function, the order  $\alpha$  anomalous magnetic moment<sup>13</sup> and the order m/M reduced mass correction<sup>14</sup> have been taken into account by a factor

$$\left(1+\frac{\alpha}{2\pi}\right)\left(1+\frac{m}{M}\right)^{-3} \cong 1+\frac{\alpha}{2\pi}-3\frac{m}{M}$$

<sup>13</sup> J. Schwinger, Phys. Rev. 73, 416 (1948).
 <sup>14</sup> G. Breit and R. E. Meyerott, Phys. Rev. 72, 1023 (1947).

PHYSICAL REVIEW

Relativistic,<sup>15,16</sup> higher-order quantum-electrodynamic,<sup>17</sup> and nuclear structure<sup>16,18</sup> effects are estimated to make contributions of the order of 1 part in 10<sup>4</sup>, so that their inclusion in this calculation is not warranted.

<sup>15</sup> G. Breit, Phys. Rev. 35, 1447 (1930).
<sup>16</sup> A. M. Sessler and H. M. Foley (to be published); abstract in Phys. Rev. 91, 444 (1953).
<sup>17</sup> N. M. Kroll and F. Pollock, Phys. Rev. 86, 876 (1952).
<sup>18</sup> V. W. Hughes and G. Weinreich, Phys. Rev. 91, 196 (1953).

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# Precision Wavelength and Isotopic Shift Measurements of Germanium Arc Lines\*

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The employment of an atomic beam light source and of interferometric equipment made it possible to obtain information about the line structure and precision wavelength of eight Ge I lines arising from transitions between the lowest even and odd energy levels of germanium. Despite the high resolving power employed, it was impossible to observe line splittings. By comparing the total width of the lines with that expected from the beam data one can estimate that the isotope shift between consecutive even Ge isotopes is smaller than 0.005 cm<sup>-1</sup>. The wavelength of the center of gravity of the different lines however, could be determined within  $\pm 0.00004$  A. This limit of error is in agreement with the wave number deviations obtained by the application of the Ritz combination principle.

#### INTRODUCTION

HE present investigation was undertaken in order to obtain information about the isotopic shift of germanium lines by means of an atomic beam light source. Previous investigations of this spectrum by use of liquid air cooled Schüler lamps showed that the isotope shift must be smaller than the line width obtained with this light source.<sup>1</sup> The only source which permits a sufficient reduction of the line width is the atomic beam source. The appreciable amount of pure germanium which was available from the Purdue University solid state group made it possible to employ this method.

The experiments were conducted in such a way that the spectrograms obtained could be used also for precision wavelength measurements. These were desirable in connection with recent investigations of the Ge I spectrum carried out in this laboratory.<sup>2</sup>

# I. Experimental Methods and Equipment

#### A. Atomic Beam Light Source

1. General assembly.—The atomic beam light source used in this investigation is a modified version of the atomic beam used by Mundie and Meissner,<sup>3</sup> by Meissner, Mundie, and Stelson,<sup>4</sup> and later by Deverall, Meissner, and Zissis<sup>5</sup> for work with magnesium, lithium, and indium, respectively. Figure 1 shows a schematic view of the general assembly. The germanium was evaporated from a graphite crucible, and the resulting vapor was collimated into a beam by the small aperture at the top of the upper furnace jacket. The beam was bombarded with electrons from two grid-filament assemblies and then condensed on the bottom of the liquid air container. The beam was viewed through a fused quartz window at the front of the upper vacuum chamber called "can" in the figure. A careful adjustment of the spectrograph is necessary to insure that the optic axis of the collimator passes through the center of the bombarded section of the beam and is perpendicular to the beam axis.

Large pump openings and high-speed pumps are essential in an atomic beam source. The upper and lower chambers are evacuated by two separate systems each consisting of a Distillation Products Inc. MC 275 diffusion pump and a fore pump. The pumping speed obtained was about 550 liter/sec at a pressure of  $10^{-5}$ mm Hg.

2. Grid filament assemblies.-The grid filament assemblies are shown in place in Fig. 1. The grid consists of water-cooled nickel tubes and the filament of two strips of platinum foil covered with emission coating and supported by tungsten power leads sealed through

<sup>\*</sup> Supported in part by the U. S. office of Naval Research.
<sup>1</sup> L. Sibaya, Current Sci. (India) 6, 152 (1937); Hack Arroe, Studier over Spektralliniers Struktur (Kopenhagen, 1951).
<sup>2</sup> K. L. Andrew and K. W. Meissner, Phys. Rev. 85, 716 (1952).
<sup>3</sup> L. G. Mundie and K. W. Meissner, Phys. Rev. 65, 265 (1944).

<sup>&</sup>lt;sup>4</sup> Meissner, Mundie, and Stelson, Phys. Rev. **74**, 932 (1948). <sup>5</sup> Deverall, Meissner, and Zissis, Phys. Rev. **91**, 297 (1953).



FIG. 1. Schematic drawing of the atomic beam light source.

a uranium glass press. To attach the platinum foil to the leads, the tungsten is first cleaned with sodium nitrite and then narrow strips of nickel foil are tacked to the front edges of the tungsten wires where the platinum filament strips are to be connected. The platinum foil is then wrapped once around the tungsten wire and spot-welded to it through the nickel foil. This technique results in good electrical contact and prevents the sputtering of the nickel in the vacuum.

3. Furnace.—The operating temperature necessary for a satisfactory germanium beam was about 1600°C. To attain this temperature a special graphite furnace was developed.<sup>6</sup> The design of this furnace was such that it produced a negligible magnetic field in the beam region in spite of the large operating currents used.

The graphite furnace containing a graphite crucible is shown in Fig. 2. This furnace permits operation at temperatures up to 1800°C. The heating section is a hollow graphite cylinder with a wall thickness of about 1 mm through which currents up to 500 amperes are passed. The conical form of the top part permits the upper water cooled power connection to be large and also assists in maintaining a favorable temperature distribution. The solid bottom part is provided with a screw thread for mounting.

The graphite crucible is suspended in the heating

section from its conical flange. Short circuiting of the heating section is prevented by a narrow centering ridge. The crucible has a graphite lid containing an axial opening of about 1.5 mm diameter which acts as the beam source (oven aperture).

The graphite furnace is mounted in a support, Fig. 3, consisting in principle of two coaxial cylindrical tubes which serve both as current leads and as supports. The threaded bottom section of the furnace is screwed into the central copper cylinder. The rim of the conical section is clamped by the top flange of the outer cylinder which is split vertically on one side to permit tightening by means of a brass screw. The upper and lower connections to the furnace are cooled by circulating tap water and the water tubes leading to the lower connection serve as power leads. In order to prevent the furnace from being broken by mechanical and thermal stresses, the mechanical support of the lower part is furnished by a sylphon bellows shown in the figure.

The outer cylinder is at ground potential and is hard soldered to the brass base plate. The inner conductor is insulated from the outer one by Teflon sleeves on the fastening screws and a "linear o-ring" gasket which seals the joint between the base plate and the small flange to which the sylphon is soldered.

#### B. Spectroscopic Instruments

1. UV spectrograph.—The spectrograph used for this investigation was a Universal Steinheil Spectrograph. In order to make it applicable for interferometric work in the region between 2000 A and 11 000 A, it was equipped with quartz-fluorite optics. The collimator and camera lenses consisted of especially designed symmetric quartz-fluorite achromates of 750-mm focal length and free apertures of 60 mm and 65 mm, respectively. The lenses were designed and made by the Perkin-Elmer Corporation, Norwich, Connecticut and met all the desired specifications. With a calcium



FIG. 2. Graphite furnace and crucible.

<sup>&</sup>lt;sup>6</sup> H. Kopfermann and G. Wessel, Z. Physik. **130**, 100 (1951). This problem was discussed with G. Wessel during his visit at Purdue.

fluoride prism as dispersing element a practically plane focal surface was obtained. The materials used for the optical parts were Homosil fused quartz and synthetic calcium fluoride. The spectrograph was mounted on a special table which minimized vibration and permitted the spectrograph to be precisely aligned so that the axis of the collimator was perpendicular to the atomic beam.

2. Interferometer.—A Perot-Fabry interferometer was used to obtain the high resolution required for this investigation. It was mounted in parallel light between the collimator and the prism and was contained in a temperature and pressure controlled housing. This was provided with plane quartz windows which were sufficiently inclined to the axis of the interferometer to throw secondary images out of the principal spectrum. The temperature was maintained within  $\pm 0.1^{\circ}$ C during the time required for exposures. The interferometer consisted of crystalline quartz plates cut perpendicular to the optic axis and hollow cylindrical invar spacers, provided with three small flat projections at each end. This type of spacer has proved to be the most satisfactory of the various designs and has the added advantage that two or three spacers can be put together in series to form the various longer spacers required. Thus, a relatively small number of spacers can be combined to form a spacer of practically any length. Our experience with such combined spacers shows that the etalon thickness can be held constant during ten-hour exposures. The spring loading devices used to hold the quartz plates in contact with the spacers and to make the final adjustment for parallelism were orginally described by Hansen.<sup>7</sup> These springs were made of Elinvar to assure that the adjustment of the interferometer would not change with temperature.

Two sets of quartz plates were used during this investigation. The first pair was coated with aluminum to a reflectivity of 85 percent in green light. The second pair had a reflectivity of 92 percent in green light and was used only for the photographs taken with the 173-mm spacer. This second pair was kindly loaned by Professor M. Czerny, Physikalisches Institut der Universität Frankfurt Main.

3. Comparator and Densitometer.—The final analysis of the photographic plates was made from readings taken with a Zeiss Abbe comparator and from densitometer traces made with a Leeds and Northrup densitometer.

4. Standard.—The wavelengths were measured with respect to the Hg<sup>198</sup> 5460 A line as standard. The standard source was a water cooled Hg<sup>198</sup> Megger's Electrodeless Discharge Tube loaned by the National Bureau of Standards; the tube was excited by means of a 250-Mc oscillator.



FIG. 3. Graphite furnace support.

### **II.** Wavelength Measurements

## A. Method of Evaluation

The method of evaluation was based upon the fundamental relation pertaining to the Perot-Fabry interferometer,

$$(p_x + \epsilon_x) = (p_s + \epsilon_s) = 2t,$$

where  $(p_x + \epsilon_x)$  and  $(p_s + \epsilon_s)$  are the order numbers of the centers of the interference fringes of an unknown and a standard line of wavelengths  $\lambda_x$  and  $\lambda_s$ , respectively. The fractional order numbers,  $\epsilon_x$  and  $\epsilon_s$ , can be obtained from measurements of the diameters of the interference rings.

Plates taken with 1.2-, 2.0-, 4.9-, 6.0-, 6.4-, and 12.4-cm spacers were measured during the investigation. Since the patterns obtained with the 6.0- and 12.4-cm spacers were intended to be used for the final determination of the wavelengths they were separately measured with great care by each of the three authors.

In every case, the innermost eight fringes, if this many appeared, were used to obtain the fractional order number  $\epsilon$  by the method of least squares.

For the preliminary determination of the etalon thickness the wavelength values of Burns and Adams<sup>8</sup> for the Hg<sup>198</sup> lines were used. Since this spectrum extends over a large range of wavelengths the corrections due to the deviation of the actual air condition from standard air conditions cannot be neglected. Therefore,

<sup>&</sup>lt;sup>7</sup> G. Hansen, Naturwiss. 15, 163 (1927).

<sup>&</sup>lt;sup>8</sup> K. Burns and K. B. Adams, J. Opt. Soc. Am. 42, 56 (1952).

Wave-Spacer length A t cm

3269

3039

2754

2709

2691

2651

2651

2592

1.2

0.4885

0.0664

0.5871

0.6231

0.3403

0.5676

0.1711

0.5333

12.4

0.48886

0.06712

0.58781

0.62372

0.34105

0.53402

TABLE I. Wavelengths of Ge I lines obtained with different spacers.

4.9

0.4885

0.0671

0.5879

0.6236

0.3408

0.5682

0.1718

0.5339

6.4

0.4890

0.0673

0.5878

0.6237

0.3408

0.5678

0.1721

0.5341

6.0

0.48887

0.06717

0.58788

0.62378

0.34112

0.56838

0.17205

0.53406

2.0

0.4888

0.0673

0.5879

0.6239

0.3410

0.5683

0.1717

0.5339

Config.	Design.	Level sep.	Present work	AELa
$4s^24p^2$	$4p^2 {}^3P_0$	FF7 4344	0.0000	0.00
•	$4p^2 {}^3P_1$	357.1341	557.1341	557.10
even	$4p^{2} P_{2}$	852.8208	1 409,9609	1 409.90
levels	$4p^{2} D_{2}^{1}$	5 /15.3380	7 125.2989	7 125.26
4s²4⊅5s	$5s  {}^{3}P_{0}^{\circ}$	050 (1(1	37 451.6893	37 451.53
1	$5s  {}^{3}P_{1}^{\circ}$	250.0101	37 702.3054	37 702.15
odd	$5s  {}^{3}P_{2}^{\circ}$	1 415.5907	39 117.9021	39 117.77
levels	$5s P_1^\circ$	902.0583	40 020.5604	40 020.43

TABLE III. Low-energy levels of Ge I.

the Hg wavelengths were corrected for the experimental conditions with the convenient tables of Meggers and Peters.<sup>9</sup> For the final results, the formula of Edlén<sup>10</sup> was used, together with his tables for the reduction of air to vacuum wavelengths.

Unfortunately, the corrections to standard temperature and pressure conditions of the germanium wavelengths ultimately obtained are in doubt since no provisions were made for the determination of the humidity in the interferometer housing, and since at the present no exact values of the refractive index of humid air in the ultraviolet are available. However, the relative wavelengths of the germanium lines and, therefore, the values of the levels, will be affected very little. In principle, the difficulty arising from air conditions could easily be overcome by evacuating the entire pressure tight housing of the interferometer and by direct determination of vacuum wavelengths and wave numbers.

#### C. Results

1. Wavelengths values.—The great variation in the wavelengths given by earlier investigators made it impossible unambiguously to determine the exact integer order number for large spacers. Therefore, the spectrogram obtained with the smallest spacer, 1.2 cm, was evaluated first. For this spacer the spectral range  $\langle \Delta \lambda \rangle = \lambda^2/2t$  has values ranging from 0.0444 A at 3269 A to 0.0279 A at 2592 A and thus the wavelength values of the MIT tables,<sup>11</sup> and those independently

 TABLE II. Final wavelength values wave numbers, and combinations.

Wavelength	Wave number	Combination
3269.48886	30 577.0065	$4p^{2} D_{2} - 5s^{3}P_{1}$
3039.06712	32 895.2615	$4p^2 D_2 - 5s P_1^2$
2754.58781	36 292.3447	$4p^{2} P_{2} - 5s P_{1}$
2709.62372	36 894.5552	$4p^2 {}^3P_1 - 5s {}^3P_0$
2691.34105	37 145.1713	$4p^2 {}^3P_1 - 5s {}^3P_1$
2651.56833	37 702.3054	$4p^2 {}^3P_0 - 5s {}^3P_1$
2651.17201	37 707.9412	$4p^2 {}^3P_2 - 5s {}^3P_2$
2592.53402	38 560.7682	$4p^2 {}^3P_1 - 5s {}^3P_2$

<sup>9</sup>W. F. Meggers and C. G. Peters, Bull. Bur. Standards 14, 697 (1919).

<sup>10</sup> B. Edlén, J. Opt. Soc. Am. 43, 339 (1953)

<sup>11</sup> MIT Wavelength Tables (John Wiley and Sons, Inc., New York, 1939).

\* See reference 12.

measured during another investigation in this laboratory, were sufficiently accurate for obtaining the integer order numbers p of the germanium lines after the correct thickness t had been determined by means of mercury lines. Employing further the fractional order numbers  $\epsilon$ , wavelengths of the germanium lines were obtained which were much more reliable than the grating values. The wavelength values resulting from the 1.2-cm spacer were then used to obtain the correct integer order numbers for the larger spacers. Since the spectral range decreases with increasing spacer thickness, the unknown wavelength has to be known within a few thousandths of an angstrom in order to find the correct integer order when working with the longest spacers employed. The smallest spectral range used in the present investigation for wavelength measurements was 0.0027 A for  $\lambda = 2592$  A and t = 12.4 cm.

Table I gives a compilation of the germanium wavelengths obtained with the different spacers. This table shows that the corrections for the dispersion of the phase shift due to reflection at the aluminized interferometer plates is negligible. A possible small phase correction would affect the final wavelength values obtained from the 6.0-cm and 12.4-cm spacers only within the limit of accuracy.

Table II contains the final values together with the wave numbers  $\sigma$  in cm<sup>-1</sup> and the transitions known from earlier investigations.<sup>12</sup> These values, except those of the lines at 2651 A, were obtained with respect to the green Hg<sup>198</sup> line as primary standard, its value being assumed to be 5460.75320 A. Since the patterns of the two lines at 2651 A were not separated with the spacer of 12.4 cm, the wavelengths of these two lines were obtained from the data for the 6.0-cm spacer. The exact value of the spacer thickness used in this case was an average value obtained by means of the other germanium wavelengths resulting from the measurements with the 12.4-cm spacer. This manner of computing seemed to be the most consistent although the direct use of the primary Hg standard led to practically the same results.

From the agreement between the values obtained

<sup>&</sup>lt;sup>12</sup> For details see Charlotte E. Moore, *Atomic Energy Levels* National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1953), Vol. 2, p. 135. We shall refer to these tables as AEL.

with the 6.0-cm and 12.4-cm spacers in Table I, and from the general error considerations, it can be deduced that the greatest possible error of the wavelengths given in Table II is  $\pm 0.00004$  A.

During the measurements of the Perot-Fabry patterns it was found that the germanium fringes could be measured more accurately than those of the Hg<sup>198</sup> as a result of greater sharpness of the lines produced in the atomic beam light source.

2. Energy levels of Ge 1.—From the wave numbers and the knowledge of the transitions involved,<sup>12</sup> there follow immediately new precision values for the energy levels. The results are contained in Table III which also gives a comparison with the AEL values.<sup>12</sup> A level diagram is given in Fig. 4.

The application of the combination principle permits a check of the accuracy obtained, since the intervals 852 cm<sup>-1</sup> and 1415 cm<sup>-1</sup> appear twice, namely as 852.8266 and 852.8270 cm<sup>-1</sup>, and 1415.5965 and 1415.5969 cm<sup>-1</sup>. This agreement supports the previously given limit of relative accuracy of our results as  $\pm 0.00004$  A.

Table IV gives a representation of all known combinations between the even and odd levels resulting from the configurations  $4s^24p^2$  and  $4s^24p5s$ , respectively. It contains also six transitions which are very well known but have not been obtained with the atomic beam. Four of them can be calculated, however, and as Table V shows the calculated values are in good agreement with the MIT values and the preliminary values recently obtained interferometrically by Meissner and VanVeld of this laboratory using a liquid air cooled hollow cathode and Krypton standards. This table also shows that Richter's values<sup>13</sup> deviate greatly from those of the other observers. The two transitions involving the even  $4p^{2} {}^{1}S_{0}$  level were not obtained with the atomic beam and the values shown in Table IV are those of Meissner and VanVeld (unpublished). The wave number differences between these lines are in good agreement with the atomic beam values.



FIG. 4. Energy level diagram for transitions observed in the germanium beam.

The great accuracy, with which the wavelength of eight germanium lines were determined in this investigation, suggests that they may be used as secondary standards in as much as reliable standards in this wavelength region are sparse. Preliminary measurements of the wavelengths of these lines have been carried out in this laboratory with a hollow-cathode source and an

$     Even     4s^2 4p^2     Odd     4s^2 4p5s $	Levels cm <sup>-1</sup>	4⊅² ³P₀ 0.0000	$4p^2 \ ^3P_1$ 557.1341	$4p^2 \ ^3P_2$ 1 409.9609	$4p^2 \ {}^1D_2$ 7 125.2989	4⊉² <sup>1</sup> S₀ 16 367.336
5s <sup>3</sup> P <sub>0</sub> °	37 451.6893		36 894.5552 obs5552			
5s <sup>3</sup> P <sub>1</sub> °	37 702.3054	37 702.3054 obs3054	37 145.1713 obs1713	36 292.3445 obs3447	30 577.0065 obs0065	21 334.969 obs969
5s <sup>3</sup> P <sub>2</sub> °	39 117.9021		38 560.7680 obs7682	37 707.9412 obs9412	31 992.6032 calculated	
5s <sup>1</sup> P <sub>1</sub> °	40 020.5604	40 020.5605 calculated	39 463.4264 calculated	38 610.5997 calculated	32 895.2615 obs2615	23 653.224 obs224

TABLE IV. Combination scheme of lines arising from transitions between the lowest even and odd levels of Ge 1.

<sup>13</sup> C. Richter, Z. wiss. Phot. 25, 380 (1928).

Wave number Calc.	Wavelength Calc.	Wavelength Richtera	Wavelength MIT <sup>b</sup>	Wave- length (Meissner and VanVeld)º
31 992.6032	3 124.8164	3 124.831	3 124.817	3 124.816
38 610.5997	2 589.1887	2 589.201	2 589.188	2 589.188
39 463.4263	2 533.2303	2 533.241	2 533.229	2 533.231
40 020.5605	2 497.9623	2 497.974	2 497.963	2 497.963

TABLE V. List of wavelengths obtained with combination principle.

<sup>a</sup> See reference 13.
<sup>b</sup> See reference 12.
<sup>c</sup> K. W. Meissner and R. D. VanVeld (unpublished).

air arc. The results of these less accurate measurements agree, within their limit of error, with the atomic beam values.

The precise term differences given in Table III permit the calculation of other classified lines in the ultraviolet or even vacuum ultraviolet region. The wavelengths of these lines can be obtained from extended interferometric measurements in the near ultraviolet and by the application of Ritz' combination principle. The possible exploitation of this method as a means of obtaining auxiliary standards in the vacuum region is the subject of an investigation now underway in this laboratory.

It may be mentioned that the wavelength values of Hg<sup>198</sup> obtained with the spacers used in the atomic beam measurements agree with those reported by Burns and Adams within  $\pm 0.0001$  A.

#### **III.** Isotopic Shift

As stated in the introduction this investigation was undertaken to study the isotopic shift of the germanium spectrum. Germanium possesses five isotopes of which four are of the even-even variety and one odd-even. The three principal isotopes (70, 72, 74) are of about equal abundance (26.6 percent, 27.4 percent, 36.4 percent, respectively). Isotope 76 has an abundance of 7.7 percent and isotope 73 of 7.8 percent. This distribution of abundances is favorable for measuring small line shifts. Theoretically one expects only small shifts due to the atomic number of germanium (32), and the fact that the terms, in the transitions observed, do not involve deeply penetrating orbits. However, by the use of an atomic beam light source and a high resolving power interferometer it was hoped to measure these small shifts.

The predicted normal shift is

$$\Delta \sigma = (\Delta M / M_1 M_2) \times 5.49 \times 10^{-4} \text{ cm}^{-1}$$

 $= 0.0085 \text{ cm}^{-1} \text{ for } \lambda = 2592 \text{ A},$ 

where  $M_1 = 70$ ,  $M_2 = 72$ ,  $\Delta M = 2$ , and  $\sigma =$  wave number of spectral line.

The specific and volume effects for this atom have not been calculated, but should be small for the electron configuration involved.

A careful microscopic study of the interferometer fringes showed no detectable splittings; therefore, densitometer traces were made of the patterns to determine whether any asymmetry could be found in the fringes of the lines. The intensity distribution was obtained from the densitometer traces by distorting the linear radius scale into a quadratic one. Since no intensity marks were provided on the plates, the replotting of the data was made under the reasonable assumption that the densities involved were in the linear section of the characteristic curve of the phtographic plates. The analysis of the traces showed that even with a large spacer (173 mm) and highly reflective coatings (92 percent in green light) no significant asymmetry could be detected. The only way to arrive at an estimation of the isotopic shifts involved was to compare the observed width of the lines with that expected from data concerning the atomic beam and the interferometer. As a result of these analyses it can be asserted that the isotope line shift between two consecutive even isotopes is less than 0.005 cm<sup>-1</sup>. This is less than the expected normal shift and it implies that the volume shift must be small and in the opposite direction to the mass shift.

The germanium used in this investigation was prepared by Miss Louise Roth of the Purdue Physics Department's Solid State Group. We wish to thank her for her very able assistance.

The densitometer traces were made at the Argonne National Laboratory. We are grateful to Dr. Mark Fred and Dr. Frank Tomkins for helpful suggestions.