Induced Radioactivity in Europium

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Europium oxide has been bombarded with slow neutrons from the cyclotron for periods ranging up to about five months, and with 7-Mev deuterons for much shorter lengths of time. By reduction of the europium to its bivalent state, it has been possible to separate this element from neighboring members of the rare earth group. By slow neutron activation, two periods of induced radioactivity have been produced in europium; one, with a half-life of 9.4±0.2 hours, is assigned to Eu^{152}, in accordance with the results of other investigators. This isotope probably decays both by the emission of negative electrons and by the capture of K electrons. The beta-spectrum, as measured in the cloud chamber, has an upper limit of 1.83 Mev. The second period, produced only after long exposure, has not decayed appreciably in six months. It has been assigned to Eu^{154}. Preliminary studies indicate that K-electron capture may also take place in the decay of this isotope. The upper limit of the beta-spectrum has been found to be 1.0±0.1 Mev. By relatively short deuteron bombardments, the 9-hour period has also been produced, and in addition two new periods of 12±4 minutes and 105±5 minutes have been obtained. These could not be separated from the 9-hour activity by chemical methods, which indicates that they are due also to isotopes of europium, probably to isomeric forms of Eu^{152} and Eu^{154}, not produced appreciably by slow neutron activation.

INTRODUCTION

RADIOACTIVITY induced in europium by the action of neutrons had previously been studied by Sugden,[1] Marsh and Sugden,[2] Hevesy and Levi,[3] and Pool and Quill.[4] Europium, like cerium, differs from other members of the rare earth group in that it may be separated from neighboring elements by a single chemical operation with satisfactory completeness, and for this reason it has been feasible to study more carefully the radioactivity induced in it by deuteron as well as by neutron bombardments. The stable isotopes of europium and adjacent elements are shown in Fig. 1, where the figures refer to percent abundance.

Previous investigators had found in europium a negative-active period of 9.2-hour half-life. On the basis of experiments with fast neutrons, this activity has been shown by Pool and Quill[4] to be due to Eu^{152}. These same experimenters have reported a period of 27 hours, which they observed only after fast neutron activation, and have assigned this to Eu^{150}, which is reported to emit positrons. In the present study, slow neutrons were used to extend the previously known results, and deuterons were also used to search for new radioactive isotopes. Cloud-chamber studies were made of the radiations from certain of the artificially produced radioelements.

MATERIALS AND APPARATUS USED

Europium oxide was obtained from Professor H. N. McCoy, who made the original purification. To remove traces of the lighter elements, such as sodium, the europium was twice precipitated from acid solution by oxalic acid, with ignition each time to the oxide. An examination of the arc spectrum of the material with a Littrow quartz spectrograph failed to reveal impurities of other rare earths, or of any of the common elements.

A further question as to the purity of the material was raised after electroscopic measurements on 0.5-gram samples showed that natural

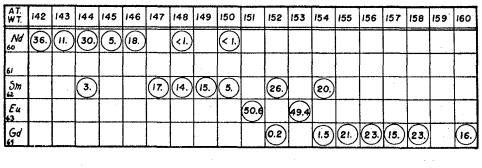

FIG. 1. Stable isotopes with their relative abundance.

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[1] S. Sugden, Nature **135**, 469 (1935).

[2] J. K. Marsh and S. Sugden, Nature **136**, 102–3 (1935).

[3] G. v. Hevesy and H. Levi, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. **14**, No. 5 (1936); also Nature **136**, 103 (1935), **137**, 185 (1936).

[4] M. L. Pool and L. L. Quill, Phys. Rev. **53**, 437–46 (1938).

radioactivity, with an intensity of the order of magnitude of the natural leak of the measuring instrument, was present before bombardment. Tests on larger samples of the europium oxide resulted in the identification of traces of mesothorium, radiothorium, thoron, and subsequent members of the natural thorium series, and a method was devised to remove all detectable natural radioactivity. The method of Kaufman[5] was used, in which a small amount of europium iodate was precipitated to act as a carrier for the less soluble thorium iodate. This was followed by the precipitation in the solution of barium sulfate to act as a carrier of radium and lead isotopes. By repeating this process, and finally reprecipitating the europium, a quantity of material was prepared in which no natural activity of any kind could be detected. This europium oxide was then used for all further experiments.

Deuterons were accelerated in the cyclotron, where a beam of from 10 to 20 microamperes at 7 Mev was usually available for direct bombardments. For the production of neutrons, beryllium was bombarded with larger currents of deuterons at somewhat lower energy.

Measurements of the radioactivity were made with a Lauritsen type electroscope. The sensitivity of this instrument was frequently checked with a standard uranium oxide source, and all readings were reduced to a constant sensitivity.

The sign of the particles emitted and the energy of beta-rays were measured in a cloud chamber 12 inches in diameter, in a magnetic field uniform to about ± 0.5 percent over the volume of the chamber. The chamber was filled with hydrogen, and alcohol and water were used as condensable vapor.

Slow Neutron Activation

Europium oxide was surrounded by paraffin and exposed to neutrons from the cyclotron. The strongest activation was obtained in an exposure which lasted from August, 1938, to January, 1939, during which time the cyclotron was operating intermittently with varying efficiency. This sample showed a strong initial decay in the previously known period, here observed to be 9.4 ± 0.2 hours, and then further decay in an extremely long period. In six months following bombardment, the intensity has remained constant within the experimental error of about one percent. The sample now has an activity about sixty times as great as the background of the electroscope, and further measurements of the decay are being made.

To make certain that the long period activity was not due to remaining traces of the naturally-active contaminant, previously detected and removed, the sample, following bombardment, was dissolved in nitric acid and barium sulfate was precipitated in the solution. The sulfate precipitate carried with it less than one percent of the long period activity, whereas the same treatment had removed almost all of the beta-activity of the natural contaminant. The bombarded sample was also much more active than could be explained on the basis of a remaining trace of radioactive impurity. It may thus be concluded that both periods observed are due to isotopes of europium produced by the capture of slow neutrons. No periods shorter than the one of 9.4 hours could be detected, even in samples bombarded for much shorter intervals of time and measured within five minutes after bombardment.

If, following the work of Pool and Quill,[4] the 9-hour activity is assigned to Eu^{152}, the long period most probably belongs to Eu^{154}. The two observed slow neutron reactions are thus:

$$Eu^{151} + n^1 \rightarrow Eu^{152} + h\nu \qquad (1)$$

$$Eu^{153} + n^1 \rightarrow Eu^{154} + h\nu. \qquad (2)$$

The observation of a new, long-lived radioactive isotope, with its assignment to Eu^{154}, explains the results of Hevesy and Levi[3] and others who have found an abnormally high absorption in europium for slow neutrons without detecting the long period.

Radiations connected with both periods have been examined. The energy spectrum of the 9-hour beta-rays was measured in the cloud chamber in a field of 334 gauss. From a distribution of 840 tracks, the observed upper limit was found to be 1.83 ± 0.05 Mev. This is in agreement with the value of 2.0 Mev found by Hevesy and

[5] L. Kaufman, J. App. Chem. (U. S. S. R.) 9, 918–24 (1936).

Levi from absorption measurements, but does not agree as well with the value of 2.6±0.4 Mev reported by Naidu and Siday.[6] Subsequent to the present work, the authors supplied a sample of the material to Mr. A. W. Tyler, who has investigated the radiations in a magnetic spectrometer. His value of 1.885±0.012 Mev for the upper limit of the electron spectrum[7] is in good agreement with that reported here.

Absorption experiments on the 9-hour radiation showed that gamma-rays of at least two different energies accompanied the beta-rays. From absorption in aluminum, the softer component was found to have an energy of about 50 kev. If Eu^{152} decayed to Sm^{152} by the capture of a K electron as well as to Gd^{152} by the emission of a beta-particle, the K radiation expected from samarium would have approximately the observed energy. Samples of europium were furnished to Dr. J. R. Richardson, who made a study of the gamma-radiation in the cloud chamber. His results[8] show gamma-ray lines at 45 kev, 0.31 Mev, and 0.9 Mev, and he has concluded that the K-electron capture is a probable process in the decay. Tyler[7] has also found these gamma-ray lines, and in addition three other lines, some of which are internally converted, and which may account in part for the presence of K radiation. It is not yet clear whether the higher energy gamma-rays are associated with an electron capture or with the beta-decay process.

The two decay mechanisms, represented by the equations

$$Eu^{152} \rightarrow Gd^{152} + e^-, \quad (3)$$

$$Eu^{152} + e^- \rightarrow Sm^{152} + h\nu + \text{neutrino}, \quad (4)$$

are in accord with the behavior predicted by Sizoo[9] for three isobaric nuclei of consecutive atomic number, the first and third of which are stable, and the second beta-radioactive.

Radiations from the long period of Eu^{154} have not been studied so completely. The particles emitted were found to be negative electrons, and gamma-radiation was also found to be present. Absorption measurements in aluminum showed that the beta-rays have an upper limit of 1.0±0.1 Mev, and this value has been confirmed by preliminary cloud-chamber measurements. The energy of the gamma-radiation has not been measured because of the low intensity available. Analogous considerations to those above suggest that Eu^{154} may also decay both by the emission of beta-particles and by the capture of K electrons. In this case also, the two product nuclei, Gd^{154} and Sm^{154}, are stable isotopes.

Deuteron Activation

Europium oxide was bombarded with deuterons for periods ranging in length up to about five hours. With the usual currents, this represented a maximum of less than 100 microampere-hours, at from 6 to 7 Mev.

Following bombardment, europium was separated chemically from other elements which might be formed. This was done by passing a solution of europium chloride through a Jones reductor, in which zinc and dilute acid reduced the trivalent europium to its bivalent form, from which it could be precipitated as $EuSO_4$, which is insoluble. The reduction process is a specific separation of europium from almost all other rare earth elements, since other members of the group can be reduced only with much greater difficulty, if at all. The nature of the separation and the conditions under which it is carried out have been described by McCoy.[10] Lanthanum chloride was added before reduction

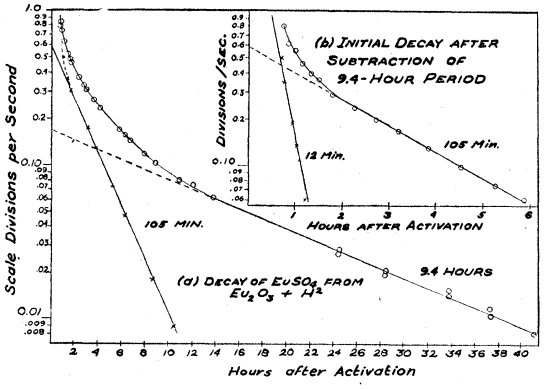

FIG. 2. Decay of Eu from Eu+H^2.

[6] R. Naidu and R. E. Siday, Proc. Phys. Soc. (London) **48**, 332–36 (1936).
[7] A. W. Tyler, Phys. Rev. **56**, 125–30 (1939).
[8] J. R. Richardson, Phys. Rev. **55**, 609–14 (1939).
[9] G. J. Sizoo, Physica **4**, 467–72 (1937).
[10] H. N. McCoy, J. Am. Chem. Soc. **58**, 1577–80, and 2279–81 (1936); **59**, 1131–2 (1937).

to serve as a carrier for the other rare earths, and was reprecipitated as the trivalent oxalate by the addition of oxalic acid, after the removal of the europous sulfate.

The decay of a sample of $EuSO_4$ from Eu_2O_3 activated by deuterons and separated in this way is shown in Fig. 2. The analysis shows three periods of decay: 9.4 ± 0.2 hours, 105 ± 5 minutes, and 12 ± 4 minutes. The decay of the unreduced fraction, which should contain any other rare earths produced by transmutation reactions, showed only these same three periods and in much lower intensity, probably due to small amounts of europium not completely reduced by the zinc.

To investigate whether the periods observed in the $EuSO_4$ were all due to isotopes of europium, the ratio of their initial intensities, corrected for an infinitely long bombardment time, was calculated and compared with the ratio extrapolated from the decay of a sample of europium oxide which was not treated chemically after bombardment. The corrected intensity ratio for the periods 9-hour : 105-minute : 12-minute, was found to be 1 : 1.5 : 10, within the limits of accuracy of the analysis, for both samples. Since the 9-hour period is known to be due to Eu^{152}, from work with neutrons, and since there was no detectable fractionation of the other two activities in the chemical separation, it seems most likely that all three are due to isotopes of europium. In addition, it may be noted that most isotopes in Gd or Sm, to which usual (H^2, n) and (H^2, α) processes from europium might lead, are stable or have known radioactive periods quite different from any of those observed here. This is in accord with the view that the periods observed are due to isotopes of europium.

Deuteron bombardments prolonged enough to produce the long period of Eu^{154} could not conveniently be performed, but the 9.4-hour period from deuteron activation was undoubtedly the same as that assigned to Eu^{152}. The two shorter lived isotopes produced by deuterons were not observed after neutron activation. Chemical evidence, which indicates that they are isotopic with the 9-hour radio-europium, suggests that they may be due to isomeric forms of Eu^{152} and Eu^{154} which, as shown, are produced much more easily by deuterons than by neutrons. It has not been possible to decide to which isotope each period belongs.

We are indebted to Professor H. N. McCoy for the europium oxide used, and to Professor J. M. Cork, Dr. B. R. Curtis, and to other members of the Department of Physics for their interest and cooperation in making the bombardments and the cloud-chamber studies. Mr. Norman Bauer and Mr. William H. Sullivan assisted in purifying the europium and in making cloud-chamber measurements. The investigation was made possible by a grant from the Horace H. Rackham Trust Fund.