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Radiations from Platinum (193) and Gold (199)*

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The 4-day platinum activity, Pt^{193}, was induced in metallic platinum irradiated by neutrons in the pile at Oak Ridge. This isotope was found to emit conversion electrons of energy 0.115 Mev and x-rays of energy 70 kev. Beta-gamma-coincidence measurements showed that the conversion electrons are coupled with little or no gamma-ray energy. Gamma-gamma-coincidences, probably gamma-(x-ray) coincidences, were found in Pt ^{193}.

Aluminum absorption gave a maximum energy of 0.38 Mev for the beta rays of the 3.3-day Au^{199}; lead absorption indicated gamma-radiation of energy 0.18 Mev. Beta-beta- and beta-gamma-coincidences were present in Au^{199}, but no gamma-gamma-coincidences were found. The absorption and coincidence measurements are combined to construct a disintegration scheme for Au^{199}.

1. INTRODUCTION

THE 4-day platinum (193) and the 3.3-day gold (199) were prepared when platinum was irradiated by slow neutrons in the pile at Oak Ridge. Platinum and gold were chemically separated, and the two fractions were subjected to further chemical purification. In the case of both isotopes, measurements of the energies of the beta- and quantum-radiations were carried out by coincidence and absorption methods which have been previously described.[1] For all coincidence measurements, a coincidence resolving time of 0.10 microsecond was employed.

2. PLATINUM (193)

It has been previously shown that the 4-day platinum period emits x-rays, gamma-rays, and soft beta-rays.[2-4] Krishnan and Nahum[3] have obtained a beta-ray energy of 0.12 Mev and have concluded from the shape of the absorption curve that only a line spectrum of conversion electrons is present. They also reported intense x-radiation and have concluded that the isotope decays by K-electron capture. More recently, Wilkinson,[4] has reached the same conclusion by bombardment of platinum by deuterons and fast and slow neutrons, and by bombardment of iridium by deuterons and alpha-particles. He has also reported x-rays, beta-rays of energy 0.1 Mev, and gamma-rays of energy 1.7 and 0.17 Mev.

The platinum fraction of the present experiments was chemically purified for the removal of iron, copper, iridium, and gold. The data of Fig. 1, an absorption curve of the beta-rays of the platinum fraction, were taken eleven days after removal of the platinum from the pile and five days after chemical purification. From the figure, it is clear that the conversion electrons of Pt^{193} have a maximum range of 0.018 g/cm^2 in aluminum, corresponding to an energy of 0.115 Mev.[5] In addition, it is also evident that a continuum of beta-rays having a visual end point at about 0.16 g/cm^2 of aluminum is also present. Feather analysis yielded an end point at 0.18 g/cm^2, corresponding to an energy of 0.56 Mev.[5] This continuum was attributed to the presence of Ir^{192}, indicating an incomplete chemical separation.

The beta-gamma-coincidence rate for Pt^{193} and accompanying iridium contamination is shown in Fig. 2 where it is seen to reach a constant value in the region of 0.018 g/cm^2 of aluminum placed before the beta-ray counter. The low value of the beta-gamma-coincidence rate at very low absorber thickness is attributed to the presence of the conversion electrons of Pt^{193} which are apparently coupled with less

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[1] C. E. Mandeville and M. V. Scherb, Phys. Rev. **73**, 141 (1948).

[2] E. McMillan, M. Kamen, and S. Ruben, Phys. Rev. **52**, 375 (1937).

[3] R. S. Krishnan and E. A. Nahum, Proc. Camb. Phil. Soc. **37**, 422 (1941).

[4] Geoffrey Wilkinson, Phys. Rev. **73**, 252 (1948).

[5] L. E. Glendenin, Nucleonics **2**, No. 1, 12 (1948).

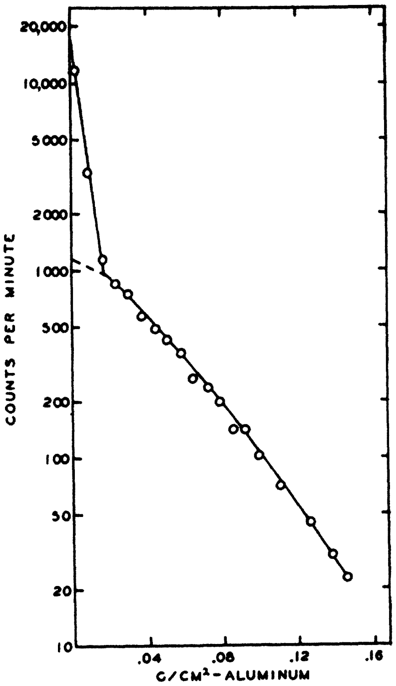

FIG. 1. Absorption in aluminum of the beta-rays of the 4-day Pt^{193}. The curve gives evidence of a line spectrum of conversion electrons of Pt^{193} superposed upon a continuum of low intensity. The continuum is ascribed to the 68-day iridium (192), present as a contaminant.

gamma-ray energy than the nuclear beta-rays of the 68-day iridium contamination. The beta-gamma-coincidence measurements are particularly sensitive to the presence of very small quantities of contamination, since beyond 0.018 g/cm² of aluminum, only the beta-rays of iridium (192) reach the beta-ray counter. The two geometries, *A* and *B*, of Fig. 2 were calibrated by the beta-gamma-coincidence rate of Sc^{46}. It was thus found that on the average, each beta-ray of the contaminant was followed by 0.6 Mev of gamma-ray energy, a known characteristic of Ir^{192}. Furthermore, as the 4-day Pt^{193} continued to decay, the points on the beta-gamma-coincidence curve below 0.018 g/cm² were found to rise to the level of the other points of the curve.

From the beta-gamma-coincidence curve, it can be concluded that the conversion electrons of the 4-day platinum are accompanied by considerably less than 0.6 Mev of gamma-ray energy and probably by no gamma-rays at all. Wilkinson[4] has reported a gamma-ray of energy 1.7 Mev to be related to the 4-day period. This gamma-ray is obviously non-coincident with the conversion electrons. No search for gamma-rays of this energy was made in the course of the investigations described in this paper.

About twelve days after removal of the irradiated material from the pile and six days after chemical purification, a beta-beta-coincidence curve was obtained, using the platinum fraction as a source. These data are given in Fig. 3. The curve is seen to have a peak in the vicinity of 0.018 g/cm² of aluminum. This curve is actually the beta-beta-coincidence curve for the 68-day iridium contamination, the first two points being reduced in magnitude by the presence of the conversion electrons of the 4-day platinum which are apparently not coupled with other beta-rays.†

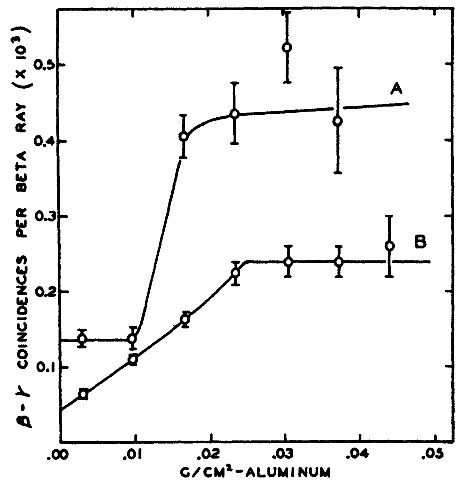

FIG. 2. Beta-gamma-coincidence curve for the platinum fraction. The coincidence rate below 0.018 g/cm² is reduced, owing to the presence of the conversion electrons of Pt^{193}. Beyond this value of absorber thickness, the beta-gamma-coincidence rate indicates that each beta-ray is followed by 0.6 Mev of gamma-ray energy, a characteristic of Ir^{192}. Since the conversion electrons of Pt^{193} are completely stopped by 0.018 g/cm² of aluminum, the remainder of the curve is very sensitive to the presence of any contamination, however small.

Curve *A* was taken with 0.2 g/cm² of aluminum before the gamma-ray counter whereas curve *B* was taken with 2.16 g/cm² of aluminum before the gamma-ray counter. The increased coincidence rate owing to the reduced absorber thickness before the gamma-ray counter simply indicates that the gamma-rays involved are for the most part relatively soft. Both geometries were calibrated by the beta-gamma-coincidence rate of Sc^{46}.

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† In making the beta-beta coincidence measurements, the aluminum absorbers were placed before *both* of the beta-ray counters.

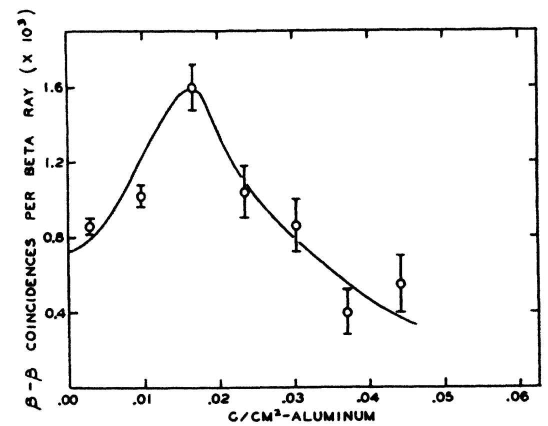

FIG. 3. Beta-beta-coincidence rate of the platinum fraction. As in the case of the beta-gamma-curve of Fig. 2, this curve is in reality characteristic of Ir^{192}. Instead of being purely exponential as is actually the case, the points below 0.018 g/cm² are reduced by the presence of the conversion electrons of Pt^{193} to give a "peaking" effect in the curve.

During the early stages of the experiment when the 4-day platinum was the predominant activity, a small amount of the platinum fraction was placed between two gamma-ray counters, each shielded by 0.2 g/cm² of aluminum. A gamma-gamma-coincidence rate of $(0.30\pm0.02)\times10^{-3}$ coincidence per gamma-ray was measured. These were very probably gamma-(x-ray) coincidences and (x-ray)-(x-ray) coincidences.

Absorption of the gamma radiation of Pt^{193} in lead revealed the presence of x-rays having an energy of about 70 Kev.

Finally, in order to ascertain positively that the long period beta emitting contamination was the 68-day iridium (192), the iridium fraction separated from the irradiated platinum metal was purified for the removal of palladium and rhodium. The purified iridium thus obtained gave a maximum beta-ray energy of 0.56 Mev, a beta-gamma-coincidence rate corresponding to 0.6 Mev of gamma-ray energy coupled with each beta-ray, and a beta-beta-coincidence curve, exponential in form, and identical in shape and absolute magnitude with that of Ir^{192} prepared by irradiation of IrO_2 by slow neutrons. These last separations and measurements show conclusively that the contamination was Ir^{192}.

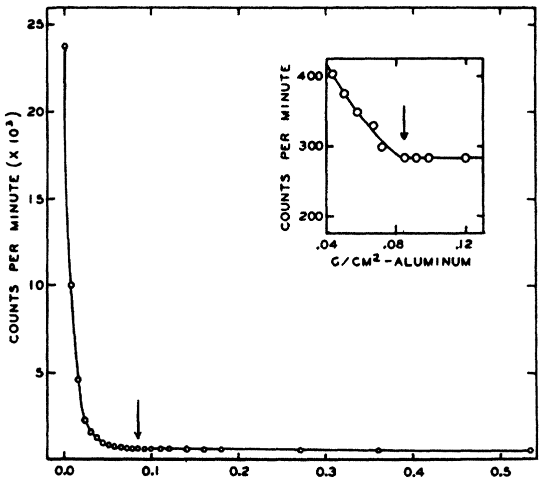

FIG. 4. Absorption in aluminum of the beta-rays of gold (199).

3. GOLD (199)

When platinum is irradiated by slow neutrons, the thirty-minute platinum parent of Au^{199} is formed. The 3.3-day Au^{199} was chemically separated from the platinum activities present, and the nuclear beta-rays were absorbed in aluminum as shown in Fig. 4. The visual limit is 0.085 g/cm², corresponding to 0.32 Mev.[5] A Feather plot gave a maximum beta-ray energy of 0.38 Mev. These beta-rays have been previously reported as "extremely soft"[2] and as of "several hundred kilovolts"[6] energy. Absorption of the gamma-radiation in lead gave evidence of a single gamma-ray having a quantum energy of 0.18 Mev. The beta-gamma-coincidence rate, shown in Fig. 5, was found to be 0.04×10^{-3} coincidence per beta-ray independent of the beta-ray energy, suggestive of a simple spectrum. No gamma-gamma-coincidences were observed in the gold fraction.***

Beta-beta-coincidences were observed in the disintegration of Au^{199}, indicating that the nuclear beta-rays are followed by a partially converted gamma-ray. The beta-beta-coincidence rate is plotted in Fig. 6 where it is seen to drop

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[6] R. Sherr, K. T. Bainbridge, and H. H. Anderson, Phys. Rev. 60, 473 (1941).

*** It is here meant that within the sensitivity of the method, no gamma-gamma-coincidences were observed. Gamma-gamma-coincidences between gamma-rays of very low energy (0.1 Mev or less) might have escaped detection owing to the low quantum efficiency of the gamma-ray counters for radiations of that energy.

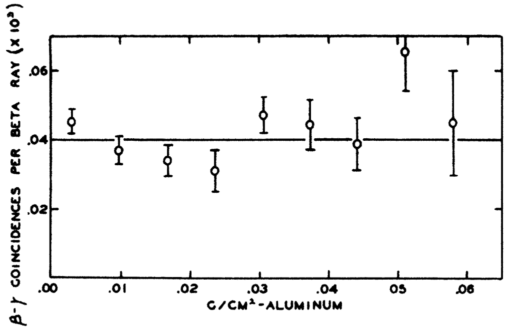

FIG. 5. Beta-gamma-coincidence rate of gold (199) as a function of the surface density of aluminum placed before the beta-ray counter.

to zero in the vicinity of 0.025 g/cm^2 of aluminum, corresponding to a conversion electron energy of about 0.135 Mev. Extrapolation to zero absorber thickness of the beta-beta- and beta-gamma-coincidence rates on a semi-logarithmic plot yielded a conversion coefficient of 26 percent.[††]

The coincidence rates and radiation energies of Au^{199} suggest the disintegration scheme of Fig. 7.

Krishnan and Nahum[3] have reported beta-rays of energy 1.01 Mev, gamma-rays of energy 0.45 Mev, and a half-period of 2.6 days for Au^{199} produced by deuteron bombardment of platinum by the Cavendish cyclotron. The reaction would be

$$Pt^{198}+D\rightarrow Au^{199}+n.$$

It is now well known that the beta-rays of the 2.7 day Au^{198} have a maximum energy of 0.97 Mev[7] and that most of the gamma-rays have an energy of 0.41 Mev.[8] It seems probable, therefore, that the radiation energies and half-period assigned to Au^{199} by Krishnan and Nahum are actually those of Au^{198} formed, in the absence of a stable Pt^{197}, by the reaction

$$Pt^{198}+D\rightarrow Au^{198}+2n.$$

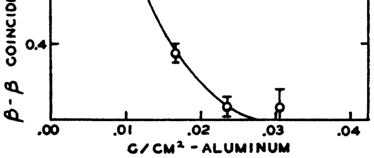

FIG. 6. Beta-beta-coincidence rate for gold (199).

APPENDIX I: CHEMICAL PROCEDURE FOR THE SEPARATION AND PURIFICATION OF GOLD AND PLATINUM

About one-half gram of irradiated metallic platinum was dissolved in *aqua regia*. After expelling the nitric acid by repeated evaporation with hydrochloric acid, the residue was dissolved in one cc of HCl. About 60 mg of gold (as $AuCl_3$ in solution) was added and diluted to 20 cc. The gold was precipitated with SO_2, filtered off, and washed with 0.1N–HCl. The precipitated gold was again dissolved in *aqua regia*; the nitric acid was removed by several evaporations with HCl. The residue was dissolved in 3 cc of HCl, 3 drops of H_2SO_4, and 75 cc of H_2O. The gold was precipitated with oxalic acid and washed with 0.1N–HCl. The precipitated gold should have been free of other metals.

The filtrate of the first precipitation, containing the platinum, was evaporated to dryness with nitric acid and gently ignited. After dissolving in *aqua regia* and destroying the nitric acid, the residue was dissolved in 1 cc of HCl, 9 cc of H_2O, and 4 cc of alcohol. The platinum was precipitated with ammonium chloride as $(NH_4)_2PtCl_6$. This precipitate was thoroughly washed with a 20 percent NH_4Cl solution. The washed precipitate was then decomposed by boiling with ammonium formate solution, and the resulting platinum was thoroughly washed with hot water. It was then boiled with HCl to remove soluble metals. The platinum was again dissolved in *aqua regia*, evaporated with HCl to destroy the HNO_3, and precipitated as $(NH_4)_2$-

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[††] This estimate may be regarded only as approximate. The ratio $(N_{\beta\beta}/N_\beta)/(N_{\beta\gamma}/N_\gamma)$ from which the conversion coefficient is calculated, is undoubtedly influenced to some extent by coincidences between nuclear beta-rays or conversion electrons and the hard x-rays of mercury which are emitted after internal conversion.

[7] P. W. Levy and E. Greuling, Phys. Rev. **73**, 83 (1948).

[8] K. Siegbahn, Proc. Roy. Soc. **A189**, 527 (1947).

$PtCl_6$. This was subsequently decomposed to platinum metal. The same procedure was repeated a third time in an attempt to prepare platinum entirely free of iron, iridium, gold, and copper.

APPENDIX II: CHEMICAL PURIFICATION OF THE IRIDIUM FRACTION

The filtrate from the $(NH_4)_2PtCl_6$ precipitation contained any iridium present, including some added as a carrier before the precipitation with NH_4Cl. Small amounts of palladium and rhodium were added, the solution diluted to 400 ml, and the palladium precipitated with dimethylglyoxime. After standing one hour, the precipitate was separated by filtration and washed with dilute (1:99) HCl and hot water. To the filtrate was added sodium nitrite, then Na_2CO_3 to make the solution neutral. After boiling, the solution was slightly acidified and Na_2S solution added to precipitate rhodium sulfide. The filtrate containing iridium was made alkaline with Na_2CO_3 and iridium sulfide was precipitated with Na_2S. The iridium precipitate was washed and ignited.

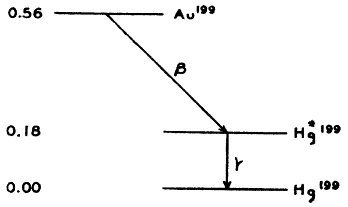

FIG. 7. Disintegration scheme of gold (199).

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Second-Order Transformations in Two-Component Systems. Application to Solutions of He^3 in He^4

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A thermodynamic treatment has been made of a second-order transformation in two-component systems. In addition to the requirement that there be no heat of transformation and no volume change, it turns out that the composition is equal in the two phases. Equations have been developed for $(dT/dx)_P$, $(dx/dP)_T$, and $(dP/dT)_x$ along the equilibrium curves. If we assume that the transformation of liquid helium remains second-order on the addition of a mole fraction x of He^3 to a He^4 solution, then for the limit of very dilute solutions

$$(dT/dx)_P=21 \text{ deg.} \quad \text{and} \quad (dx/dP)_T=6\times10^{-4} \text{ atmos.}^{-1}.$$

I. INTRODUCTION

IN order to give a thermodynamic treatment of the change in temperature of the lambda-point of liquid helium with pressure, Ehrenfest[1] was led to the concept of thermodynamic transitions of higher order. In the usual phase transitions there is a discontinuity in the temperature and pressure derivatives of the free energy (the entropy and volume, respectively) but the free energy is equal in the two phases. Such a transformation was called first-order by Ehrenfest. At the lambda-point of liquid helium the free energy and its first derivatives are equal on both sides of the transformation but there is a discontinuity in the second derivatives of the free energy in crossing a line in the pressure-temperature plane along which the transformation occurs. This was called a transformation of the second order. Similarly, a transformation of the *n*th order is one in which a discontinuity first appears in the *n*th derivative of the free energy.

Recent experimental investigations of the properties of dilute solutions of the isotope He^3 in ordinary helium make it of interest to investigate the thermodynamics of higher order transitions in systems of more than one com-

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[1] P. Ehrenfest, Comm. Leiden Suppl. No. 75b.