# Atomic Masses in the Region about Mass 40

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The double-focusing mass spectrometer developed for the precise determination of atomic masses has been improved. A redetermination of the mass doublets  $4C^{12}-S^{32}O^{16}$ ,  $2O^{16}-S^{32}$ , and  $C^{12}H_4-O^{16}$  lead to the following masses:  $H^1 = 1.008146 \pm 3$ ,  $C^{12} = 12.003842 \pm 4$ , and  $S^{32} = 31.982236 \pm 7$ . The relation of these results to those of other investigators is discussed.

Mass doublet comparisons between hydrocarbon fragments and S<sup>32</sup>, S<sup>33</sup>, S<sup>34</sup>, Cl<sup>35</sup>, Cl<sup>37</sup>, A<sup>36</sup>, A<sup>38</sup>, K<sup>39</sup>, K<sup>41</sup>, Ca<sup>42</sup>, Ca<sup>43</sup>, Ca<sup>44</sup>, Ca<sup>48</sup>, and Sc<sup>45</sup> have been made and mass values for these nuclides tabulated assuming both mass spectroscopic and nuclear reaction determined mass values for H1 and C12.

The packing fraction curve in the mass 40 region follows the general trends predicted by a formula such as that of Bohr and Wheeler, except at masses 40 and 48 where there appear to be marked discrepancies.

DOUBLE-FOCUSING mass spectrometer has A been described<sup>1</sup> which has proved useful for the precise measurement of atomic masses. Mass values for H1, H2, He4, C12, N14, Ne20, S32, A36, A40, and other isotopes have been reported.<sup>2,3</sup> The instrument employs a 90° electrostatic analyzer followed by a  $60^{\circ}$  magnetic analyzer. Ions are produced by electron impact of gases or emitted thermionically from filaments. A small single-focusing mass spectrometer tube mounted in the same magnetic field as the main tube acts as part of a control device to compensate for fluctuations in the magnetic and electric fields in the main tube. The small tube is the input element of an inverse feedback loop which produces the stabilization.

A mass spectrum in the main tube is obtained by varying the position of a tap on a voltage divider. If  $\Delta m$  represents the mass difference between two ions whose masses are compared, the equation

$$\Delta m/m = (\Delta R/R)[G/(G+1)] \tag{1}$$

gives the relation between the fractional difference in mass and the fractional shift in the resistance in the voltage divider circuit. With the apparatus as constructed, G, the open circuit gain of the feedback loop, has to be held below 100 to prevent oscillations. Because of the precise nature of the measurements, G must be measured accurately.

## I. IMPROVEMENTS IN THE INSTRUMENT

# A. Control System

In operation it turned out that the determination of G required as much or more effort than the measurement of  $\Delta R/R$ . Moreover, because of the difficulty in making the G measurements, one could not be completely certain that small systematic errors might not have been present. Accordingly, an "integral control" mechanism has now been added to the feedback circuit.<sup>†</sup>

In Fig. 1 of reference 1 the output of the differential amplifier no longer goes only to the high voltage supply as shown. In addition, it is fed into the input circuit of a Brown Electronik Amplifier.<sup>4</sup> The output of this amplifier drives a reversible motor which has a potentiometer coupled to its shaft across which a battery is connected. The voltage between the tap and a center tap on the potentiometer is then fed into the high voltage supply, in series with the output of the differential amplifier.

In practice, the integral controller serves to hold the output of the differential amplifier at zero for slow changes in the circuit such as take place as one sweeps a mass spectrum. Thus the gain may be considered as infinite in the formula (1) above. For rapid fluctuations, due to disturbances in the circuits, the compensation is not complete, the gain remaining G.

## **B.** Detection System

The vibrating reed electrometer previously employed has been replaced by a 10-stage electron multiplier of the Allen type.<sup>5</sup> The output of it is fed into an inverse feedback amplifier employing an electrometer tube for the input stage. Grid resistors up to 1011 ohms are employed satisfactorily, the time response of the circuit being considerably better than with the vibrating reed electrometer previously used. The increased sensitivity resulting from the use of the electron multiplier detector permits the study of rare isotopes.

## C. Miscellaneous Improvements

Most of the electronic components have been rebuilt to give better regulation and more reliable performance. A description of the rebuilt apparatus will be published separately.

## **II. PERFORMANCE OF THE INSTRUMENT**

The continuous measurement of the ion beam current allows several tests of the proper performance of the

<sup>\*</sup> Research supported by joint program of ONR and AEC.
<sup>1</sup> A. O. Nier and T. R. Roberts, Phys. Rev. 81, 507 (1951).
<sup>2</sup> T. R. Roberts, Phys. Rev. 81, 624 (1951).
<sup>3</sup> A. O. Nier, Phys. Rev. 81, 624 (1951).
<sup>4</sup> The second seco

<sup>&</sup>lt;sup>†</sup> The authors wish to express their appreciation to Professor N. B. Nichols of the Electrical Engineering Department who suggested the use of the controller.

<sup>&</sup>lt;sup>4</sup> J. C. Mouzon, Adaptability of the Measuring Circuit, Input Circuit and Amplifier of the Brown Electronic Potentiometer, Bulletin No. B 15-10, 1948, Brown Instrument Company, Philadelphia, Pennsylvania. <sup>5</sup> J. S. Allen, Rev. Sci. Instr. 12, 484 (1941); 18, 739 (1947).



FIG. 1. Mass spectrum at mass 28 showing (C<sup>12</sup>)<sub>2</sub>H<sub>4</sub>, (N<sup>14</sup>)<sub>2</sub>, and C<sup>12</sup>O<sup>16</sup>. Actually, the resolution was improved after print was made, and for most of the work in the present paper (N<sup>14</sup>)<sub>2</sub> and C<sup>12</sup>O<sup>16</sup> were completely resolved.

instrument to be made periodically during runs. These tests are carried out frequently in an attempt to remove systematic errors and to improve the statistical errors.

Known possible sources of systematic error include control circuit gain not effectively infinite, leakage current to ground from the potential divider, and charge on the electrostatic analyzer plates. In general these errors will multiply the doublet difference by a constant and can be detected by measuring a known "doublet" such as  $C_3H_8-C_3H_7$  in which the difference is a hydrogen mass or 1.00814. Regular measurements are made of the hydrogen mass doublet in the region of masses being investigated. If the result is consistently in error by more than a few parts in 10<sup>4</sup> the measurements are discarded until a remedy is found.

We have found that an error can arise from small variations in the energy focusing of the instrument when measuring a doublet containing an ion fragment with appreciable kinetic energy from chemical binding. The energy focusing is checked by varying the 6000-v accelerating potential by about 40 volts and looking for a small shift in the position of a peak. A small movement of the whole spectrometer tube in or out of the magnetic field can correct any shift so that it is less than  $\Delta M/M = 10^{-5}$ . As an example, consider the measurement of the  $O_2$ -S doublet. When the S<sup>+</sup> ion is obtained from H<sub>2</sub>S, almost all of the kinetic energy released in the dissociation process accompanies the light hydrogen fragments. In this case the energy focusing has little effect on doublet difference. When  $SO_2$  is the source of S<sup>+</sup> ions the fragments are of equal mass and the doublet shows a strong dependence on the energy focusing. It has been found necessary to check the focusing daily, and for every new mass region, if results consistent within the statistics for each run are to be expected.

The region of good angular focusing contains the position of perfect energy focusing, and with proper adjustment the peaks have a width at half-height of  $\Delta M/M = 1/4600$  (Fig. 1). The theoretical value based on slit widths alone and assuming perfect angular and energy focusing is 1/5000. We have found recently that charges on the electrostatic analyzer plates can move the energy focus position out of coincidence with the position for narrow peaks. In practice this provides a test for the accumulation of foreign material on the plates more sensitive than the hydrogen mass doublet measurement.

Statistical errors arise from noise in the electronic circuits. The stability of the control circuit is checked by tuning the spectrometer to a steep side of a peak (Fig. 2). Instability of the main amplifier and emission regulator appears as excessive fluctuation of the top of a peak. Under best conditions the noise is the shot effect of the ion beam itself. In practice statistical errors in reading the charts are not important.

#### III. DOUBLETS CONTAINING ELEMENTS FROM SULFUR TO SCANDIUM

Table I lists doublets containing nuclides in the neighborhood of mass 40 which we have measured recently. Three methods were used in the production of the ions. The gases SO<sub>2</sub>, HCl, and argon were admitted to the source through capillary leaks, as were the hydrocarbons used for comparison. Potassium and calcium metals were evaporated from a small furnace and ionized by the electron beam.  $ScO^+$  ions were obtained from a tungsten ribbon filament coated with  $ScO_3$ ; the comparison peak in this case came from ethyl acetate vapor.

The peaks were matched in intensity; a run consists of at least ten consecutive tracings with alternate forward and backward sweep. Runs were taken on different days over a period of several months, and the probable errors are calculated solely from the statistics. Where necessary the doublets have been corrected for a C<sup>13</sup> isotope peak on the low side of the hydrocarbon comparison. A similar correction was necessary for S<sup>32</sup>O<sup>17</sup> and S<sup>32</sup>O<sup>18</sup> isotope peaks under S<sup>33</sup>O<sup>16</sup> and S<sup>34</sup>O<sup>16</sup>.



FIG. 2. Mass spectrum illustrating stability of regulating system. Mass doublet having a separation  $\Delta m/m = 1/1000$  was swept from left to right. On way down and at steepest point on second peak the scanning mechanism was stopped for a period longer than required to normally scan a mass doublet. A deliberate change in  $\Delta R/R$  or 1/100,000 produced a shift which may be seen on chart. Note that normal fluctuations are considerably lower than the artificial disturbance.

During these measurements six determinations were made on doublets differing by one hydrogen unit. The average value for the hydrogen mass doublet was 1.0082, a value we regard as constituting a satisfactory check of the performance of the instrument.

## IV. SECONDARY STANDARD MASSES

Before the doublets can be converted to useful masses or packing fractions, it is necessary to know the masses of H1 and C12. An abundance of evidence exists indicating that masses quoted prior to 1950 are incorrect, but results of various laboratories are not consistent. At present this laboratory is concentrating on a set of doublets previously reported by Nier<sup>3</sup> in which carbon si determined directly from sulfur compounds. Thus, if

 $2O^{16} - S^{32} = a$ , and  $4C^{12} - S^{32}O^{16} = b$ ,

TABLE I. Doublets for nuclides near mass 40.

Doublet	No. of runs	Source of ions	Av. in 10 <sup>-4</sup> amu.	Previous work
C4H-S33O	4	$SO_2$ gas	$413.85 \pm 0.46$	
$C_4H_2 - S^{34}O$	5	$SO_2$ gas	$529.00 \pm 0.40$	
$C_3 - HCl^{32}$	5	HCl gas	$233.41 \pm 0.44$	225 $\pm 7^{*}$
	-			$246.7 \pm 1.7^{b}$
$C_3H_2 - HCl^3$	5	HCl gas	$420.14 \pm 0.46$	$412 \pm 7^{\text{a}}$ $4217 \pm 0.0^{\text{b}}$
				$421.7 \pm 0.9^{\circ}$
$C_3 - A^{36}$	4	enriched A <sup>36</sup>	$325.01 \pm 0.33$	$\frac{419.0 \pm 1.1^{\circ}}{326 \pm 7^{\circ}}$
$H_{9}O - A^{36}/2$	6	enriched A <sup>36</sup>	$268.19 \pm 0.28$	$271 + 3.6^{a}$
	U			$267.0 \pm 0.4^{\circ}$
C3H2-A38	5	enriched A <sup>38</sup>	$529.10 \pm 0.40$	
C2H2-K39	6	K metal	$599.05 \pm 0.26$	
$C_{1}H_{1} - K^{41}$	Š	K metal	$773.61 \pm 0.33$	
$C_{1}H_{1} - C_{2}^{42}$	3	Ca metal	$882.47 \pm 0.34$	
$C H_{-} C c 43$	4	Ca metal	$060.40\pm0.52$	
$C_{3}\Pi_{7} - Ca^{*}$	4	Ca metal	$900.40\pm0.32$	
$CO_2 - Ca^{**}$	1	Ca metal	$340.07 \pm 0.39$	
$C_4 - Ca^{48}$	5	Ca metal	$4/5.90 \pm 1.0$	
$C_2O_2H_5-Sc^{45}O$	4	ScO <sub>3</sub>	$783.17 \pm 0.41$	

 F. W. Aston, Proc. Roy. Soc. (London) A163, 391 (1937).
 <sup>b</sup> Okuda, Ogata, Aoki, Sugawara, Phys. Rev. 58, 578 (1940). See reference 1.

then

$$C^{12} = 12 + (a-b)/4.$$

Hydrogen may then be determined from any suitable hydrocarbon—oxygen doublet, in our case  $C_3H_8$ — $CO_2$ , a doublet which has just twice the mass difference of the common CH<sub>4</sub>-O doublet. Our recent results are given in Table II. The best conditions of focusing were maintained throughout this experiment, and daily measurements of a hydrogen mass doublet had an average of 1.0083. Probable errors were computed for each run; each set of runs showed internal consistency, and the quoted errors, which are purely statistical, were calculated on this basis. These doublets give the masses  $H^1 = 1.008146 \pm 3$ ,  $C^{12} = 12.003842 \pm 4$ . The differences from results previously reported by Nier can probably be attributed to the general improvement of the instrument, particularly the elimination of the gain measurement mentioned earlier.

TABLE II. Doublets determining H<sup>1</sup> and C<sup>12</sup>.

Doublet	No. of runs	Source of ions	$\Delta M$ in 10 <sup>-4</sup> Present results	amu Nier*
C <sub>4</sub> -SO	5	C <sub>4</sub> H <sub>6</sub> SO <sub>2</sub>	$331.32 \pm 0.13$	$331.82 \pm 0.28$
$O_2 - S$	6	$O_2$ H <sub>2</sub> S	$177.64 \pm 0.07$	
$\rm CO_2 - \rm CS$				$177.82 \pm 0.25$
$C_3H_8-CO_2$	6	$\begin{array}{c} \mathrm{C}_{3}\mathrm{H}_{8}\\ \mathrm{CO}_{2} \end{array}$	$728.54 \pm 0.15$	$729.67 \pm 0.41$

See reference 3.

The recent results of several investigations are compared in Table III. Li et al.<sup>6</sup> calculated masses by means of a chain of nuclear reactions extending from H<sup>1</sup> to O<sup>16</sup>. Ewald<sup>7</sup> has recently reported new values for the fundamental doublets used by earlier investigators. The results agree remarkably well considering the differences in the methods employed. However, our result for C12 from the very direct sulfur method is not consistent with those of Ewald<sup>7</sup> or Li et al.<sup>6</sup> For us to obtain  $C^{12} = 12.003804$ , either the mass difference  $4C^{12} - S^{32}O^{16}$ would have to be less than  $330 \times 10^{-4}$  amu, or  $20^{16} - S^{32}$ would have to be greater than  $179 \times 10^{-4}$  amu. Ewald<sup>7</sup> finds  $2O^{16} - S^{32} = (177.16 \pm 0.20) \times 10^{-4}$  amu, a good agreement with our value, but at present there are no other determinations of 4C12-S32O16. It is hoped that other mass spectroscopists will make a check of this important doublet.

Although our value for  $C^{12}H_4 - O^{16}$  is substantially higher than that of Li et al.,6 and Ewald,7 the values for H1 obtained are in good agreement. Ogata's8 determination for  $C^{12}H_4 - O^{16}$  lends support to the higher value for this doublet. Again, it is to be hoped that other independent determinations of this all-important doublet will be made. Since the disagreements in Table III do not appear to be statistical in nature, it would appear wrong to average the results in an attempt to find more accurate masses. The difficulty can be resolved only by further experimental work.<sup>‡</sup>

TABLE III. Recent determinations of secondary standards.

Mass in 10 <sup>-</sup>	excess 4 amu	$\Delta M$ in 10 <sup>-1</sup> amu		
$H_1$	C12	$C^{12}H_4 - O^{16}$	Method	Reference
	$38.50 \pm 0.0938.04 \pm 0.1738.07 \pm 0.1138.42 \pm 0.04$	$\begin{array}{c} 364.84 \pm 0.21 \\ 363.72^{\rm b} \pm 0.19 \\ 363.71 \pm 0.12 \\ 364.47 \pm 0.04 \\ 364.27 \pm 0.08 \end{array}$	sulfur doublets nuclear reactions standard doublets sulfur doublets	Nier <sup>a</sup> Li <i>et al.</i> ° Ewald <sup>d</sup> Ogata <sup>a</sup> This paper
* See refer b Compute	ence <b>3.</b> ed from H <sup>1</sup> and	1 C <sup>12</sup> . • See reference	• See refer d See refer 8.	ence 6. rence 7.

<sup>6</sup>Li, Whaling, Fowler, and Lauritsen, Phys. Rev. 83, 512 (1951).

(1951).
<sup>7</sup> H. Ewald, Z. Naturforsch. 6a, 293 (1951).
<sup>8</sup> K. Ogata and H. Matsuda, Phys. Rev. 83, 180 (1951).
<sup>‡</sup> Nole added in proof: At the Symposium on Mass Spectroscopy, National Bureau of Standards, U.S.A., September 6-8, 1951, Ogata reported values of 177.27±0.05 and 331.27±0.07 for 20<sup>16</sup>-S<sup>28</sup> and 4C<sup>12</sup>-S<sup>28</sup>O<sup>16</sup> respectively. Mattauch and Bieri reported provisional value of 364.52±0.10 for C<sup>12</sup>H<sub>4</sub>-O<sup>16</sup>. These new results support the values presented in this paper. new results support the values presented in this paper.

Standards used		H <sup>1</sup> 1.008146 $\pm 3^{\circ}$ C <sup>12</sup> 12.003842 $\pm 4^{\circ}$
S32	$31.982236 \pm 7$	$31.982236 \pm 7$
S <sup>33</sup>	32.98197 + 8	32.98213 + 5
S <sup>34</sup>	$33.97860 \pm 8$	$33.97876 \pm 5$
Cl <sup>35</sup>	$34.97993 \pm 7$	$34.98004 \pm 5$
Cl <sup>37</sup>	$36.97754 \pm 7$	$36.97766 \pm 5$
A <sup>36</sup>	35.97892 ±4ª	35.97900 ±3*
A 38	$37.97479 \pm 7$	$37.97491 \pm 4$
A40	$39.97502 \pm 4^{b}$	39.97513 ±3 <sup>b</sup>
K <sup>39</sup>	$38.97593 \pm 6$	$38.97606 \pm 3$
<b>K</b> <sup>41</sup>	$40.97476 \pm 6$	$40.97490 \pm 4$
Ca40	39.97534 ±9°	39.97545 ±9°
Ca42	$41.97202 \pm 6$	$41.97216 \pm 4$
Ca43	$42.97237 \pm 8$	$42.97251 \pm 6$
Ca <sup>44</sup>	$43.96920 \pm 6$	$43.96924 \pm 6$
Ca <sup>48</sup>	$47.96763 \pm 12$	$47.96778 \pm 10$
Sc45	$44.97000 \pm 6$	$44.97010 \pm 5$

TABLE IV. Masses of nuclides from sulfur to scandium determined by mass spectroscopy.

 Weighted average of the masses from the two A<sup>30</sup> doublets.
 b Weighted average from C<sub>1</sub>H<sub>4</sub>-A<sup>40</sup>, D<sub>2</sub>O-A<sup>40</sup>/2, Ne<sup>30</sup>-A<sup>40</sup>/2 a: D<sub>2</sub>O-Ne<sup>90</sup> (A. O. Nier and T. R. Roberts, Phys. Rev. 81, 507 (1951)).
 • From Ca<sup>40</sup>-A<sup>40</sup>=3.2±0.8, Nier and Roberts, see reference b. . -A40/2 and

<sup>d</sup> See reference 6. • Values from this paper.

## V. COMPUTED MASSES IN 40 REGION

The masses in Table IV have been calculated from the doublets using two sets of hydrogen and carbon masses, the values of Li et al.,<sup>6</sup> and those given in this paper. The probable errors are purely statistical, and the discrepancies in the errors come from the errors in the standards used. Thus, more consistent values for hydrogen and carbon will smaller errors are required before the full accuracy of doublets in this region can be utilized. This table also includes for completeness two nuclides computed from doublets reported previously by this laboratory. The importance of the small difference between the two sets of masses may be judged by computing the energy for the possible reaction  $Ca^{43}(d, p)Ca^{44}$ . Masses computed using the standards of Li et al. lead to Q = 2.96 Mev, while the standards of this paper give Q = 3.20 Mev.

TABLE V. Mass ratio Cl<sup>35</sup>/Cl<sup>37</sup>.

Investigations	Method	Value
Astona	Mass spectroscopy	$0.9459806 \pm 300$
Okuda et al.b	Mass spectroscopy	$0.9459452 \pm 65$
Townes et al.º	Microwave (I Cl)	$0.9459801 \pm 50$
Gilbert et al.d	Microwave (F Cl)	$0.9459775 \pm 40$
Townes et al.º	Microwave (Cl CN)	$0.9459906 \pm 120$
Pollard <sup>f, g</sup>	Nuclear reaction	$0.9459893 \pm 110$
This paper	Mass spectroscopy	$0.9459777 \pm 20$

F. W. Aston, Proc. Roy. Soc. (London) A162, 191 (1937).
 <sup>b</sup> See reference b of Table I.
 <sup>e</sup> Townes, Merritt, and Wright, Phys. Rev. 73, 1334 (1948).
 <sup>d</sup> Gilbert, Roberts, and Griswold, Phys. Rev. 76, 1723 (1949).
 <sup>e</sup> Townes and Shulman, reported by W. Low and C. H. Townes, Phys. Rev. 80, 608 (1950).
 <sup>e</sup> E. C. Pollard, Phys. Rev. 57, 1086 (1940).
 <sup>e</sup> J. H. Shrader and E. C. Pollard, Phys. Rev. 59, 277 (1941).

From nuclear From Table IV reactions Reactions used amu amu  $0.99989 \pm 5$ S<sup>33</sup>-S<sup>32</sup>  $0.99970 \pm 2$  $S^{32}(dp)S^{33a}$ Cl37-A36  $0.99866 \pm 6$  $0.99864 \pm 3$ Cl37(pn)A37b A<sup>36</sup>(*dp*)A<sup>37</sup>c A<sup>38</sup>-Cl<sup>37</sup>  $0.99725 \pm 6$ 0.99705  $Cl^{37}(n\gamma)Cl^{38d}$  $Cl^{38}(\beta)A^{38e}$ Ca42-K41  $0.99726 \pm 6$ 0.99720  $K^{41}(n\gamma)K^{42d}$  $K^{42}(\beta)Ca^{42e}$ 

TABLE VI. Comparison with some nuclear reactions.

Strait, Van Patter, Buechner, and Sperduto, Phys. Rev. 81, 747 (1951).
<sup>b</sup> H. T. Richards and R. V. Smith, Phys. Rev. 74, 1257 (1948).
<sup>c</sup> Davison, Buchanan, and Pollard, Phys. Rev. 76, 890 (1949).
<sup>d</sup> Kinsey, Bartholomew, and Walker, Phys. Rev. 78, 481 (1950)
A. C. G. Mitchell, Revs. Modern Phys. 22, 36 (1950).

In the case of Cl<sup>35</sup> and Cl<sup>37</sup> several independent checks of the mass ratio Cl<sup>35</sup>/Cl<sup>37</sup> are possible. Table V gives the comparisons. The agreement of the present results with the recent microwave and nuclear reaction values is gratifying. Differences between masses of some nuclides listed in Table IV may be compared with recent nuclear disintegration data. This is done in Table VI.

The present study constitutes the first systematic effort to determine precisely the masses of all the naturally occurring nuclides in an extended intermediate mass range. Because of their extreme rarity only S<sup>36</sup>, K<sup>40</sup>, and Ca<sup>46</sup> had to be excluded. In Fig. 3 (solid curve) are shown the packing fractions corresponding to the atomic masses in the last column in Table IV. It is interesting to compare this with a semiempirical mass formula such as that of Bohr and Wheeler.9 For a precise comparison one should adjust the empirical constants in the formula to take account



FIG. 3. Packing fraction variation with mass number as determined from masses in last column of Table IV. Dotted curve given by Bohr-Wheeler formula. Note agreement in general form except at masses 40 and 48.

<sup>9</sup> N. Bohr and J. A. Wheeler, Phys. Rev. 56, 426 (1939).

of the newer experimental data. Actually our plot of the formula does take account of the newer values for the masses of the neutron and proton.

The present study is being systematically extended to higher masses. The results obtained, when supplemented by masses for the unstable isotopes in the region, will provide a large block of coherent data. Such information will make it possible to determine more precisely the numerical values for the various terms in formulas proposed for nuclear binding energies and should shed light on shell structure theories. In Fig. 3 it is interesting to note the close correspondence in

undulations of the two curves and to observe the apparent discontinuities occurring at masses 40 and 48.

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# Application of the Bethe-Weiss Method to the Theory of Antiferromagnetism

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The P. R. Weiss method developed in the theory of ferromagnetism is applied to antiferromagnetism by introducing sublattices. Atomic lattices (spin  $\frac{1}{2}$  per atom) with negative Heisenberg exchange coupling J between the nearest neighbors are investigated. It has been found that two-dimensional lattices cannot sustain antiferromagnetic order. The Curie temperatures of the simple cubic and b.c.c. structure are, respectively, 2.004 |J|/k and 3.18 |J|/k. That the f.c. lattice cannot be ordered by the interactions among the nearest neighbors is deduced from the disorder of a quadratic layer and the ineffectiveness of the interactions between layers in a f.c.c. lattice in producing order. This helps to understand why the ordering pattern of spins in Mn ions in MnO should be such as observed by Shull. Curves are obtained for reciprocal susceptibility and for short-range order vs temperature above the Curie point  $T_e$ . The experimental formula  $\chi = const/(T+\theta)$ is compared with our theory. We obtain for the simple cubic and b.c.c. lattice  $\theta = 1.5T_c$  and  $1.25T_c$  respectively if we extrapolate our theoretical curve from extremely high temperatures, and  $\theta$  is slightly higher than these values if we extrapolate from the temperature range at which experimental readings are taken. This compares more favorably with the experimental data than the prediction  $\theta = T_c$  of the molecular field theory. The general validity of our theory and its failure in the range of low temperatures are discussed.

## I. INTRODUCTION

MAGNETIC medium with negative exchange A coupling between the neighboring atoms cannot be ferromagnetic, but under certain circumstances the spins of the neighboring atoms are ordered antiparallel at low temperatures. This ordering effect is called antiferromagnetism. Its existence was first suggested by the discovery of an anomalous specific heat in MnO near the ordering transition temperature, at which a maximum susceptibility has also been observed.<sup>1</sup> The latter phenomenon made possible the proper understanding of this transition. We can imagine that, as the temperature is lowered, the inner field which causes the staggering of spins becomes stronger and makes it harder for the applied field to align the spins in one direction. Quite a few substances are found to show antiferromagnetic transitions; among them are most of the ionic salts of transition metals. Theoretical interpretations of this phenomenon have been given by Néel,<sup>2</sup> Bitter,<sup>3</sup>

and Van Vleck<sup>4</sup> using the molecular field method in which the ordering "force" is assumed to be uniquely determined by the existing degree of order over all the lattice. Increasing attention has turned to antiferromagnetism since the development of the neutron diffraction technique, which makes possible a direct investigation of the ordering pattern.<sup>5</sup> Using this technique, Shull et al.<sup>6</sup> have found in MnO a rather unexpected structure: The spins of Mn++ are ordered in such a manner that spins are lined up antiparallel in each of the four simple cubic sublattices of which the facecentered cubic lattice of Mn ions is composed. This indicates that the exchange interaction between the next-nearest neighboring Mn ions is more effective in ordering spins than that between the immediate neighboring Mn ions. A satisfying explanation of the strong exchange force between next-nearest neighbors has been offered by Anderson,7 in which he takes into considera-

<sup>4</sup> J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).
<sup>5</sup> C. G. Shull and J. S. Smart, Phys. Rev. 76, 1256 (1949).
<sup>6</sup> Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951).
<sup>7</sup> P. W. Anderson, Phys. Rev. 79, 350 (1950).

<sup>&</sup>lt;sup>1</sup>See the review article, J. H. Van Vleck, Revs. Modern Phys. 17, 27 (1945).
 <sup>2</sup> L. Néel, Ann. phys. 17, 64 (1932); 5, 256 (1936).

<sup>&</sup>lt;sup>3</sup> F. Bitter, Phys. Rev. 54, 79 (1938).



FIG. 1. Mass spectrum at mass 28 showing  $(C^{12})_2H_4$ ,  $(N^{14})_2$ , and  $C^{12}O^{16}$ . Actually, the resolution was improved after print was made, and for most of the work in the present paper  $(N^{14})_2$  and  $C^{12}O^{16}$  were completely resolved.



FIG. 2. Mass spectrum illustrating stability of regulating system. Mass doublet having a separation  $\Delta m/m = 1/1000$  was swept from left to right. On way down and at steepest point on second peak the scanning mechanism was stopped for a period longer than required to normally scan a mass doublet. A deliberate change in  $\Delta R/R$  or 1/100,000 produced a shift which may be seen on chart. Note that normal fluctuations are considerably lower than the artificial disturbance.