P^{35} can be produced only by the gamma-ray irradiation of S^{36} which is present in 0.016 percent isotopic abundance. Therefore, the relative amounts of P^{34} or P^{35} to that of P^{32} should be very small, since P^{32} can be produced by the gamma-ray bombardment of either S^{33} or S^{34} which have the isotopic compositions 0.75 percent and 4.2 percent respectively. The results quoted above show that the yield of the weak component is almost equal to the yield of P^{32}. The results of the chlorine irradiation are similar. Therefore this activity is neither P^{34} nor P^{35}.

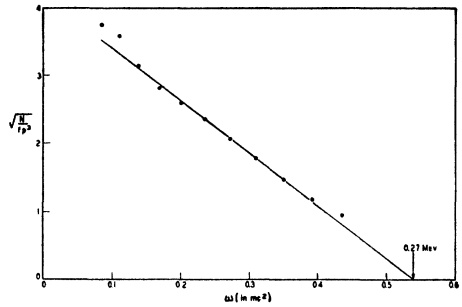

FIG. 7. Fermi plot of the weak component in 27-day old carrier-free phosphorus from Oak Ridge. $E_{max}=0.27\pm0.02$ Mev.

The evidence against the observed radiation resulting from an isomeric state of P^{32} is (1) No isomeric transitions occur this low in mass number, nor are they to be expected on the basis of the one particle nuclear model of M. G. Mayer.[10] One does not expect to find a spin difference great enough to account for long-lived isomeric transitions in this region of mass number. (2) Since the energy difference between the two betas is 1.45 Mev, an isomeric state would decay with high probability by isomeric transition. From spin considerations at least one isomeric transition must not be strictly forbidden. However, no gammas are found associated with the transition. Therefore the activity cannot be an isomeric state of P^{32} or S^{32}.

By elimination, this 0.27-Mev 25-day negative beta-emitting phosphorus must be P^{33}. The decay scheme is shown in Fig. 8. P^{33} is either an $s_{\frac{1}{2}}$ or a $d_{\frac{1}{2}}$ state. Using the rule that adding two neutrons to a nucleus does not change the spin one obtains the same state for P^{33} as for P^{31} which is known to be $s_{\frac{1}{2}}$. The transition

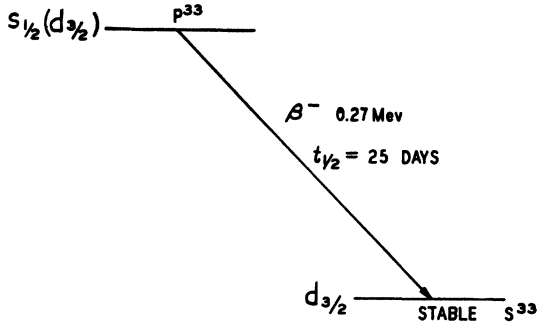

FIG. 8. Decay scheme of P^{33}.

† *Note added in proof:* Our new measurements show the end-point energy to be 0.26±0.01 Mev.

[10] M. G. Mayer, Phys. Rev. 78, 16 (1950).

$s_{\frac{1}{2}} \rightarrow d_{\frac{3}{2}}$ is L-forbidden with an expected log$ft \sim 7$. The measured logft is 5.2. This is evidence in favor of a strict shell model $d_{\frac{3}{2}}$ state for P^{33}. S^{33} is known to be in a $d_{\frac{3}{2}}$ state.

Low and Townes[11] report the atomic mass of S^{33} as 3.298058 ± 10. This is not an absolute mass but is relative to the mass chosen for S^{32}, which is 31.98089. If one assumes the simple decay scheme shown in Fig. 8, the mass for P^{33} is 32.98088 ± 10.

At Oak Ridge, P^{32} is produced by the $S^{32}(n,p)P^{32}$ reaction. This explains the existence of a small amount of P^{33} in the P^{32} sample because the same reaction will transform S^{33} into P^{33}. The ratio of P^{33} activity to that of P^{32}, after correction for decay, is 1.9 percent. Taking the cross section of the reaction $S^{32}(n,p)P^{32}$ to be 0.012 barn for pile neutrons[3] the cross section of the reaction $S^{33}(n,p)P^{33}$ is then ~ 0.029 barn, assuming that the sulfur was in the pile for the usual 6 weeks.

VI. DISCUSSION AND CONCLUSION

The isotope P^{33} has also been reported by Yaffe and Brown[1] to exist as a 22-sec beta-activity of high energy. This was produced by bombarding P^{32} with neutrons in the pile. The P^{32} was made by $S^{32}(n,p)P^{32}$. An (n,γ) reaction on P^{33} would produce P^{34} previously reported as a 12.4-second half-life with 5.1 and 3.2-Mev betas. In view of the complexity of the decay curve of Yaffe and Brown this may be the 22-sec activity observed by them. If this short-lived activity is actually P^{34}, this would be strong evidence in favor of its assignment as P^{33} since P^{34} could only be produced by (n,γ) on P^{33}.

This isotope may have some value as a phosphorus tracer because of its long half-life. Its use in plant physiology is especially apparent. Thus, for example, at the end of a 150-day growing season the activity of P^{33} would have 15 times as much activity as P^{32}.

The low energy of the radiation may be a defect in making detection difficult; however, it makes it possible to use higher specific activities because the radiation damage would be less than with the high energy beta of P^{32}.

It is suggested that the P^{33} can be best obtained by allowing samples of very intense carrier-free P^{32} from Oak Ridge to decay over a period of 10–12 months. The resulting activity would be from 90–98 percent P^{33}.

The authors wish to acknowledge the interest and advice of Professors Nathan Sugarman, Herbert L. Anderson, and Willard F. Libby in this work. Thanks are also due Mr. Charles McKinney and the betatron operating crew.

[11] W. Low and C. H. Townes, Phys. Rev. **80**, 608 (1950).

PHYSICAL REVIEW VOLUME 83, NUMBER 5 SEPTEMBER 1, 1951

Experiments on Proton-Proton Scattering from 120 to 345 Mev*

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(Received April 30, 1951)

The differential scattering cross section for elastic collisions of 345-Mev protons with protons has been measured in the angular range 11° to 90° (center of mass system). The same cross section has been measured over more limited ranges of angles at lower energies. The cross section (in the center of mass system) at 90° is remarkably independent of energy. The cross section at 345 Mev is very independent of angle, being close to 3.8×10^{-27} cm²/steradian (center of mass system). The agreement with existing phenomenological theories based on static potentials is rather poor, especially in the case of scattering at small angles at 345 Mev.

INTRODUCTION

THE results of experimental investigations of n-p scattering have previously been reported and we have given preliminary reports on our study of p-p scattering.[1,2]

At the end of one preliminary report, we indicated some possible improvements in technique which we have now accomplished. In this paper we give our final results on the differential cross section of proton-proton scattering as a function of the angle of scattering and of the energy of the protons. The results of our preliminary paper are confirmed, but the present investigation extends the data to lower energies and increases the precision of the determinations. While these experiments were in progress, Oxley, Schamberger, and Towler[3] have investigated the p-p scattering at 240 Mev, and Birge[4] has done the same at 100 Mev. Their results overlap our own in part, and agree with us in the common part.

A summary of the results is presented in Tables I, II, and III and in Fig. 10.

EXPERIMENTAL

Our source of high energy protons is the external beam of the 184-inch Berkeley cyclotron. In this beam is placed a hydrogenous target, either polyethylene

* Through the Radiation Laboratory this work has been supported by the U.S. AEC.

[1] Hadley, Kelly, Leith, Segrè, Wiegand, and York, Phys. Rev. **75**, 351 (1949); Kelly, Leith, Segrè, and Wiegand, Phys. Rev. **79**, 96 (1950).

[2] O. Chamberlain and C. Wiegand, Phys. Rev. **79**, 81 (1950); Chamberlain, Segrè, and Wiegand, Phys. Rev. **81**, 284, 661 (1951).

[3] Oxley, Schamberger, and Towler, Phys. Rev. **82**, 295(A) (1951).

[4] R. W. Birge, Phys. Rev. **80**, 490 (1950).