# Mass Measurements with a Magnetic Time-of-Flight Mass Spectrometer\*

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A new mass spectrometer has been used to measure the time of flight of ions for a number of complete revolutions in a magnetic field. This spectrometer is especially suitable for heavy masses; the following results have been obtained so far:

Element		Mass	Element M	Mass	
S <sup>32</sup>	31.983	$\pm 0.001$	Rb <sup>87</sup> 86.9295	$\pm 0.0020$	
$Cl^{35}$	34.9805	$\pm 0.0005$	I <sup>127</sup> 126.9415	$\pm 0.0025$	
$K^{41}$	40.975	$\pm 0.002$	Xe <sup>129</sup> 128.9455	$\pm 0.0015$	
$\mathrm{Br}^{79}$	78.944	$\pm 0.001$	Xe <sup>130</sup> 129.945	$\pm 0.002$	
$\mathrm{Br}^{81}$	80.943	$\pm 0.001$	Xe <sup>131</sup> 130.944	$\pm 0.002$	
Kr <sup>84</sup>	83.938	$\pm 0.001$	Xe <sup>132</sup> 131.945	$\pm 0.002$	
Rb <sup>85</sup>	84.931	$\pm 0.0015$	Xe <sup>134</sup> 133.947	$\pm 0.002$	

The precision as tabulated is estimated from the consistency between independent runs. The "probable error" is about three times smaller.

### I. BASIC PRINCIPLES

A MASS spectrometer<sup>1</sup> has been constructed which measures the time of flight of ions describing a number of revolutions in a uniform magnetic field. For N revolutions in a homogeneous field of H gauss the time of flight T is given by

$$T = 652NM/H \quad \mu \text{sec.} \tag{1}$$

The mass M is in amu.<sup>2</sup> Conventional mass spectrometers decrease in accuracy with increasing mass. In the time-of-flight spectrometer, the mass-time proportionality and the time-measuring equipment give an essentially constant precision for all masses. In our particular instrument this accuracy is one or two millimass units.

In the present apparatus a pulsed ion source is placed about 12 cm above an ion detector in a vertical magnetic field of about 450 gauss. Some ions leave the source with a vertical velocity component, and travel in a helix, reaching the ion detector after one, two, three, or more revolutions, depending on the initial vertical velocity. Because of the finite size of source and detector only a limited number of revolutions can be observed; ions moving on a helix with a small pitch are intercepted by the rear structure of the source after a single revolution. In the present apparatus about 12 revolutions can be recorded with sufficient intensity for measurement. It must be noted that heat motion of the ions in the source is sufficient to give them the required vertical components of velocity; a special deflecting field is not necessary.

The ion detector records pulses received after one to about fifteen revolutions. The time interval usually measured is between the second and ninth pulse, giving N=7 in Eq. (1). The field is chosen so that this time interval corresponds to about 10  $\mu$ sec per mass unit; thus *H* is about 450 gauss. Since the time intervals can be measured to 0.01  $\mu$ sec, this yields a mass determination with a precision of 0.001 atomic mass unit.

For complete revolutions in a perfectly uniform magnetic field, the time of flight is entirely independent of direction and magnitude of the initial velocity of the ions; ions with different velocities move along different paths. In addition to this time focusing, the field produces a space focusing: after each revolution the ions focus along a field line passing through source. These focusing characteristics are very advantageous for the intensities of the higher orders of revolution. The focusing properties offer also the advantage that this spectrometer does not require narrow defining slits. However, it is actually necessary to restrict the circular path of the ions somewhat by means of baffles. One reason for this limitation is that ions traveling on small circles have a very low kinetic energy, and are easily scattered. For a radius of R cm the kinetic energy E is

$$E = H^2 R^2 / (144)^2 M \text{ ev.}$$
 (2)

With our radius of 12.5 cm and our magnetic field H=450, this gives  $E\sim10$  ev for M=150. This energy decreases with the square of decreasing radii.

From Eq. (1) it seems at first advisable to use as small a field H as possible in order to increase the time T and thus the accuracy of the measurement. However Eq. (2) shows that the energy of the ions is proportional to  $H^2$  and a weaker field means slower ions and more scattering resulting in lower intensity and decreased sharpness of the recorded pulses. In fact, for heavy ions a field of 450 gauss mentioned above gives suitable pulses only up to about six revolutions in our present apparatus. Increasing the field to about 600 gauss im-

<sup>\*</sup> Work performed at the Brookhaven National Laboratory, under the auspices of the AEC.

<sup>&</sup>lt;sup>1</sup>S. A. Goudsmit, Phys. Rev. 74, 1537 (1948).

<sup>&</sup>lt;sup>2</sup> In all formulas, we shall express time in microseconds, length in centimeters, mass in atomic mass units ( $O^{16}=16.0000$ ), and kinetic energy *E* in electron volts. In these units a very convenient approximation, correct to three percent, is  $E = \frac{1}{2}Mv^2(v)$  in cm/ $\mu$ sec). If in addition *H* is in gauss and electric field *F* in volts/cm, the force on a singly charged ion is  $F + (v \times H)/100$  and its momentum  $p = H_P/100$ . All equations will be written for singly charged particles but can easily be modified for higher ionizations.

proves the higher orders considerably and allows measuring to about the 12th order.

TABLE I. Masses measured with new spectrometer.

#### **II. DEVIATIONS FROM LINEARITY**

According to Eq. (1) the time interval is proportional to the mass of the ion.<sup>3</sup> In an ideal case it would only be necessary to compare the time for an unknown mass with that for a standard ion. Unfortunately, small perturbing electric fields, discussed in more detail below, cause slight deviations from linearity. Moreover, these fields, which are caused by deposits on the wall of the vacuum chamber, are slowly varying with time. Instead of Eq. (1) we must now write

$$T = aM(1 + \epsilon M). \tag{3}$$

The coefficient  $\epsilon$  has been less than 10<sup>-5</sup> in our work. It is therefore necessary to measure simultaneously the time of flight for two standards and the unknown mass. As standards we have selected a number of suitable hydrocarbons. By observing how the time ratio of the two standards differs from their known mass ratio, the quadratic correction is obtained and can be applied to the unknown mass. By choosing one of the two standards near the unknown mass the correction due to nonlinearity can be made small; it usually amounts to a few milli-mass-units. We have checked this method by measuring three known hydrocarbons and found agreement within our limits of precision.

Since changes in standards occur from time to time it is useful to know how this affects the evaluation of the masses. If A and B are the present values for the masses of the standards and  $\delta A$  and  $\delta B$  some future corrections, the correction  $\delta M$  in the mass M is given by

$$\delta M/M = (\delta A/A)(M-B)/(A-B) + (\delta B/B)(M-A)/(B-A).$$
(4)

In the foregoing expression it is usually sufficient to use mass numbers instead of the actual masses.

### III. RESULTS

Table I gives a list of masses measured with the new spectrometer, together with the reference standards used in each case. It must be noted that the indicated limits of accuracy are estimated from the consistency of a number of independent measurements. If we apply the usual procedure of determining the "probable error," these limits of accuracy would be about three times smaller; we prefer however the more conservative values. Under favorable conditions of low pressure, steadiness of field, negligible surface potentials and good intensity, the present apparatus can measure to 0.001 amu, which accuracy we have reached in a few cases. We doubt, however, that even with the best performance of the present instrument it is possible to go much beyond this limit. For Cl the precision is higher because we measured the ion  $CCl_3^+$ .

Element	Ma	ISS <sup>a</sup>	Measured ion	Sta	ndards <sup>b</sup>
S <sup>32</sup>	31.983	$\pm 0.001$	CS <sub>2</sub> +	CeH12	C <sub>3</sub> H <sub>6</sub> O
Cl <sup>35</sup>	34.9805	$\pm 0.0005$	$CCl_3^+$	$C_6H_{12}$	$C_8H_{10}$
K41	40.975	$\pm 0.002$	K <sup>+</sup>	K <sup>39</sup>	- 0 20
Br <sup>79</sup>	78.944	$\pm 0.001$	$C_2H_4Br^+$	C <sub>6</sub> H <sub>6</sub>	$C_8H_{10}$
Br <sup>81</sup>	80.943	$\pm 0.001$	$C_2H_4Br^+$	C <sub>6</sub> H <sub>6</sub>	C <sub>8</sub> H <sub>8</sub>
Kr <sup>84</sup>	83.938	$\pm 0.001$	Kr+	C <sub>6</sub> H <sub>6</sub>	C <sub>s</sub> H <sub>s</sub>
Rb <sup>85</sup>	84.931	$\pm 0.0015$	Rb+	$C_6H_{12}$	•••
Rb <sup>87</sup>	86.9295	$\pm 0.0020$	$Rb^+$	Rb85	
I <sup>127</sup>	126.9415	±0.0025°	$CH_{3}I^{+}$	$C_6H_{12}$	CCl235Cl37
Xe <sup>129</sup>	128.9455	$\pm 0.0015$	Xe <sup>+</sup>	C <sub>8</sub> H <sub>9</sub>	$C_9H_{12}$
Xe <sup>130</sup>	129.945	$\pm 0.002$	$Xe^+$	$C_9H_{12}$	Xe <sup>129</sup>
Xe <sup>131</sup>	130.944	$\pm 0.002$	Xe <sup>+</sup>	$C_9H_{12}$	Xe <sup>129</sup>
$Xe^{132}$	131.945	$\pm 0.002$	$Xe^+$	$C_9H_{12}$	$\mathrm{Xe}^{129}$
Xe <sup>134</sup>	133.947	$\pm 0.002$	Xe <sup>+</sup>	$C_9H_{12}$	Xe <sup>129</sup>

 The precision as tabulated is estimated from the consistency between independent runs. The "probable error" is about three times smaller.
<sup>b</sup> Basic values used are H = 1.0081386, C = 12.003895 from K. Bainbridge, Phys. Rev. 81, 146 (1951). For Cl<sup>55</sup> and Cl<sup>37</sup> we used the values derived by Henry Motz (private communication) from disintegration data, namely, 34.97996, 36.97769.
Preliminary value.

#### IV. SHORT DESCRIPTION OF APPARATUS

The magnet consists of a brass sphere of 20-in. inner diameter, wound with coils in such a way as to produce a homogeneous field over the whole volume inside the sphere. It was designed and constructed several years ago by E. U. Condon and J. A. Hipple, at that time on the staff of the Westinghouse Research Laboratories. We are very fortunate to have obtained this magnet on a loan from Westinghouse. The field has been tested with a proton probe, and by means of small shims the homogeneity has been improved over a cylindrical shell of about 5-in. radius, 5-in. height, and about  $\frac{1}{2}$ -in. thickness. Submarine batteries furnish a current of 20 amperes at 48 volts, to give a field of 400 gauss. The two halves of the sphere can be connected in parallel and the field increased up to about 800 gauss with present equipment.

A cylindrical vacuum chamber is built inside the sphere and is provided with a removable gold-plated liner to reduce the effect of contact and surface potentials. Shields surround the source and detector so that the ion beam sees only the gold plated surfaces. A few baffles restrict the ions to a helical path lying on a cylinder of 5-in. radius and a width of about  $\frac{1}{2}$  in. The pressure during measurements is 1 to  $5 \times 10^{-6}$  mm Hg.

As detector for the ion pulses one can use a simple Faraday cage or a scintillation detector.<sup>4</sup> By far the best detector is an electron multiplier especially designed for this purpose by Smith and described in detail elsewhere.<sup>5</sup>

## **V. THE ION SOURCE**

The ion source is of conventional design. An electron beam, collimated by the magnetic field, ionizes vapor in the small source chamber of about 3-mm depth by  $\frac{1}{2}$ -in. square. In some of the sources the rear wall is a hot filament on which salts can be deposited to produce

 $<sup>^{3}</sup>$  Actually this is true for a fixed path in a magnetic field of arbitrary shape.

<sup>&</sup>lt;sup>4</sup> E. E. Hays and P. I. Richards, Rev. Sci. Instr. **21**, 99 (1950). <sup>5</sup> L. G. Smith, Rev. Sci. Instr. **22**, 166 (1951).



FIG. 1. The second to eighth order of rubidium isotopes 85 and 87 displayed on a 1000  $\mu$ sec sweep. The deflections are downward and saturated; the upward pulses are amplifier kickbacks. The first order is very weak. The background shows weak pulses due to other alkali ions; the fifth order of Cs lies just before the eighth order of Rb.

alkali ions. The voltage of the ionizing electron beam is variable, but the best ion pulses are obtained with energies of 10 to 20 volts at 0.5 milliamp.

The front plate of the source, containing a  $\frac{1}{16}$ -in. exit slit, is insulated from the rest of the structure and can be given pulses up to 600 volts and lasting  $\frac{1}{4}$  µsec,  $\frac{1}{2}$  µsec or longer. An important feature of the source is the following: because of the short duration of the pulse, heavy ions reach the exit slit after the pulse has stopped. In this manner ions heavier than a certain mass (depending upon pulse voltage, pulse duration and source depth) will not receive the full energy but all will obtain the same momentum. All ions therefore follow the same helical paths in the magnetic field and can be made to move in paths determined by the baffles. Thus ions of a large range of masses can be observed and measured simultaneously; it is not necessary to readjust the source parameters for each mass. This obviously facilitates relative measurements and increases reliability and accuracy.

Since the radius is restricted by baffles to the value R, ions below a certain mass cannot be observed. The maximum energy ions can get is equal to the pulse voltage; the smallest observable mass can thus be obtained from Eq. (2) by putting E equal to the pulse voltage. If no baffles are used all masses can be recorded, as the lighter ions move then on smaller radii.

## VI. MEASURING TECHNIQUE

A most essential part of the apparatus is, of course, the time-measuring equipment. It follows the principle of Loran<sup>6</sup> navigation receivers and has been adapted to our needs by the Electronics Division of Brookhaven National Laboratory where it was designed by W. Higinbotham.

The essential features are the following. One scope displays the whole sweep; Figs. 1–3 show examples of various displays. Two separately movable electronic markers select two pulses, which then appear on two separate fast traces on a second scope. By turning the dials which control the markers the two pulses on the second scope can be made to coincide. The dial setting then reads directly the time interval between the two pulses. In order to facilitate the measurements, the two traces on the fast scope can be separated or made to coincide at will, and the relative amplification of the two pulses can be varied so as to make them look more alike. In this way good pulses can be matched to 0.01  $\mu$ sec even if they are as long as a  $\frac{1}{2}$  µsec. Figure 4 shows an example; this picture shows the fastest sweeps of about 2  $\mu$ sec which are used for precision measurements. Experience proves that a skilled observer can match to almost 0.01 µsec even those pulses which fluctuate considerably in intensity. The sweep repetition rate is about 300/sec and is not critical.



FIG. 2. The eighth order of Rb<sup>85</sup> and Rb<sup>87</sup> on a delayed sweep of 25  $\mu sec$  at about 950  $\mu sec$  from the start. The separation is 22  $\mu sec$ .

The organic standards and unknown mass are introduced into the source simultaneously through suitable leaks. A reading consists in matching say the second and tenth pulses of each ion, using the same pair of orders for the standards and the unknown. In order to eliminate the effect of slow drifts in the magnetic field, readings are taken in a symmetrical order.<sup>7</sup> If Aand B denote the standards and M the mass to be determined, the order of measurement is, for example,

## $M A B B A M M A B B A M \cdots$

Not only does this procedure eliminate slow drift by averaging, but inspection of individual sequences also gives an indication of sudden variations so that consistent runs may be selected. Each reading takes about a minute, a run about ten minutes.

## VII. THE PULSE LENGTH

The magnetic field does not necessarily have to be homogeneous. Particles following the same orbits have equal momenta in any magnetic field, and the time of travel between two points is proportional to the mass. It is of course advantageous that the field be homogeneous, since the beam defining slits can then be wide and full use made of space focusing properties. Nonhomogeneity lengthens the pulses and decreases the accuracy of pulse matching, unless the slits are made very narrow.

<sup>&</sup>lt;sup>6</sup> See "Loran," Vol. 4 of Massachusetts Institute of Technology Radiation Lab Services (McGraw-Hill Book Company, Inc., New York, 1949).

<sup>&</sup>lt;sup>7</sup> We are currently installing a regulator for the magnetic field.

Observations indicate that the minimum length recorded depends primarily upon the depth of the source. The pulse leaving the source is a small cloud of ions of about 0.3 cm thickness along its path. This cloud spreads out vertically and also perpendicularly to its path, but after every complete revolution its dimension along its path is ideally again 0.3 cm. The recorded over-all pulse duration  $\tau$  is thus given by the time it takes for this cloud to enter the detector. Denoting the length of the cloud by s, and the time for one revolution by T, we have

$$\tau = (s/2\pi R)T \sim 100 sM/HR \ \mu sec; \tag{5}$$

thus the pulse duration increases with the mass. For M=150, H=450 gauss, R=12.5 cm, and s=0.3 cm we find  $\tau=0.8 \ \mu$ sec. The observed values of the base width of the pulses agree well with the computation; the recorded pulses are perhaps somewhat narrower. We have not succeeded in constructing shallower sources to reduce the size of the pulse below 0.3 cm.

Equation (5) gives another reason for using baffles to eliminate ions moving on small circles. The relative size of ion cloud to path length would be large and produce long pulses.

## VIII. INTENSITY

The intensities of the various orders can be computed by assuming that the vertical velocity components of



FIG. 3. The eighth order of xenon isotopes 128, 129, 130, 131, 132, 134, and 136 on a sweep of about 90  $\mu$ sec delayed about 1050  $\mu$ sec from the start. The separation between consecutive isotopes is about eight  $\mu$ sec.

the ions obey a Maxwell distribution corresponding to an absolute temperature  $\theta$ . We call *a* the height of the exit slit of the source, assuming for simplicity that it equals the entrance slit of the detector, and we denote by *l* the vertical distance between them. A simple geometrical consideration gives for the fraction *I* of ions that reach the detector after *N* revolutions

$$I = 0.067 a H / N(M\theta)^{\frac{1}{2}} \exp(-0.0142 l^2 H^2 / N^2 M\theta).$$
(6)

Note that even when the exponential factor is negligible the intensity decreases only with the first power of the number of revolutions. This is due to the space focusing. The intensity has a maximum for the order N near the value

$$N_{\max} = (0.0284l^2H^2/M\theta)^{\frac{1}{2}}.$$
 (7)

Since l=12 cm one finds, for a temperature of 1000°K and a field of 450 gauss, that the third order will be the strongest for M=100. It also becomes clear why for

large l the first order is very weak. For the order of maximum intensity Eq. (6) gives  $I \sim a/4l$ , or about 2 percent for a=1 cm. However, in reality it is probably much smaller since Eq. (6) is based on idealized and simplified assumptions.

Formula (6) does not take into account the decrease in intensity due to scattering. This would add another exponential factor with a negative exponent proportional to the path traversed, or to N, the number of revolutions.

## IX. SCATTERING

An advantageous feature is that single scattering of the ions does not in general lengthen the recorded pulse; it merely removes ions from the pulsed beam. The change in direction and energy experienced in a collision with residual gas molecules usually causes a change in path such that the scattered ions cannot reach the entrance slit of the detector. If the scattering happens to occur near  $180^{\circ}$  from source and detector, the approximate  $180^{\circ}$  focusing invalidates this statement, but such occurrences are rare. If the pressure is so high that multiple scattering takes place, the pulses are lengthened and considerably weakened. It is indeed comforting that under favorable operating conditions the pulses of the various orders are quite similar, an important factor in accurate pulse matching.

Whether a scattered ion will reach the detector depends on where in its path the deflection occurred. The change in arrival time caused by the scattering is also a function of the position and the amount of deflection. A detailed theoretical treatment, though elementary, would be uselessly complex. We shall merely state that geometrical consideration shows that a deflection by a



FIG. 4. Pulse matching. In the top picture the shift is 0.1  $\mu$ sec, in the middle picture it is 0.02  $\mu$ sec, and in the bottom picture the pulses are matched. The sweep is 2  $\mu$ sec.

small angle  $\phi$  causes, on the average, a change  $\phi T_1/2\pi$ in arrival time. In order to keep the pulses sharp we want this change to be less than  $\frac{1}{4} \mu \sec$  or

$$\phi < H/400M$$
 radians. (8)

The gas scattering will be primarily due to dipole moments induced in residual gas molecules by the moving ions. In this case the potential energy will be of the form  $k/r^4$ . The value of k depends upon the polarizability of the gas molecules and is of the order of  $10^{-31}$  ev cm<sup>4</sup>. For organic molecules such as pump oil or our standards, the value k may be several times larger. The probability that an ion experiences a deflection larger than a small angle  $\phi$  can be expressed in terms of a cross section  $\sigma$ . A straight-forward application of mechanics shows that

$$\sigma^2 \sim 100 k / \frac{1}{2} M v^2 \phi. \tag{9}$$

With the help of Eqs. (2) and (8) we find

$$\sigma \sim 3 \times 10^4 k^{\frac{1}{2}} M/RH^{\frac{3}{2}}.$$
 (10)

With k at least  $10^{-31}$  ev cm<sup>4</sup>, this shows that for M = 150, H = 450 gauss, R = 12.5 cm, the value of  $\sigma$  is at least  $1.2 \times 10^{-14}$  cm<sup>2</sup>. At a pressure of  $5 \times 10^{-6}$  mm Hg this results in a mean free path L such that

$$L < 350 \text{ cm.}$$
 (11)

This is almost doubled if we increase the field from 450 gauss to 600 gauss.

#### X. SURFACE POTENTIALS

If surface potentials cause a radial component of electric field averaging F volts/cm, the time of flight T is changed by an amount  $\Delta T$  given by

$$\Delta T/T \sim 10^4 F M/H^2 R. \tag{12}$$

Combining this with Eqs. (1) and (3) gives for the correction coefficient  $\epsilon$ 

$$\epsilon = 10^4 F / H^2 R. \tag{13}$$

Since  $\epsilon$  was found to be less than 10<sup>-5</sup> it indicates that the average perturbing field F is less than 2 mv/cm (indicating potentials of the order of 20 mv).

If surface potentials produced a fairly uniform field they would not cause serious difficulties even if the field varied slowly in time. We have, however, some evidence that these fields are probably irregularly distributed and thus cause deflections of the ions similar to scattering. It is not possible to give an *a priori* estimate of this effect but it is considerably reduced by occasional careful cleaning of the gold-plated liner. This "scattering" probably behaves as if it were caused by fixed dipoles and not induced dipoles as was the case for molecular scattering. If that is so, the mean free path is proportional to  $E\phi = H^3R^2/M^2$ . The disturbing effects will decrease rapidly with increasing the magnetic field.

#### XI. LIMITATIONS IN PRECISION

It has not been ascertained whether surface potentials or gas scattering determine the mean free path in the present apparatus. Considering the latter only, it is possible to study the limit of precision of which this type of mass spectrometer is capable without making radical changes in technique. In order to do this we make the following assumptions:

(a) It is not practical at present to measure time intervals with higher precision than 0.01  $\mu$ sec.

(b) In order to make full use of the time measuring precision, the pulses must be shorter than 1  $\mu$ sec.

(c) It is not easy to obtain pressures below  $10^{-6}$  mm Hg in the volumes needed for this type of spectrometer  $(4 \times 10^{10} \text{ particles per cc})$ .

(d) It is not practical to produce an ion cloud much smaller than about 0.2 cm.

(e) The total path length between source and detector should not exceed one mean free path in order to avoid pulse distortion due to scattering, and the value of k in Eq. (9) is not less than  $10^{-31}$  ev cm<sup>4</sup>.

The parameters at our disposal are the field strength H and the radius R. Using Eq. (10) the mean free path L is

$$L = (4 \times 10^{10} \sigma)^{-1} \sim 3RH^{\frac{3}{2}}/M.$$
(14)

The slowest speed the ions can have is determined by (b) and (d), namely,  $0.2 \text{ cm}/\mu\text{sec}$ . The maximum time to traverse L is thus

$$T = 15RH^{\frac{1}{2}}M \ \mu \text{sec.} \tag{15}$$

If this is measured to 0.01  $\mu$ sec the optimum precision is one part in  $1500RH^{\frac{1}{4}}/M$ . With R=12.5 cm, H=450gauss and M=100 this gives almost  $2\times10^6$ . The time T would be  $2\times10^4$   $\mu$ sec and the path 5000 cm.

Since k is most likely several times larger than assumed here, and since our pressure is also five times higher, it is not surprising that the precision obtained so far is from 20 to 40 times less than computed. By increasing H and R it seems possible to improve the precision considerably, provided surface potentials or other factors do not prevent ions from remaining in their prescribed orbit for the long time that is required.

The present apparatus has the disadvantage that the length of the ion paths is essentially limited by geometry to about 15 revolutions or 1200 cm. Various modifications have been suggested to avoid this limitation; the most promising method seems to be one proposed by Smith.<sup>8</sup>

## XII. CONCLUSIONS

Though the results obtained should still be considered preliminary, they indicate that the basic principle used in this spectrometer leads to reasonably high precision mass measurements for heavy ions; more work is needed before we understand fully the nature of some of the

<sup>&</sup>lt;sup>8</sup> L. G. Smith, Rev. Sci. Instr. 22, 115 (1951).

difficulties encountered in the operation of this new instrument. We plan to measure a few more heavy masses and shall also attempt to improve our precision so as to reach in all cases the limit of one milli-massunit.

We wish to thank Dr. Joseph Slepian of the Westinghouse Research Laboratories for the loan of the CondonHipple magnet, Dr. L. G. Smith for many valuable suggestions during the early stages of this work, and Mr. A. Tuthill for his technical assistance. Thanks are also due to Dr. W. A. Higinbotham of our Electronics Division for the design of the timing equipment and to members of the Chemistry Department for much valuable advice.

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# Electron-Hole Production in Germanium by Alpha-Particles

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The number of electron-hole pairs produced in germanium by alpha-particle bombardment has been determined by collecting the internally produced carriers across a reverse-biased n-p junction. No evidence is found for trapping of carriers in the barrier region. Studies of individual pulses show that the carriers are swept across the barrier in a time of less than  $2 \times 10^{-8}$  sec. The counting efficiency is 100 percent. The energy lost by an alpha-particle per internally produced electron-hole pair is  $3.0\pm0.4$  ev. The difference between this and the energy gap is attributed to losses to the lattice by the internal carriers. It is concluded that recombination due to columnar ionization is negligible in germanium.

## INTRODUCTION

IN the theories of external secondary emission and of bombardment conductivity, it is desirable to know the actual number of electrons freed in a solid by a bombarding particle. The rate of loss of energy by the bombarding particle has been studied extensively by measurements of stopping power and treated theoretically by Bohr, Bethe, and others1 for high energy particles. This energy loss is the result of electron excitation and ionization, lattice excitation, and nuclear displacement. Much of the energy may be lost in the production of high energy internal secondary electrons which, in turn, produce tertiaries and so forth. Consequently, only approximate estimates of the number of free electrons produced per bombarding particle can be obtained from theory. No satisfactory method has been devised to obtain this quantity experimentally for metals. For phosphors, the light output per incident particle can be measured but its interpretation in terms of a number of free electrons is complicated by the existence of nonradiative transitions. A better method, which has been used for certain insulators, is bombardment conductivity.<sup>2</sup> It is the purpose of this report to describe an accurate determination by this method of the average energy lost by an alpha-particle in producing one electron-positive hole pair in germanium. The use of germanium is predicated by the fact that it is a valence bonded crystal, with the same structure as

diamond for which the average energy lost by an alphaparticle in producing one electron-positive hole pair has been measured.<sup>3</sup> Moreover, large single crystals of germanium of known composition and known electrical properties can now be prepared.

#### THEORY OF THE METHOD

Consider a rod of germanium of which one half is *n*-type and the other half p-type. If the *n*-type end is made positive with respect to the p-type end, the n-pbarrier will develop a very high resistance and virtually all of the voltage drop along the rod will be concentrated across the n-p barrier. This can be crudely likened to a thin insulator separating two conductors. If the bombarding particles strike the barrier itself so that the resultant holes and electrons are produced in this high field region, they will be swept across the barrier, thereby registering in the external circuit and will eventually disappear in the main body of the germanium. Although the field is not constant throughout the barrier, that is irrelevant as long as trapping or recombination do not take place within the barrier, i.e., as long as the sum of the voltage drops traversed by a given electron-hole pair is substantially equal to the total voltage drop across the specimen. To date, no evidence has been observed for the existence of trapping or recombination within a well made n-p barrier in germanium. Moreover, the injected current densities normally used are much too small to set up a space charge field which could perturb the barrier field appre-

<sup>&</sup>lt;sup>1</sup>N. F. Mott and H. Massey, *Theory of Atomic Collisions* (Oxford University Press, London, 1934). <sup>2</sup> Reviews of this work as applied to crystal counters have been published by R. Hofstadter, Nucleonics 4, No. 4, 2 (1949); 4, No. 5, 29 (1949); Proc. Inst. Radio Engrs. 38, 726 (1950).

<sup>&</sup>lt;sup>8</sup> A. J. Ahearn, Phys. Rev. 73, 1113 (1948); K. G. McKay, Phys. Řev. 77, 816 (1950).



FIG. 1. The second to eighth order of rubidium isotopes 85 and 87 displayed on a 1000  $\mu$ sec sweep. The deflections are downward and saturated; the upward pulses are amplifier kickbacks. The first order is very weak. The background shows weak pulses due to other alkali ions; the fifth order of Cs lies just before the eighth order of Rb.



FIG. 2. The eighth order of Rb<sup>85</sup> and Rb<sup>87</sup> on a delayed sweep of 25  $\mu sec$  at about 950  $\mu sec$  from the start. The separation is 22  $\mu sec$ .



FIG. 3. The eighth order of xenon isotopes 128, 129, 130, 131, 132, 134, and 136 on a sweep of about 90  $\mu$ sec delayed about 1050  $\mu$ sec from the start. The separation between consecutive isotopes is about eight  $\mu$ sec.



FIG. 4. Pulse matching. In the top picture the shift is 0.1  $\mu$ sec, in the middle picture it is 0.02  $\mu$ sec, and in the bottom picture the pulses are matched. The sweep is 2  $\mu$ sec.