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New mass measurements of samarium and gadolinium and a mass table for the light rare earths*

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The 41-cm double-focusing mass spectrometer at the University of Minnesota has been used to measure the atomic masses of ^{152}Sm and ^{154}Sm and the isotopic mass differences of most Sm and Gd isotopes. Through the use of a new generalized error signal technique, measurements on the narrow doublets of Sm and Gd chlorides gave improved mass differences over previous work in this mass region. Where intense peaks were available, the results are consistent with errors of 0.4 to 1.0 μu. The conventional wide doublet technique was used to measured Sm-hydrocarbon doublets, yielding the masses of ^{152}Sm and ^{154}Sm with errors of less than 4 μu. This new mass data, when combined with other mass measurements and reaction data of comparable accuracy, is used in a least-squares mass adjustment in the range of 141 to 160 u.

[NUCLEAR STRUCTURE ^{152}Sm, ^{154}Sm measured atomic mass. Sm, Gd measured mass differences. Mass adjustment for $A = 141$ to 160.]

INTRODUCTION

In the past 20 years the precision of atomic mass and mass difference data has steadily increased. In the case of reaction data, improved techniques for the measurement of (n, γ) and β-decay reactions have produced several connections with errors in the range of 0.4 to 1.0 keV.[1] Mass spectrometric results have improved both as a result of new larger machines and because of refined measurement techniques. At Minnesota, beginning with the work of Benson, a 1 u mass doublet could be measured with an accuracy as high as 4 μu. Special mass doublets which give the differences ^{1}H, ^{2}H, and ^{37}Cl-^{35}Cl were measured to 0.03, 0.05, and 0.6 μu, respectively.[2] In the last few years improved instrumentation on the Minnesota machine has increased the consistency of wide doublet measurements by an additional factor of 2 or more. However, wide doublet measurements are most seriously affected by certain types of systematic errors, and in the light rare earths region this type of measurement has not given the best mass difference data. Those measurements at Minnesota exhibited unexplained disagreement between two or more independent mass difference measurements which must yield the same mass difference.[3] In order to further investigate these disagreements we have measured an additional set of metal-metal mass differences using narrow metal chloride doublets[4] and have remeasured selected metal-hydrocarbon doublets, from which the atomic masses of ^{152}Sm and ^{154}Sm are determined. These new measurements are described in the first part of this paper, and the resulting values are compared with presently available data. The final section discusses a new local least-squares mass adjustment which is based upon these new values.

INSTRUMENT

The basic mass spectrometer remains unchanged and has been described elsewhere.[5-7] However, certain adjustments and new instrumentation have improved the performance of the machine and will be mentioned briefly. Much of the existing electronics has been improved or replaced. As a result, system instabilities were minimal during the present measurements. All diffusion pumps were eliminated from the spectrometer tube to guard against the effects of oil films on conducting surfaces. A new Nicollet Instruments model 1062 instrument computer was installed to improve data collection efficiency. When the 1062 is run in the analog-to-digital mode it provides at least a factor of 100 improvement in signal averaging efficiency over the previous analyzer, so that the reproducibility of a measurement depends primarily upon the voltage divider error, the spectrometer resolution, and the statistics of the number of ions collected. Pulse counting electronics has been added and its use will be described later. This counting mode allows a direct determination of the collector current which was typically 10^4 to 10^5 ions/sec.

TECHNIQUE

Wide doublets

The wide doublet measurement technique has been described by Benson and Johnson.[2] The required voltage divider network was constructed by the same authors and has remained stable in time. With periodic calibration it gives a ratio $\Delta R/R$ which is known with an error of 1 ppm or $(0.02\ \Omega/\Delta R)$ ppm, whichever is greater. Operational checks of the spectrometer can be made through the measurement of known wide doublets. During the present work these checks included four runs of the doublet type $C_nH_n^+ - C_nH_{n-m}^+ = mH$ and two runs of the doublet type ${}^{A}Sm^{37}Cl^+ - {}^{A+2}Sm^{35}Cl^+ = {}^{37}Cl - {}^{35}Cl$. The average of the six mass checks indicates that any systematic error which is proportional to the doublet width must be 2 μu/u or less. The resolution, defined as the mass of the particular ion divided by the width of the peak at one-half maximum, was usually 150 000 to 200 000.

Narrow doublets

Using the standard error signal technique it is possible to measure wide doublets of up to 2 mass units with an accuracy of a few μu. For very narrow doublets a practical operating limit of this technique is reached when the tails of the ion peaks begin to overlap and confuse the error signal. For the Minnesota machine operating at mass 200, this limiting separation is about 4 to 5 mu. Metal chloride doublets in the rare earths region are typically 5 mu or less, as are some metal-metal narrow doublets, so that this technique cannot always be used with our instrument. A solution to the resolution problem was developed at this laboratory and has been previously noted.[8] The method requires that a mass doublet (or triplet) spectrum be stored in the 1062 memory and then read out to magnetic tape for off-line numerical resolution. A detailed description of the process will be the subject of a separate paper; however, the basic ideas are outlined in the remainder of this section.

If each peak in a mass spectrum is assumed to have an identical functional form $f(t)$, then the M-point spectrum may be described by a linear combination $g_N(t)$ of N such functions on $1 \leq t \leq M$, where

$$g_N(t) = f(t) + \sum_{j=1}^{N} A_j f(t - b_j),$$

$$b_1 \neq b_2 \neq \cdots \neq b_N \neq 0, \quad A_j > 0 .$$

If other contributions such as noise and baseline are present, they can be included in a term $r(t)$ and the total spectrum is represented by $G_N(t)$:

$$G_N(t) = g_N(t) + r(t) .$$

From $G_N(s)$, the Laplace transform of $G_N(t)$, one may derive what we wish to call a generalized error signal $H_N(t)$, defined by

$$H_N(t) \equiv \sum_{n=0}^{\infty} (-1)^n \sum \frac{n!}{n_1!\, n_2! \ldots n_N!} \times \left(\prod_{j=1}^{N} B_j^{n_j}\right) G_N(t - \vec{\beta}\cdot\vec{n}) ,$$

$$n_1 + n_2 + \cdots + n_N = n,$$

where $\vec{\beta}\cdot\vec{n} = \beta_1 n_1 + \beta_2 n_2 + \cdots + \beta_N n_N$, the B_j are approximations to A_j, and the β_j are approximations to b_j. $H_N(t)$ can be shown to obey the recursion relationship

$$H_N(t) = G_N(t) - \sum_{K=1}^{N} B_K H_N(t - \beta_K)$$

and has the property that when $B_j = A_j$ and $\beta_j = b_j$ for all j, then

$$H_N(t) = f(t) + \rho_N(t) ,$$

where $\rho_N(t)$ represents the noise and baseline contribution. Figure 1 is an example of a doublet $(N=1)$ generalized error signal $H_1(t)$. If it is assumed that $G_N(t) \equiv 0$ except where $1 \leq t \leq M$; then the quantity q, defined by

$$q(\vec{B}, \vec{\beta}) = \frac{1}{L} \sum_{t=M+1}^{M+L} \frac{H_N^2(t)}{\mathrm{var}[H_N(t)]} , \quad L = [\beta_N]$$

will have a local minimum with the expected value $\langle q \rangle = 1$ when $B_j = A_j$ and $\beta_j = b_j$ for all j. Where $G_N(t)$ results from pulse counting, the baseline correction is the background count rate and the variance of $H_N(t)$ $\{\mathrm{var}[H_N(t)]\}$ may be estimated from $G_N(t)$. The computer program that was used for the present measurements minimizes $q(\vec{B}, \vec{\beta})$

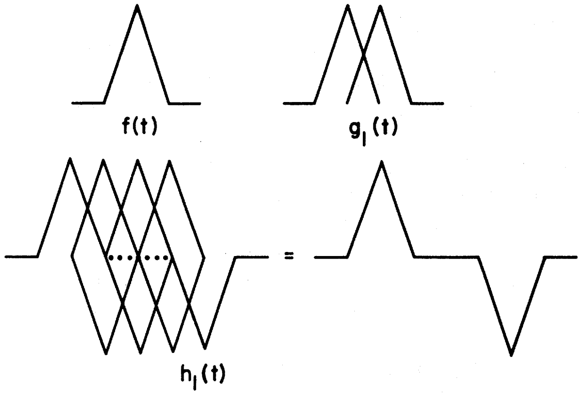

FIG. 1. Example of a doublet generalized error signal $h_1(t)$ where only the first four terms are computed.

to obtain the separations B_j in units of channels. A mass-to-channel conversion factor must then be established in order to obtain the difference in units of mass.

To this end the mass spectrometer operating mode was altered. A precise sawtooth generator is placed in series with the constant electrostatic analyzer voltage supply (V_0) in order to sweep the beam across the collector slit. An additional sawtooth generator is required for the accelerating voltage supply to maintain the correct voltage ratio. The doublet or triplet spectrum is then stored in the 1062 analyzer using the pulse count mode. During sweeps 1, 3, 5, . . . , the voltage which is delivered to the electrostatic analyzer is of the form $V(t) = V_0(1 + \alpha t)$. During sweeps 2, 4, 6, . . . , the voltage divider is switched, giving $V'(t) = V(t)/(1 + \Delta R/R)$. Figures 2 and 3 are examples of the resulting spectra. By means of Bleakney's theorem a mass-to-channel equivalence can be derived, giving the result

$$\Delta M = \phi M(\Delta R/R)/S(\phi) ,$$

where ϕ is the ratio of one of the narrow doublet separations to the separation of the repeated pattern. Each stored spectrum then gives two determinations of ϕ. The function $S(\phi)$ is a near-unity function of the doublet position within the spectrum. In order to minimize systematic errors, measurements are taken with the sweep voltage increasing or decreasing, switching relays energized at high or low mass and with the current direction through the voltage divider normal or reversed. A run consists of 24 stored spectra, three for each of the 8 permutations.

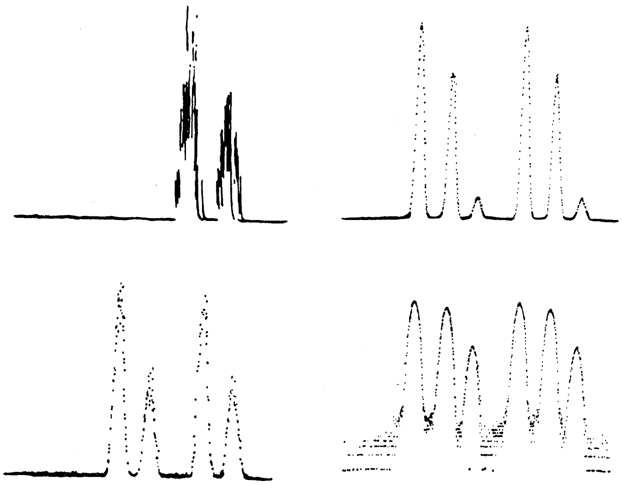

FIG. 2. Typical doublet and triplet spectra measured. The upper left is a trace of one sweep where the maximum intensity is 12 000 counts/sec. The lower left is a typical stored doublet spectrum. Ions are $^{150}Sm^{35}Cl^{+}$ and $^{148}Sm^{37}Cl^{+}$. The upper right is a typical stored triplet spectrum. Ions are $^{160}Gd^{35}Cl_2^{+}$, $^{158}Gd^{35}Cl^{37}Cl^{+}$, and $^{156}Gd^{37}Cl_2^{+}$. The lower right is a logarithmic plot of the same spectrum. The resolution is 200 000 with a maximum of 3400 counts/channel = 133 000 counts/sec.

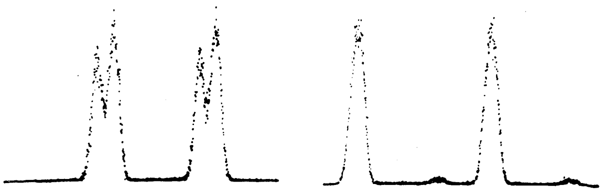

FIG. 3. Unusual doublets which were measured. The left is a very narrow doublet $\Delta m = 1.343$ mu. Ions are $^{154}Gd^{+}$ and $^{154}Sm^{+}$ at 200 000 resolution. The right is a wide narrow doublet $\Delta m = 14.282$ mu. Ions are $^{155}Gd^{35}Cl_3^{+}$ and $^{149}Sm^{37}Cl_3^{+}$. There are 350 ions in each small peak.

MEASUREMENTS

Wide doublets

There have been no new accurate absolute mass values reported in the light rare earths since the measurement of the masses of ^{142}Nd and ^{143}Nd by Benson and Johnson.[2] These absolute masses, when they are combined with the more commonly measured mass differences, have been the basis for atomic mass calculations in the light rare earths. However, at increasing distances from the measured masses, small systematic errors in the mass difference data may accumulate, to give erroneous computed values. In order to test for this possibility in the light rare earths, the masses of ^{152}Sm and ^{154}Sm were measured against ions derived from biphenyl $C_{12}H_{10}$. Table I lists the average values of the measured doublets and masses, along with their estimated errors. The error is based upon the sensitivity of the error signals during a measurement and upon the esti-

TABLE I. Measured wide doublets.

Doublet or mass	Measured (u)	Est. error (μu)	Δ[a] (μu)	Adopted error (μu)
$C_{12}H_8$-^{152}Sm	0.142 867 0	3.0	· · ·	5
^{154}Sm-$C_{12}H_9$	0.851 789 0	3.0	· · ·	8
$C_{12}H_{10}$-^{154}Sm	0.156 035 7	2.0	· · ·	4
$^{1}H_{1}$	1.007 824 6[b]	3.6	−0.4	· · ·
^{154}Sm-^{152}Sm	2.002 482[b]	3.6	5	· · ·
^{152}Sm	151.919 733[b]	3.0	5	· · ·
^{154}Sm	153.922 215[b]	2.0	4	· · ·

[a] Deviation from the best value of Wapstra and Gove or present work.

[b] Derived from measured values.

TABLE II. Measured narrow doublets.

Doublet	$[\chi^2/(N-1)]^{1/2}$ Found	$[\chi^2/(N-1)]^{1/2}$ Expect [a]	Mass difference (μu)	Error (μu)	Metal doublet [b]	Mass difference (u)	Error (μu)
^{149}Sm^{35}Cl-^{147}Sm^{37}Cl	0.50	1 ± 0.35	5239.8	0.8	^{149}Sm-^{147}Sm	2.002 289 6	0.8
^{150}Sm^{35}Cl-^{148}Sm^{37}Cl	1.35	1 ± 0.25	5404.8	0.6	^{150}Sm-^{148}Sm	2.002 454 6	0.6
^{152}Sm^{35}Cl-^{150}Sm^{37}Cl	1.65	1 ± 0.71	5402.7	0.8	^{152}Sm-^{150}Sm	2.002 452 6	0.8
^{152}Sm^{35}Cl$_2$-^{148}Sm^{37}Cl$_2$	1.66	1 ± 0.71	10 807.9	1.4	^{152}Sm-^{148}Sm	4.004 907 6	1.4
^{154}Sm^{35}Cl-^{152}Sm^{37}Cl	0.75	1 ± 0.32	5427.2	0.4	^{154}Sm-^{152}Sm	2.002 477 0	0.4
...	1.16	1 ± 0.35	...	...	^{154}Sm-^{154}Gd	0.001 342 8	0.8
^{156}Gd^{35}Cl-^{154}Gd^{37}Cl	1.03	1 ± 0.41	4203.0	1.0	^{156}Gd-^{154}Gd	2.001 252 9	1.0
^{157}Gd^{35}Cl-^{155}Gd^{37}Cl	0.68	1 ± 0.32	4289.0	0.7	^{157}Gd-^{155}Gd	2.001 338 9	0.7
^{158}Gd^{35}Cl-^{156}Gd^{37}Cl	0.59	1 ± 0.41	4930.8	0.7	^{158}Gd-^{156}Gd	2.001 980 6	0.7
^{160}Gd^{35}Cl-^{158}Gd^{37}Cl	1.21	1 ± 0.32	5900.0	0.5	^{160}Gd-^{158}Gd	2.002 949 9	0.5
^{155}Gd^{35}Cl$_3$-^{149}Sm^{37}Cl$_3$	1.72	1 ± 0.41	14 282.4	6.3	^{155}Gd-^{149}Sm	6.005 432 0	6.3

[a] $[\chi^2/(N-1)]^{1/2}$ in this case is a test of consistency among N runs on a given doublet.
[b] Measured doublet $+n(^{37}\text{Cl}-^{35}\text{Cl})$ differences, where appropriate.

mated voltage divider error. Because the peaks of the Sm-hydrocarbon doublets originate from different molecular species, their modes of formation in the source are dissimilar and may introduce systematic errors. A necessary if not sufficient check of this possibility is obtained through the derived quantities of Table I. It is seen that the derived value of $^1\text{H}_1$ is in agreement with the accepted value taken from Table VII. Likewise, the derived difference ^{154}Sm-^{152}Sm is consistent with the more precise value measured in this work. A further check results from the least-squares adjustment, in which the present values for Sm are linked to those for ^{142}Nd and ^{143}Nd. In a later section it is seen that good agreement is obtained. However, as an additional precaution, each estimated error has been increased by an amount equal to 8 ppm of the doublet width to reflect possible systematic errors of this type. In Table I the new errors are listed as adopted errors.

Narrow doublets

Mass differences involving most of the stable isotopes of samarium and gadolinium were measured with the new technique. These measurements employed metal and metal chloride narrow doublets of natural isotopic composition. Only the ^{154}Gd-^{154}Sm difference was measured at M$^+$. More than half of the measurements used doublets of the type $^{A+2}\text{M}\,^{35}\text{Cl}^+$-$^{A}\text{M}\,^{37}\text{Cl}^+$. These doublets are not intense so that their weighting in the final average is small. However, they serve as an independent internal check on the other determinations.

TABLE III. Comparisons with other sources.

Doublet	Manitoba Adopted [a] (μu)		Manitoba Least-squares output [b] (μu)		All composites (μu)		Wapstra [c] (μu)		Present work (μu)	
^{157}Gd^{35}Cl-^{155}Gd^{37}Cl	4287	3	4286.7	2.2			4286.1	3.6	4289.0	0.7
^{149}Sm^{35}Cl-^{147}Sm^{37}Cl	5231	3	5234.7	1.7	5237.5	1.8 [d]	5236.8	1.5	5239.8	0.8
^{155}Gd^{35}Cl$_3$-^{149}Sm^{37}Cl$_3$	...		...		14 284.0	3.3 [b]	14 277	...	14 282.4	6.3
^{160}Gd^{35}Cl-^{158}Gd^{37}Cl	5900.1	2.3	5897.8	1.7			5899	4	5900.0	0.5
^{158}Gd^{35}Cl-^{156}Gd^{37}Cl	4925.6	1.5	4926.3	1.4			4930.7	3.6	4930.8	0.7
^{156}Gd^{35}Cl-^{154}Gd^{37}Cl	4203.7	1.4	4205.0	1.3			4203	7	4203.0	1.0
^{154}Sm-^{154}Gd	1337.9	3.8	1342.8	2.9			...		1342.8	0.8
^{154}Sm^{35}Cl-^{152}Sm^{37}Cl	5417	4	5422.4	3.0			5418	5	5427.2	0.4
^{152}Sm^{35}Cl-^{150}Sm^{37}Cl	5403.2	2.6	5405.4	2.2			5402.7	3.9	5402.7	0.8
^{152}Sm^{35}Cl$_2$-^{148}Sm^{37}Cl$_2$	10 806.6	1.6	10 806.5	1.6			...		10 807.9	1.4
^{150}Sm^{35}Cl-^{148}Sm^{37}Cl	5402.9	2.4	5401.1	1.6	5403.3	1.4 [d]	5402.8	1.3	5404.8	0.6
^{154}Sm^{35}Cl$_2$-^{150}Sm^{37}Cl$_2$	...		10 827.8	5			...		10 832.9	5.2

[a] See Ref. 9.
[b] See Ref. 11.
[c] See Ref. 10.
[d] Composite of (n,γ) reactions.

TABLE IV. Mass differences used in the adjustment.

Difference	Input (u)	σ_i (μu)	Output (u)	σ_0 (μu)	r_i (μu)	r_i/σ_i	Source
^{143}Nd-^{142}Nd	1.002 084 0	5.0	1.002 089 0	1.6	−5.0	−0.99	a
^{144}Nd-^{142}Nd	2.002 357 8	3.0	2.002 361 2	1.7	−3.4	−1.14	b
^{144}Nd-^{142}Nd	2.002 366 0	7.0	2.002 361 3	1.7	4.7	0.68	a
^{144}Nd-^{143}Nd	1.000 273 0	5.0	1.000 272 3	0.9	0.7	0.14	a
^{144}Sm-^{144}Nd	0.001 911 1	1.1	0.001 910 7	1.0	0.4	0.36	b
^{145}Nd-^{143}Nd	2.002 753 7	3.6	2.002 758 6	1.4	−5.0	−1.40	b
^{145}Nd-^{143}Nd	2.002 751 0	7.0	2.002 758 7	1.4	−7.7	−1.10	a
^{145}Nd-^{144}Nd	1.002 480 0	5.0	1.002 486 4	1.2	−6.4	−1.27	a
^{146}Nd-^{144}Nd	2.003 031 1	0.9	2.003 030 0	0.8	1.1	1.23	b
^{146}Nd-^{144}Nd	2.003 026 0	7.0	2.003 030 0	0.8	−4.0	−0.58	a
^{146}Nd-^{145}Nd	1.000 536 0	5.0	1.000 543 7	1.0	−7.7	−1.53	a
^{147}Sm-^{145}Nd	2.002 313 8	4.0	2.002 314 0	1.6	−0.1	−0.02	b
^{148}Nd-^{144}Nd	4.006 800 2	1.9	4.006 802 3	1.4	−2.1	−1.09	b
^{148}Nd-^{146}Nd	2.003 773 0	7.0	2.003 772 2	1.5	0.8	0.11	a
^{148}Nd-^{146}Nd	2.003 772 0	2.7	2.003 772 2	1.5	−0.3	−0.11	b
^{148}Sm-^{144}Sm	4.002 818 9	2.6	4.002 816 7	1.5	2.2	0.86	b
^{149}Sm-^{147}Sm	2.002 289 6	0.8	2.002 289 3	0.7	0.3	0.38	c
^{150}Nd-^{146}Nd	4.007 768 9	1.2	4.007 768 1	1.0	0.8	0.65	b
^{150}Nd-^{148}Nd	2.003 988 0	7.0	2.003 995 9	1.7	−7.9	−1.13	a
^{150}Nd-^{148}Nd	2.003 988 8	4.0	2.003 995 8	1.7	−7.0	−1.76	b
^{150}Nd-^{150}Sm	0.003 616 5	1.0	0.003 616 4	0.9	0.1	0.06	b
^{150}Sm-^{148}Sm	2.002 454 6	0.6	2.002 454 3	0.5	0.3	0.50	c
^{151}Eu-^{149}Sm	2.002 668 7	2.6	2.002 671 3	1.7	−2.6	−0.99	b
^{152}Sm-^{148}Sm	4.004 907 6	1.4	4.004 907 1	0.8	0.5	0.37	c
^{152}Sm-^{150}Sm	2.002 452 6	0.8	2.002 452 8	0.7	−0.2	−0.23	c
^{154}Sm-^{150}Sm	4.004 932 6	5.2	4.004 929 9	0.8	2.7	0.52	c
^{154}Sm-^{152}Sm	2.002 477 0	0.4	2.002 477 1	0.4	−0.1	−0.25	c
^{154}Sm-^{154}Gd	0.001 342 8	0.8	0.001 342 5	0.8	0.3	0.39	c
^{154}Gd-^{152}Gd	2.001 068 3	2.0	2.001 068 8	1.9	−0.5	−0.24	b
^{155}Gd-^{149}Sm	6.005 432 0	6.3	6.005 427 2	1.8	4.8	0.77	c
^{155}Gd-^{153}Eu	2.001 394 1	2.4	2.001 393 0	2.1	1.1	0.47	b
^{156}Gd-^{154}Gd	2.001 252 9	1.0	2.001 253 1	1.0	−0.3	−0.30	c
^{157}Gd-^{155}Gd	2.001 338 8	0.7	2.001 338 8	0.7	0.1	0.12	c
^{158}Gd-^{156}Gd	2.001 980 6	0.7	2.001 980 8	0.7	−0.1	−0.12	c
^{160}Gd-^{158}Gd	2.002 949 8	0.5	2.002 949 8	0.5	0.0	0.00	c

[a] Benson and Johnson, Ref. 2.
[b] Manitoba, Refs. 9 and 11.
[c] Present work.

TABLE V. Atomic mass determinations used in the adjustment.

Doublet	Input (u)	σ_i (μu)	Output (u)	σ_0 (μu)	r_i (μu)	r_i/σ_i	Source
^{143}Nd-$C_{11}H_9$	0.837 335	16	0.837 315 8	3.0	19.2	1.20	Ref. 2
$C_{11}H_{10}$-^{142}Nd	0.170 490	16	0.170 509 3	3.0	−19.3	−1.21	Ref. 2
^{143}Nd-$C_{11}H_9$	1.839 406	8	1.839 404 8	2.6	1.2	0.15	Ref. 2
^{143}Nd-$C_{11}H_{10}$	0.831 578	5	0.831 579 7	2.6	−1.7	−0.33	Ref. 2
$C_{12}H_8$-^{152}Sm	0.142 867 0	5	0.142 863 5	2.4	3.5	0.70	Present work
^{154}Sm-$C_{12}H_9$	0.851 788 5	8	0.851 788 7	2.4	−0.2	−0.02	Present work
$C_{12}H_{10}$-^{154}Sm	0.156 035 8	4	0.156 036 4	2.4	−0.6	−0.16	Present work

Peak intensities at MCl_2^+ are much greater than those at MCl^+ and the most accurate results were obtained with this type of ion. Also, one doublet at MCl_3^+ was run in order to measure ^{155}Gd-^{149}Sm.

Figure 2 shows typical doublet and triplet spectra, in which the separations are about 5 mu and the count rates are about 5000/sec. It is clear that even 200 000 resolution does not fully resolve the members of the triplet. Figure 3 shows two unusual doublets which could be successfully measured and which provide the most rigorous tests of the new error signal technique. The very narrow doublet $^{154}Gd^+$-$^{154}Sm^+$ would require a resolution of about 400 000 to be measured with a standard peak matching technique. By contrast, the doublet $^{155}Gd^{35}Cl_3^+$-$^{149}Sm^{37}Cl_3^+$ is well separated, but the intensity of the $SmCl_3^+$ ion was very low. The final value for this doublet was assigned an error of 6.3 μu and was determined from a total of 80 000 $^{149}Sm^{37}Cl_3^+$ ions.

Table II lists all of the narrow doublet measurements, both as metal chloride differences (where appropriate) and as metal-metal differences. The final mass difference is a weighted average of all determinations, some of which were derived from both MCl^+ and MCl_2^+. The assigned error of the average represents the deviation from the mean as computed from the errors assigned to each run. The statistic $(\chi^2/f)^{1/2}$ and its expected value are given as a check on the consistency of the individual determinations. Because the number of ions in each run is known, a good theoretical estimate of the expected accuracy of the measurement can be made.[8] A comparison of this estimate with the assigned error will indicate whether there are additional sources of random error which are limiting the accuracy of a measurement. Apparently no difficulties of this nature exist for the present measurements, because almost all of the assigned errors were found to be 1.2 to 2.5 of the theoretical. As an over-all check, closed loops can be constructed using part or all of the present data with selected (n,γ) data from Table VII. It is found that these loops close within the limits of error. The metal-metal mass differences are computed using the ^{37}Cl-^{35}Cl value of Smith as given in Table VI. The quoted error of this value contributes only 0.13 μu to the assigned error of the mass difference.

Table III gives a comparison of the present results with those from other sources. The adopted values of Barber *et al.*[9] and two composite values which are based upon the (n,γ) reactions of Table VII represent independent determinations of the doublet mass differences. The least-squares outputs of Wapstra and Gove[10] and Meredith and Barber *et al.*[11] incorporate data from all sources and are not independent values for the doublet differences. Generally, where there are comparison values with sufficiently small errors, these values agree with the present results. A notable exception is the Manitoba value for $^{158}Gd^{35}Cl$-$^{156}GD^{37}Cl$, which is 5.2(±1.5) μu low with respect to the present measurement. It is also seen that the older McMaster doublets are generally low, in two cases by at least twice the quoted error.

MASS ADJUSTMENT

Input data

The apparent quality of the new measurements motivated the authors to do a least-squares adjustment of the best adjacent mass spectroscopic and nuclear reaction data in order to obtain improved absolute masses and mass differences in the region Pr through Gd. This adjustment should also provide an additional check on the errors which were assigned to the present mass measurements.

Table IV lists all of the input mass differences, their adjusted values, the residuals r_i, and the normalized residuals r_i/σ_i. The Nd doublets of Benson are input with his original errors multiplied by a consistency factor of 2.5, which resulted from his local least-squares adjustment.[2] All of the Manitoba and some of the earlier McMaster Nd doublets are included with their original error estimates,[9] although these estimates may be slightly optimistic. For Sm and Gd, available Manitoba doublets are included where they are comparable in precision with the present values. Also, where the present measurements do not cover connections of the naturally occurring isotope from Nd to Gd, Manitoba doublets are used.

Table V lists all of the atomic mass determinations used in the adjustment. Input errors in the present Sm-hydrocarbon doublets have been increased to reflect possible systematic errors of 8 μu/u. The size of the input errors for the Benson Nd-hydrocarbon doublets was assigned from the

TABLE VI. Constants used in the adjustment.

Constant	Value[a]
^1n	1.008 665 02 ± 4 u
^1H	1.007 825 05 ± 1 u
^2H	2.014 101 82 ± 2 u
^4He	4.002 602 94 ± 27 u
^{37}Cl-^{35}Cl	1.997 049 85 ± 13 u
Mass to energy conversion[b]	931 504 ± 10 keV/u

[a] Based upon the latest work of Smith as cited in Ref. 10.

[b] See discussion in Ref. 10.

TABLE VII. Reaction data used in the adjustment.

Reaction	Input (keV)	σ_i (keV)	Output (keV)	σ_0 (keV)	r_i (keV)	r_i/σ_i	Source
$^{141}\mathrm{Pr}(n,\gamma)^{142}\mathrm{Pr}$	5843.4	1.5	5843.5	0.8	−0.1	−0.05	67KE03[a]
$^{141}\mathrm{Pr}(n,\gamma)^{142}\mathrm{Pr}$	5843.5	1.0	5843.5	0.8	0.0	0.03	b
$^{142}\mathrm{Pr}(\beta-)^{142}\mathrm{Nd}$	2164.0	2.0	2164.0	2.0	0.0	0.00	b2-1[c]
$^{142}\mathrm{Nd}(n,\gamma)^{143}\mathrm{Nd}$	6122.9	2.0	6125.6	1.5	−2.9	−1.36	d
$^{143}\mathrm{Pr}(\beta-)^{143}\mathrm{Nd}$	931.0	2.0	931.0	2.0	0.0	0.00	b2-1[c]
$^{143}\mathrm{Nd}(n,\gamma)^{144}\mathrm{Nd}$	7815.5	2.0	7817.8	0.9	−2.5	−1.17	d
$^{143}\mathrm{Nd}(n,\gamma)^{144}\mathrm{Nd}$	7817.2	1.1	7817.8	0.9	−0.7	−0.59	e
$^{144}\mathrm{Pr}(\beta-)^{144}\mathrm{Nd}$	2994.0	3.0	2994.0	3.0	0.0	0.00	b2-1[c]
$^{144}\mathrm{Sm}(n,\gamma)^{145}\mathrm{Sm}$	6762.7	2.0	6762.7	2.0	0.0	0.00	70SM02[a]
$^{145}\mathrm{Nd}(n,\gamma)^{146}\mathrm{Nd}$	7565.7	1.1	7565.1	1.0	0.7	0.57	e
$^{145}\mathrm{Pm}(\mathrm{EC})^{145}\mathrm{Nd}$	141.0	1.0	141.0	1.0	0.0	0.00	b2-1[c]
$^{147}\mathrm{Nd}(\beta-)^{147}\mathrm{Pm}$	897.0	2.0	895.2	0.8	2.0	0.92	b2-4[c]
$^{147}\mathrm{Nd}(\beta-)^{147}\mathrm{Pm}$	894.5	1.0	895.2	0.8	−0.7	−0.67	f
$^{147}\mathrm{Nd}(\beta-)^{147}\mathrm{Pm}$	896.0	2.0	895.2	0.8	0.9	0.42	g
$^{147}\mathrm{Pm}(\beta-)^{147}\mathrm{Sm}$	224.6	0.6	224.6	0.6	0.0	0.00	b2-4[c]
$^{147}\mathrm{Sm}(\alpha)^{143}\mathrm{Nd}$	2295.0	6.0	2300.5	1.5	−5.9	−0.92	b2-4[c]
$^{147}\mathrm{Sm}(n,\gamma)^{148}\mathrm{Sm}$	8139.9	1.2	8139.4	0.7	0.5	0.38	e
$^{147}\mathrm{Sm}(n,\gamma)^{148}\mathrm{Sm}$	8140.6	1.8	8139.4	0.7	1.2	0.64	h
$^{148}\mathrm{Sm}(n,\gamma)^{149}\mathrm{Sm}$	5872.5	1.0	5871.0	0.5	1.6	1.48	70SM02[a]
$^{149}\mathrm{Nd}(\beta-)^{149}\mathrm{Pm}$	1669.0	10.0	1669.0	10.0	0.0	0.00	64GO08[a]
$^{149}\mathrm{Pm}(\beta-)^{149}\mathrm{Sm}$	1071.0	2.0	1071.0	2.0	0.0	0.00	5-2-20[c]
$^{149}\mathrm{Sm}(n,\alpha)^{146}\mathrm{Nd}$	9428.0	5.0	9428.5	1.2	−0.5	−0.11	65BE33[a]
$^{149}\mathrm{Sm}(n,\gamma)^{150}\mathrm{Sm}$	7986.4	1.8	7985.7	0.5	0.7	0.36	h
$^{149}\mathrm{Sm}(n,\gamma)^{150}\mathrm{Sm}$	7986.8	1.0	7985.7	0.5	1.1	1.05	b
$^{149}\mathrm{Sm}(n,\gamma)^{150}\mathrm{Sm}$	7985.4	0.8	7985.7	0.5	−0.4	−0.43	i
$^{150}\mathrm{Sm}(n,\gamma)^{151}\mathrm{Sm}$	5591.7	2.0	5592.9	1.5	−1.3	−0.60	70SM02[a]
$^{151}\mathrm{Sm}(\beta-)^{151}\mathrm{Eu}$	75.9	0.6	76.0	0.6	−0.1	−0.18	59A28[a]
$^{151}\mathrm{Eu}(n,\gamma)^{152}\mathrm{Eu}$	6305.2	0.5	6305.2	0.5	0.0	0.05	70KA21[a]
$^{152}\mathrm{Sm}(n,\gamma)^{153}\mathrm{Sm}$	5869.3	2.0	5867.2	0.4	2.3	1.07	j
$^{152}\mathrm{Sm}(n,\gamma)^{153}\mathrm{Sm}$	5867.0	0.4	5867.2	0.4	−0.2	−0.42	69RE04[a]
$^{152}\mathrm{Eu}(\beta-)^{152}\mathrm{Gd}$	1828.0	7.0	1822.9	2.5	5.5	0.73	5-6-37[c]
$^{152}\mathrm{Gd}(d,t)^{151}\mathrm{Gd}$	−2333.0	10.0	−2333.0	10.0	0.0	0.00	k
$^{152}\mathrm{Gd}(d,p)^{153}\mathrm{Gd}$	4022.0	10.0	4024.6	7.1	−2.8	−0.26	k
$^{153}\mathrm{Sm}(\beta-)^{153}\mathrm{Eu}$	804.0	5.0	817.0	2.2	−13.9	−2.60	l
$^{153}\mathrm{Eu}(n,\gamma)^{154}\mathrm{Eu}$	6415.9	1.0	6416.2	1.0	−0.3	−0.31	b
$^{154}\mathrm{Sm}(n,\gamma)^{155}\mathrm{Sm}$	5814.2	2.0	5814.2	2.0	0.0	0.00	70SM02[a]
$^{154}\mathrm{Eu}(\beta-)^{154}\mathrm{Gd}$	1978.0	5.0	1985.7	2.3	−8.3	−1.54	l
$^{154}\mathrm{Gd}(d,t)^{153}\mathrm{Gd}$	−2638.0	10.0	−2640.6	7.1	2.8	0.26	k
$^{155}\mathrm{Eu}(\beta-)^{155}\mathrm{Gd}$	247.0	3.0	247.0	3.0	0.0	0.00	l
$^{155}\mathrm{Gd}(n,\alpha)^{152}\mathrm{Sm}$	8331.0	6.0	8331.5	1.6	−0.5	−0.09	j
$^{155}\mathrm{Gd}(n,\gamma)^{156}\mathrm{Gd}$	8530.0	4.0	8532.2	1.2	−2.4	−0.55	62GR33[a]
$^{157}\mathrm{Gd}(n,\gamma)^{158}\mathrm{Gd}$	7934.0	1.0	7934.2	0.9	−0.2	−0.19	b

[a] Source codes due to Wapstra and Gove, Rev. 10.

[b] N. C. Rasmussen, V. J. Orphan, and Y. Hukai, Proceedings of the Third International Conference on Atomic Masses, edited by R. C. Barber (University of Manitoba Press, Winnipeg, 1967), p. 278.

[c] Reference code as used in *Nuclear Data*, edited by K. Way (Academic, New York, 1967).

[d] N. C. Rasmussen, V. J. Orphan, Y. Hukai, and T. Ihoye, private communication cited in L. V. Groshev *et al.*, Nucl. Data A5 (No. 1) (1968).

[e] E. R. Reddingius, Ph.D. thesis, University of Leiden, Netherlands (unpublished).

[f] M. J. Canty and R. D. Connor, Nucl. Phys. A104, 35 (1967).

[g] H. Beckhuis, P. Boskma, J. Van Klinker, and H. DeWaard, Nucl. Phys. 79, 220 (1966).

TABLE VII *(Continued)*

[h] D. J. Buss and R. K. Smither, Phys. Rev. C 2, 1513 (1970).
[i] E. R. Reddingius, private communication cited in Ref. 11.
[j] R. K. Smither, private communication cited in Groshev *et al.*, Nucl. Data A5 (No. 1) (1969).
[k] P. Tjøm and B. Elbek, see Ref. 11, p. 1219.
[l] J. H. E. Mattauch, W. Thiele, and A. H. Wapstra, Nucl. Phys. 67, 73 (1965).

results of his local least-squares adjustment. Table VI lists the energy conversion constant and the secondary standards which are used in the adjustment. They are taken from Wapstra and Gove[10] and are based upon the recent work of L. G. Smith. Table VII lists the selected reaction data which are used in the adjustment. This list is taken from a more extensive list given by Meredith and Barber.[11] A few additional values are to be found in Wapstra and Gove. For the present adjustment, where a closed loop is involved, we have used only those data whose quoted errors are comparable to the errors of the new mass differences.

RESULTS

Table VIII summarizes the statistics which result for data in closed loops. The remaining data are not changed by the adjustment and do not contribute to χ^2. We find that the consistency factor $(\chi^2/f)^{1/2}=1.05$, where 1.0 ± 0.11 is expected. Here χ^2 is the sum of the squared normalized residuals and f is the number of degrees of freedom. It is seen that the 11 mass differences of the present work contribute only 1.78 to χ^2, again confirming the original error assignments.

The group of $\beta+$ and $\beta-$ reactions contributes 11.0 for 7 data values; however, 6.4 of the contribution is due to one reaction, that of ^{153}Sm($\beta-$)^{153}Eu reported as 804.0±5 keV and adjusted to 817.0±2 keV. Both this reaction and another one which is known to be incorrect[11] [^{153}Gd (EC) ^{153}Eu] were reported by Chumin *et al.*[12] It should be noted that the mass differences of both Benson and Manitoba contribute slightly larger amounts to χ^2 than would be expected, for if the contributions from all data were as great, we would have $\chi^2=60$ and $\chi^2=64$, respectively. Finally, we conclude that the atomic mass determinations are consistent with the linking doublet values.

Table IX lists the adjusted atomic masses and compares these values with the Manitoba mass evaluation[11] and the 1971 mass evaluation of Wapstra and Gove.[10] Agreement with the Manitoba adjustment is generally good when the effect of the McMaster doublets is considered. It is now evident that their only absolute mass input was taken from the output of Benson's least-squares adjustment, which gave errors of 8 to 13 μu for each of seven masses ^{142}Nd through ^{150}Nd. The Manitoba adjustment then gave a further error reduction to 3.6 μu in all output atomic masses. Clearly, however, the four original measured doublets themselves should have been input to give a smallest error of 8 μu for each mass derived from the adjustment.

In the extensive adjustment of Wapstra and Gove[10] another body of atomic mass determinations was introduced. In the region from Pr to Gd, these data are due to Demirkhanov *et al.*[13] On the basis of consistency tests, Liran and Zeldes conclude that these data are inconsistent and should be excluded.[14] In the 1971 adjustment, however, the reported errors are multiplied by a consistency factor of 5 and much of the data are used in the adjustment. Also, the atomic masses of Benson are given larger errors, and the net effect is to weigh each determination of Demirkhanov *et al.* almost equally with those of Benson. As a result the atomic masses of Wapstra and Gove are determined

TABLE VIII. Summary of statistics for closed loop input data.

Table reference	Type of input data	Number of data	Contribution to χ^2
IV	Mass differences (Benson)	9	8.25
IV	Mass differences (Present work)	11	1.78
IV	Mass differences (Manitoba)	14	11.60
V	Absolute masses (Benson)	4	3.04
V	Absolute masses (Present work)	3	0.52
VII	(n,γ)	19	10.20
VII	$\beta+, \beta-$, EC	7	11.17
VII	α, (n,α)	3	0.87
VII	(d,t), (d,p)	2	0.14
	Totals:	72	47.57
	Expect($f=N-n$; $n=46$)	⋯	43.00± 4.6
	Totals (all input data)	$N=89$	$\chi^2=47.57$

TABLE IX. Adjusted atomic masses. Δ ≡ comparison value − present value.

				This work			Manitoba *LSQ*			Wapstra *LSQ*		
N	Z	A	El.	Mass (u)	Mass excess (μu)	σ_0 (μu)	Mass excess (μu)	σ_0 (μu)	Δ (μu)	Mass excess (μu)	σ_0 (μu)	Δ (μu)
82	59	141	Pr	140.907 672 5	−92 327.5	3.8	−92 328.9	4.1	−1.4	−92 302	11	25
83	59	142	Pr	141.910 064 3	−89 935.7	3.7	−89 937.0	4.1	−1.3	−89 911	11	25
82	60		Nd	141.907 741 2	−92 258.8	3.0	−92 259.5	3.8	−0.7	−92 234	11	25
84	59	143	Pr	142.910 829 6	−89 170.4	3.4	−89 170.1	4.2	0.3	−89 144	12	26
83	60		Nd	142.909 830 2	−90 169.8	2.6	−90 169.6	3.6	0.2	−90 144	11	26
85	59	144	Pr	143.913 316 6	−86 683.4	4.1	−86 683.2	4.8	0.2	−86 654	12	29
84	60		Nd	143.910 102 5	−89 897.5	2.6	−89 897.1	3.6	0.4	−89 871	11	26
82	62		Sm	143.912 013 2	−87 986.8	2.7	−87 986.1	3.7	0.7	−87 926	12	61
85	60	145	Nd	144.912 588 8	−87 411.2	2.7	−87 412.5	3.7	−1.3	−87 390	11	21
84	61		Pm	144.912 740 2	−87 259.8	2.9	−87 260.9	3.8	−1.1	−87 207	14	53
83	62		Sm	144.913 418 2	−86 581.8	3.5	−86 585.0	9.0	−3.2	−86 522	12	60
86	60	146	Nd	145.913 132 5	−86 867.5	2.6	−86 869.4	3.6	−1.9	−86 847	11	21
87	60	147	Nd	146.916 104 9	−83 895.1	2.8	−83 892.8	4.0	2.3	−83 874	12	21
86	61		Pm	146.915 143 9	−84 856.1	2.6	−84 854.1	4.0	2.0	−84 834	11	22
85	62		Sm	146.914 902 8	−85 097.2	2.5	−85 095.5	3.9	1.7	−85 075	11	22
88	60	148	Nd	147.916 904 7	−83 095.3	2.9	−83 097.6	3.8	−2.3	−83 071	12	24
86	62		Sm	147.914 829 8	−85 170.2	2.5	−85 169.6	3.9	0.6	−85 149	11	21
89	60	149	Nd	148.920 133 6	−79 866.4	11.2	−79 870.0	11.0	−3.6	−79 847	16	19
88	61	149	Pm	148.918 341 9	−81 658.1	3.3	−81 661.1	4.5	−3.0	−81 638	12	20
87	62		Sm	148.917 192 1	−82 807.9	2.5	−82 810.7	3.9	−2.8	−82 789	11	19
90	60	150	Nd	149.920 900 6	−79 099.4	2.5	−79 102.2	3.9	−2.8	−79 079	12	20
88	62		Sm	149.917 284 2	−82 715.8	2.5	−82 718.8	3.9	−3.0	−82 697	11	19
89	62	151	Sm	150.919 945 0	−80 055.0	3.0	−80 062.0	4.6	−7.0	−80 036	12	19
88	63		Eu	150.919 863 4	−80 136.6	3.0	−80 143.5	4.6	−6.9	−80 117	12	20
87	64		Gd	150.920 360 0	−79 640.0	11.2	−79 637.0	11.0	3.0	−79 619	16	21
90	62	152	Sm	151.919 736 9	−80 263.1	2.4	−80 265.0	4.6	−1.9	−80 245	12	18
89	63		Eu	151.921 759 6	−78 240.4	3.0	−78 246.0	6.0	−5.6	−78 221	12	19
88	64		Gd	151.919 802 7	−80 197.3	3.2	−80 195.0	6.0	2.3	−80 183	13	14
91	62	153	Sm	152.922 103 3	−77 896.7	2.5	−77 897.0	4.6	−0.3	−77 878	12	19
90	63		Eu	152.921 226 3	−78 773.7	3.4	−78 770.0	5.0	3.7	−78 740	12	34
89	64		Gd	152.921 759 0	−78 241.0	8.1	−78 240.0	9.0	1.0	−78 481	12	−240
92	62	154	Sm	153.922 214 1	−77 785.9	2.4	−77 794.0	5.0	−8.1	−77 778	12	8
91	63		Eu	153.923 003 3	−76 996.7	3.5	−76 999.0	7.0	−2.3	−76 986	14	11
90	64		Gd	153.920 871 6	−79 128.4	2.5	−79 126.0	5.0	2.4	−79 109	13	19
93	62	155	Sm	154.924 637 4	−75 362.6	3.2	−75 362.0	10.0	0.6	−75 354	12	9
92	63		Eu	154.922 884 5	−77 115.5	4.3	−77 112.0	6.0	3.5	−77 099	12	17
91	64		Gd	154.922 619 3	−77 380.7	2.9	−77 377.0	5.0	3.7	−77 364	12	17
92	64	156	Gd	155.922 124 7	−77 875.3	2.7	−77 874.0	5.0	1.3	−77 857	12	18
93	64	157	Gd	156.923 958 1	−76 041.9	2.9	−76 040.0	5.0	1.9	−76 028	12	14
94	64	158	Gd	157.924 105 5	−75 894.5	2.8	−75 895.0	5.0	−0.5	−75 877	12	17
96	64	160	Gd	159.927 055 3	−72 944.7	2.8	−72 952.0	6.0	−7.3	−72 929	12	16

mostly by the Demirkhanov *et al.* data. These masses are seen to be generally high from the present work by 15 to 20 μu with a quoted error of 12 μu.

Plots of the nuclear systematics which result from the present adjustment have not been included. It is readily seen from Table IX that these plots would differ from existing ones by only a few μu.

[*] Work supported by Contract No. N00014-67-A-0113-0018 with the Office of Naval Research, a grant from the Graduate School of the University of Minnesota, and Grant No. MPS74-19408 from the National Science Foundation.

[1] See, for instance, N. C. Rasmussen *et al.*, in *Proceedings of the Third International Conference on Atomic Masses*, edited by R. C. Barber (Univ. of Manitoba Press, Winnipeg, 1967), p. 278.

[2] J. L. Benson and W. H. Johnson, Jr., Phys. Rev. 141, 1112 (1966).

[3] M. C. Hudson, Ph.D. thesis, University of Minnesota, 1969 (unpublished).

[4] These doublets were originally suggested by Duckworth and involve combinations of metal chloride ions, such as ${}^{A+2}M^{35}Cl^{+}-{}^{A}M^{37}Cl^{+}$ and ${}^{A+4}M^{35}Cl_2^{+}-{}^{A}M^{37}Cl_2^{+}$, from which he and his co-workers have determined 2 u mass differences with a typical error of 1.0 to 2.0 μu (see Barber *et al*, Ref. 9).

[5] R. R. Ries, R. A. Damerow, and W. H. Johnson, Jr., Phys. Rev. 132, 1662 (1963).

[6] H. Hintenberger, *Nuclear Masses and Their Determination* (Pergamon, London, 1957), Session VII, p. 185.

[7] E. G. Johnson and A. O. Nier, Phys. Rev. 91, 10 (1953).

[8] D. C. Kayser, R. A. Britten, and W. H. Johnson, in *Atomic Masses and Fundamental Constants 4*, edited by J. H. Sanders and A. H. Wapstra (Plenum, New York, 1972), p. 172.

[9] R. C. Barber, R. L. Bishop, J. O. Meredith, F. C. Southon, P. Williams, A. E. Duckworth, and P. Van Rockhuyzen, Can. J. Phys. 50, 1, 34 (1972).

[10] A. H. Wapstra and N. B. Gove, Nucl. Data A9 (Nos. 4 and 5), 267 (1971).

[11] J. O. Meredith and R. C. Barber, Can. J. Phys. 50, 11, 1195 (1972).

[12] V. G. Chumin, K. Y. Gromou, B. Makhumdov, and Z. T. Zhelev, Joint Institute for Nuclear Research, Dubna, Report No. E-2721, 1966 (unpublished).

[13] See references denoted 64 DE15 and 65 DE13 in Wapstra and Gove.

[14] S. Liran and N. Zeldes, Nucl. Phys. A136, 190 (1969).