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A Microcalorimetric Determination of the Mean Energy of β-Rays from Radium E*

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A very precise microcalorimetric method of determining the mean energy of Ra E β-rays is described. The method involves an adiabatic change of temperature of a small calorimeter whose heat capacity is measured by determining the change in temperature produced by several strong sources of polonium. With the aid of Mme. P. Curie's absolute apparatus, the absolute value of the polonium content in these sources as well as in the Ra E samples after the decay of the parent substance could be determined with an accuracy of from 1 to 2 percent. The average value of the β-ray mean energy of Ra E deduced from these experiments is 320,000 $\pm$5000 ev. The measurements made in air gave a mean energy of 323.6$\pm$3.5 kev, or slightly higher than those carried out in nitrogen (317.6$\pm$2.5 kev). It has been pointed out that the most probable value is nearer the lower limit. The results have been compared with those derived from other calorimetric determinations as well as with the values calculated from β-ray spectra of Ra E established by different authors.

I. INTRODUCTION

THE total or mean energy of β-rays from radioactive bodies may be determined by integration of the continuous spectrum of emitted electrons or by calorimetric measurements. The chief advantage of the first is that the mean energy may be calculated independent of both the amount of radioactive substance present and the number of electrons emitted by each disintegrating atom. Its accuracy is, however, limited by the correctness of the energy distribution curve for electrons escaping from the parent nuclei. In the calorimetric method, the total energy evolved in the form of heat by the emitted radiation is measured independently of secondary processes and with the same precision for slow and fast particles. If β-rays alone are emitted, the results depend only on calorimetric measurements, which now may be made with an error of about 2 percent.[1] Ra E is suitable for calorimetric study, as its β-activity is not accompanied by any other radiation of appreciable intensity,[2] its initial quantity can always be determined with very great accuracy by measuring the polonium accumulated in the source and finally it appears[3] certain that each Ra E atom emits one electron per disintegration.

Early determinations of the mean energy of disintegration of Ra E by the calorimetric method yielded values from 3.44 to 3.37×10^5 ev with errors of 10 to 15 percent.[4, 5] More precise measurements with improved technique and stronger Ra E sources seemed desirable.[6]

II. EXPERIMENTAL PROCEDURE

Preparation of Ra E sources

The Ra E was prepared from radio-lead from Joachimstahl pitchblende by Foucauld's extraction method.[7] The Ra E is practically free of radioactive impurities other than polonium, and can be further purified by spontaneous deposition on nickel or by electrolysis with Pt electrodes in

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* The above work was carried out jointly with M. Lecoin during the school year 1938–39 [see M. Lecoin and I. Zlotowski, Nature **144**, 440 (1939)]. Because of the exigencies of war, the writer was not able, despite many attempts, to reach M. Lecoin and as a result some details and data of the electrometric measurements, as well as a discussion of the discrepancies between the determinations of the mean energy values for Ra E β-rays and the value obtained in former work by M. Lecoin had, of necessity, to be omitted. It is sincerely hoped that M. Lecoin will be in a position to publish these data in a separate publication at some later date.

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[1] See I. Zlotowski, J. de phys. et rad. [7] 6, 242 (1935).

[2] According to S. Bramson [Zeits. f. Physik **66**, 721 (1930)] there is from 0.25 to 0.5 γ per 100 Ra E atoms and from the recent work of G. v. Droste [Zeits. f. Physik **104**, 335 (1937)] it may be stated that the total γ-ray energy per disintegration ($h\nu > 0.3$ mC^2) represents less than 0.004 percent of the mean energy of β-rays.

[3] N. Riehl, Zeits. f. Physik **46**, 478 (1928).

[4] C. D. Ellis and W. A. Wooster, Proc. Roy. Soc. **A117**, 109 (1927).

[5] L. Meitner and W. Orthmann, Zeits. f. Physik **60**, 143 (1930).

[6] A preliminary report has been published by M. Lecoin and I. Zlotowski, Nature **144**, 440 (1939).

[7] P. Foucauld, J. chim. phys. **29**, 479 (1932).

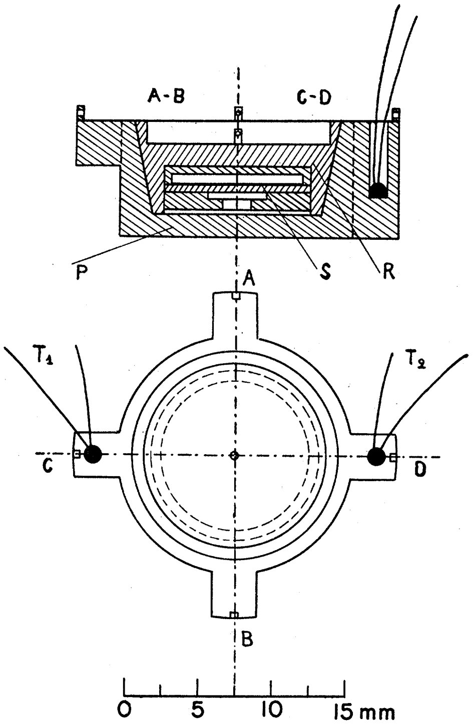

Fig. 1. Calorimeter in which source (*S*) of Ra E was placed.

the presence of tartaric acid. The removal of Po was then effected by deposition on silver leaves. The final solution thus purified was either evaporated in an atmosphere of argon, or electrolyzed onto one side of a nickel cathode which was later used as the source support in the calorimeter. Two sources were prepared containing about 45 and 80 millicuries of Ra E, respectively. The Po content in both the sources was less than 300 e.s.u.

Calorimetric method

The method, an adaptation of Swietoslawski's adiabatic microcalorimeter,[8] involves the maintenance of the same temperature of the calorimeter and the surrounding water bath. The difference of temperature of bath and calorimeter never exceed 0.001°C. If, then, the heat capacity of the calorimeter is determined and its increase in temperature measured by determining the change of temperature in the sourrounding bath, the amount of heat produced by the radiation can be calculated.

The calorimeter (Fig. 1) was used as an absorbing shield for all rays emitted by the source and consisted of a hollow nickel cylinder *P* suspended by means of four silk threads inside the calorimetric vessel and of a well-fitted cover *R*, whose function was to allow introduction of the small disks *S* of nickel with the radioactive deposits. Although the mass of the calorimeter was small (about 10 g) no rays emitted by the source could escape from the calorimeter without passing through at least 3 mm of nickel, a thickness quite satisfactory for a practically complete stoppage of Po α-rays and Ra E β-rays.[9] The calorimetric cylindrical vessel (about 18 cm in diameter) containing the calorimeter was surrounded by water in a closed tank about 75 cm in diameter.

The adiabatic equilibrium in our experiments was rigorously controlled by means of two copper-constantan thermocouples, the junctions of which were placed in the calorimeter mass and in the walls of the surrounding vessel. The junctions were separated from the source by at least 4 mm of nickel to avoid eventual influence of the thermoelectric circuits by β-rays. A Zernicke type galvanometer with a sensitivity of 1.8×10^{-8} volt per mm at 2 m, which corresponded to 0.0005°C, was used with the thermocouple. An equilibrium between the surrounding bath and the calorimeter was maintained by adding hot water through a pipe with numerous small openings at the bottom of the tank. Saturated air bubbling through the tank stirred the whole mass of water.

The temperature rise of the surrounding water, and therefore of the calorimeter, was determined by two carefully calibrated Beckmann thermometers. The calibration of these was carried out against an "ultra-Beckman" [10] in the same bath and under conditions identical with those

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[8] W. Swietoslawski and A. Dorabialska, Comptes rendus **185**, 763 (1927); W. Swietoslawski, Ann. de chim. **16**, 251 (1931); W. Swietoslawski and E. Bartoszewicz, Bull. Acad. Sci. Pol. A 1931, 336; W. Swietoslawski, Bull. Acad. Sci. Pol. A 1934, 80.

[9] The primary γ-rays are practically negligible (if they exist at all) and the secondary γ-rays in nickel, which represent about 2 percent of the energy emitted, are extremely soft. For details see: E. Stahel and J. Guillissen, J. de phys. et rad. [8] **1**, 12 (1940).

[10] According to *PTR* in Berlin, the accuracy of the temperature readings on the "ultra-Beckmann" was 2×10^{-4}°C.

in which the measurements were made. All temperatures are reported to the nearest 0.001°C.

Calorimetric measurements

The calorimetric capacity for each series of measurements was tested and determined by measuring the heat given off by several sources of polonium deposited on a nickel foil, the strength of which was near the amount of Po built up in the used Ra E source after the practically complete decay of the parent substance. The measurements with six sources of Po between 400 and 4000 e.s.u. (1 millicurie Po equals 1340 e.s.u.; solid angle 2π) yielded an increase of temperature of 0.0166°C per hr. for each 1000 e.s.u. of Po with no determination varying more than 0.0001° from the mean. It is obvious that the precision depends directly upon the accuracy of the electrometric evaluation of the Po source. By using the Mme. Curie absolute apparatus,[11] with its precision of 1 to 2 percent, it appears reasonable to assume that all calorimetric capacity values were correct to within 2 percent.

With precautions to obtain thermal equilibrium before readings were taken, Ra E sources of 40 to 80 millicuries were used and the temperature rise (0.2° to 0.4°C) over four-hour periods noted. Such sets of readings were made daily over a period of about 30 days until the parent Ra E had practically disappeared. The regularity of the curves when decrease in thermal effect is plotted against the time (Fig. 2) best indicates the accuracy of all the measurements. However, in each set of experiments the values found in the first 36 hours were systematically high. Since the first set was carried out in air, it was supposed that supplementary effects had been produced by some chemical reactions with oxygen. Hence, a second series of measurements was carried out in an atmosphere of nitrogen, but despite this precaution the effect was not suppressed. The actual explanation of this phenomenon is given later.

Method of calculation

In calculating the mean energy for Ra E β-rays, the Po content at the beginning, and the contribution of the Po formed later, must be taken into account. If X denotes the number of millicuries of Ra E, Y the number of millicuries of Po present in the Ra E deposit at the moment of its final purification, and C the heat capacity of the calorimeter, the mean energy of disintegration of a Ra E atom ($E_{\mathrm{Ra\,E}}$ in kev) may readily be calculated for each calorimetric measurement by means of the following equation:

$$
\begin{aligned}
Q = C\cdot\Delta T_t = {} & k_1\cdot X\cdot\exp(-\lambda_{\mathrm{Ra\,E}}\cdot\theta)\cdot E_{\mathrm{Ra\,E}} \\
& + k_2\cdot Y\cdot\exp(-\lambda_{\mathrm{Po}}\cdot\theta)\cdot E_{\mathrm{Po}} \\
& + k_3\cdot X\Bigg[\frac{1-\exp(-\lambda_{\mathrm{Po}}\cdot t)}{\mathrm{Po}}\cdot\exp(-\lambda_{\mathrm{Po}}\theta) \\
& \quad -\frac{1-\exp(-\lambda_{\mathrm{Ra\,E}}\cdot t)}{\mathrm{Ra\,E}}\cdot\exp(-\lambda_{\mathrm{Ra\,E}}\cdot\theta)\Bigg]\cdot E_{\mathrm{Po}},
\end{aligned}
$$

where ΔT_t is the temperature rise during time t, θ the age of the source (i.e., the time elapsed between its preparation and the starting moment of the measurement), E_{Po} the disintegration energy of Po (per atom), and k_1, k_2 and k_3 numerical constants depending upon the units of measurement used. The value of E_{Po} is taken as 5.4×10^6 ev.[12]

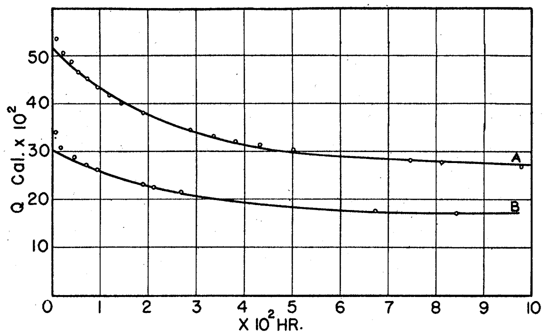

FIG. 2. Diagram of the heat evolution from Ra E sources. Curve A, Ra E source of 80 mC. Curve B, Ra E source of 45.5 mC.

The quantity Y of Po present at any moment in the Ra E source can also be determined by Mme. Curie's absolute apparatus after all the β-rays are deflected by a sufficiently strong magnetic field. Careful consideration of the errors in the determination of Y, which never exceeded

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[11] Mme. P. Curie, J. chim. phys. **22**, 142 (1925).

[12] G. H. Briggs, Proc. Roy. Soc. **A143**, 604 (1934); G. Mano, Ann. de physique **1**, 504 (1934).

300 e.s.u., and of the absorption of α-rays in the active deposit itself showed that in the experiments carried out with strong Ra E sources, both suggested sources of error do not affect the accuracy of our measurements.

Determination of Ra E

The electrometric measurements of Ra E based on β-ray ionization measurements carried out with the so-called P chamber (for penetrating radiation) suggested by Mme. Curie,[13] yielded results with a probable error of about 5 percent. Nevertheless, taking into account the difficulties of calibration of this chamber, it is reasonable to expect that the actual systematic error in all the evaluation may be much greater. The calorimetric determination is believed to be much more accurate.

If Y, the initial amount of polonium in the radioactive deposit is known, the calorimetric measurement of the amount of Po at the end of the experiments permits the evaluation of the quantity X of Ra E, present at the beginning of the experiment to within 1 or 2 percent. Therefore, calculations have been effected in each case with several values of Y, all within the limits fixed by the accuracy of the electrometric determinations of Po, as well as by the eventual absorption of α-rays by the radioactive Ra E deposit.

Thus, for source No. 1, where no trace of Po was found at the beginning, calculations carried out, with $Y=0$, 55 and 110 e.s.u., gave the following values for X: 81.5, 80.0 and 78.9 millicuries, figures not very far off from those obtained by electrometric determination (78.5 mC). Taking into account the precision of the calorimetric measurements, we finally adopted 80 mC as the most probable value.

TABLE I. *Temperature of surrounding water bath.*

Source No. 1 Experiment on April 2, 1939			Source No. 2 Experiment on June 23, 1939		
	Temperature			Temperature	
Time p.m.	Thermometer I	Thermometer II	Time p.m.	Thermometer I	Thermometer II
4:00	2.736°C		7:30	2.814°C	
4:10		2.743°C	7:45		2.817°C
4:30	2.776		8:00	2.832	
4:45		2.784	8:15		2.835
5:00	2.817		8:30	2.850	
5:15		2.824	8:45		2.854
5:30	2.859		9:00	2.868	
5:45		2.865	9:15		2.872
6:00	2.899		9:30	2.887	
6:15		2.907	9:45		2.891
6:30	2.940		10:00	2.905	
6:45		2.947	10:15		2.910
7:00	2.982		10:30	2.925	
7:15		2.988	10:45		2.928
7:30	3.022		11:00	2.943	
7:45		3.029	11:15		2.947
8:00	3.062		11:30	2.961	
8:15		3.069	11:45		2.965
ΔT (4 hr.)	0.326	0.326	ΔT (4 hr.)	0.147	0.148
	0.326°C			0.147_5°C	

With source No. 2, where 233 e.s.u. of Po were found to be present at the beginning of the experiment by direct electrometric measurement, similar calculations, with the following values for Y: 233, 270, and 300 e.s.u. gave 46.2, 45.5, and 44.9 millicuries, respectively, for the value of X. For reasons discussed above, the following values were adopted: 45.5 mC for X and 270 e.s.u. (0.202 mC) for Y.

Determination of the Ra D content in the Ra E sources

Because of the carefully controlled purification of the Ra E sources, it was almost certain that they would be practically free from any trace of Ra D. Nevertheless, a series of calculations were carried out, based on data from our electrometric and calorimetric measurements, in order to confirm these expectations, as well as to establish in what proportion very small amounts of Ra D could affect the final results of our determinations. Calculations show that all measurements made during the first 30 days are quite independent of the presence of less than 1 percent Ra D. The fact that the results of our measurements conform, within an experimental error of about 3 percent, with those obtained in longer experiments (50 and 80 days) is evidence for assuming that the Ra D content in our Ra E sources was always below 1 percent.

III. EXPERIMENTAL RESULTS

Typical data are shown in Table I. These indicate the consistency of our measurements. The measurements made during the first 24 to 36 hours after the last purification of the source give values for $E_{\text{Ra E}}$ which are systematically too high. The measurements made in air (mean value: 323.6±3.5 kev) are also slightly higher than those made in nitrogen (mean value: 317.6±2.5 kev) and less coherent. It appears at first that the observed discrepancies are due to

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[13] I. Curie, J. chim. phys. **22**, 471 (1925).

TABLE II. *Experimental data. Source No. 1* (*X*=*80 mC of* Ra E; *Y*=*55 e.s.u. of* Po. *Last elimination of* Po *on March 27, 4* P.M.). *For the significance of all symbols see section, Method of calculation.*

No.	Thermo-couple	Date of the Experiment	θ Hours	ΔT_4 $\times 10^3$	Q Cal. $\times 10^2$	B Cal. $\times 10^2$	C Cal. $\times 10^2$	A Cal. $\times 10^2$	$E_{\mathrm{Ra\,E}}$ kev
1	I	Mar. 28, 0.00	8.0	435	53.43	0.461	1.790	51.18	336.5
2	I	Mar. 28, 3.30 P.M.	23.5	411	50.50	0.460	4.288	45.75	329.2
3	I	Mar. 29, 9.30 A.M.	41.5	397	48.80	0.459	6.903	41.44	330.7
4	II	Mar. 29, 10.00 P.M.	54.0	380	46.66	0.457	8.582	37.62	322.9
5	II	Mar. 30, 4.00 P.M.	72.0	369	45.31	0.455	10.75	34.01	323.9
6	II	Mar. 31, 3.00 P.M.	95.0	354	43.47	0.453	13.20	29.82	324.1
7	II	Apr. 1, 4.30 P.M.	120.5	339	41.63	0.452	15.56	25.62	322.7
8	II	Apr. 2, 4.00 P.M.	144.0	326	40.03	0.449	17.42	22.16	319.8
9	I	Apr. 4, 3.00 P.M.	191.0	310	38.07	0.444	20.41	17.22	326.1
10	I	Apr. 8, 3.30 P.M.	287.5	282	34.62	0.435	24.29	9.89	326.5
11	I	Apr. 10, 4.00 P.M.	336.0	272	33.41	0.431	25.48	7.30	323.8
12	II	Apr. 12, 2.30 P.M.	382.5	263	32.30	0.427	26.26	5.61	321.0
13	II	Apr. 14, 4.00 P.M.	432.0	256	31.47	0.423	26.82	4.23	322.0
14	II	Apr. 17, 2.00 P.M.	502.0	248	30.53	0.417	27.27	2.84	323.5
15	I	Apr. 27, 9.00 P.M.	749.0	230	28.24	0.396	27.16	0.69	323.5
16	I	Apr. 30, 1.00 P.M.	813.0	226	27.75	0.391	26.93	0.47	326.5
17	I	May 7, 10.30 A.M.	979.5	218	26.77	0.378	26.21	0.18	324.3
								Mean value	323.6±5.0 kev

some secondary chemical phenomenon taking place either in the material of the source support or in the radioactive deposit under the action of the oxygen in the air, or to traces of some oxidizing agents not eliminated from the source by the preparatory treatment. This assumption seems to find confirmation in the fact that, after a comparatively short period of time, all measurements carried out during many subsequent days lead to $E_{\mathrm{Ra\,E}}$ values lying within experimental error.

Table II gives a summarized comparison of the results obtained in one set of measurements; the values A, B, and C contain the heat due respectively to Ra E, Po from initial contamination and Po built up by Ra E disintegration. Besides the first three measurements, the spread between the extreme values of $E_{\mathrm{Ra\,E}}$ is not greater than 2.2 percent. It is interesting to note that the accuracy of our determination seems to be practically independent of the amount of Ra E present in the source. As a matter of fact, the calculated $E_{\mathrm{Ra\,E}}$ values are pretty constant, although at the end of experiments the total heat effect due to Ra E represented only 0.5 percent of the initial heat evolution.

The fair agreement observed in our experiments shows that the Po accumulated in the Ra E sources does not give any additional heat effect of the type observed by Sanielevici in the case of very strong pure Po deposits.[14] Since the Po content in a Ra E source rises with the decay of the parent substance, a direct consequence of such an effect would be a systematic increase in the calculated mean values of the Ra E disintegration energy. Moreover, we have also verified with exactness that our Po sources, used for check calibration of the calorimeter, did not reveal any abnormal heat evolution.

IV. DISCUSSION AND INTERPRETATION OF RESULTS

The mean value of the energy of disintegration of Ra E, deduced from our measurements, is 320,000±5000 ev. If the amount of Ra E is expressed in millicuries, the heat effect due to the emitted β-rays is equal to 1.61±0.03 cal./mC of Ra E hr. As the measurements made in air and in the first 36 hours are always slightly higher, it would seem reasonable to suppose that the most probable value is nearer the lower limit of our final result. It is interesting to compare these results with other values obtained from calorimetric experiments carried out by other authors, as well as with the values calculated from the β-ray spectra established by various authors.

Ellis and Wooster[4] obtained by calorimetric methods values somewhat higher (350,000 ±40,000 ev) than ours. An analysis of their data and methods leads one to expect a value too high.

The various sources of error mentioned in the work of Meitner and Orthmann,[5] as well as the

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[14] A. S. Sanielevici, J. chim. phys. 33, 759 (1936).

strength of their Ra E deposits (1.7 and 4.0 mC), make it seem likely that the error of their measurements was substantially larger than 6 percent. The determination of Ra E, based on the ionization carried out in the presence of Po, could not be very precise. The evaluation of Po itself was not any more accurate than that of Ellis and Wooster. Moreover, in the same sets of measurements, the $E_{\mathrm{Ra\,E}}$ values varied from 325,000 ev to 355,000 ev, depending on the method used for the determination of polonium at the beginning of the experiments. These, with other calibration errors, lead one to expect an error of about 10 percent.

The integration of the continuous spectra of Ra E β-rays, obtained by various workers, leads to an average energy value differing little from 330,000 ev. The most probable value given by Sargent,[15] as a result of an analysis of all experimental papers published between 1915 and 1933, is 340,000 ev. Recently, Neary[16] found a similar figure from a new experimental study of β-ray distribution. However, it should be pointed out that the first precise evaluation made by Magdwick,[17] by means of magnetic focusing and an ionization chamber, gave 395,000 ev for $E_{\mathrm{Ra\,E}}$, Scott[18] found $E_{\mathrm{Ra\,E}}=400{,}000$ ev by using a Geiger counter, and Ho and Wang[19] found $E_{\mathrm{Ra\,E}}$ equal to 401,000 ev from measurements on Wilson cloud-chamber tracks. In both of these studies the high mean energy values are accompanied by an evident over-emphasis of the high velocity limit determinations ($H_{\max}=6600$ and 7500 g cm, respectively).

On the other hand, Alichanow, Alichanian and Dzelepow,[20] using a magnetic focusing arrangement with Geiger-Müller counters, found $E_{\mathrm{Ra\,E}}$ equal to about 300,000 ev, and more recently Lecoin[21] deduced a value of 250,000 ev from measurements of the magnetic curvature of Wilson tracks, which figure seems to be too low. A comparison of our calorimetric results with those based on the study of the β-ray spectra leads to the conclusion that the number of electrons with energies below the average limit fixed by spectral analysis (20–50 kev) must be very small, and that certainly no more than 1 or 2 percent of the β-ray energies lie below 1 Mev.

It is to be noted that the mean energy of Ra E disintegration calculated by Martin and Townsend[22] in 1939, by careful investigation of the β-ray spectrum, was equal to 321,000 ev, and the very precise energy distribution (down to 5 kev) published by Flammersfeld,[23] after our work was completed, leads to a value of from 315,000 to 320,000 ev, which nearly agrees with our evaluation.

ACKNOWLEDGMENTS

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[15] B. W. Sargent, Proc. Roy. Soc. **A139**, 659 (1933).

[16] G. J. Neary, Proc. Roy. Soc. **A175**, 71 (1940).

[17] E. Magdwick, Proc. Camb. Phil. Soc. **23**, 982 (1927).

[18] F. A. Scott, Phys. Rev. **48**, 391 (1935).

[19] P. C. Ho and M. H. Wang, Chinese J. Phys. **2**, 1 (1936).

[20] A. I. Alichanow, Physik. Zeits. Sowjetunion **1**, 78 (1936); A. I. Alichanian, A. I. Alichanow and P. S. Dzelepow, Bull. Acad. Sci. USSR, Ser. Phys. [19] **5**, 375 (1938).

[21] M. Lecoin, J. de phys. et rad. [7] **9**, 81 (1938).

[22] L. H. Martin and A. A. Townsend, Proc. Roy. Soc. **A170**, 190 (1939).

[23] A. Flammersfeld, Zeits. f. Physik **112**, 727 (1939).