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Arc Spectrum of Bismuth Bi I

S. Mrozowski
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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The arc spectrum of bismuth was investigated in three orders of the best 30-foot Chicago grating. The light source consisted of a heated quartz tube containing bismuth metal, filled with a few mm of helium and excited by a 4-meter oscillator. At a sufficiently high vapor pressure of bismuth only the arc spectrum is excited and is so intense, that not only almost all previously known lines but also many new lines were studied. Because of the very high quality of the grating and the sharpness of the lines, pictures were obtained which show in the third order an exceptionally high resolution of about 400,000, which constitutes the highest resolving power ever obtained with a diffraction grating. The results of measurements of the hyperfine structures for 55 lines are presented in Tables I and IV; the wavelengths for the components corresponding to the transitions between hyperfine structure levels with highest F quantum numbers, and the exact term values for the atomic energy levels derived from them are collected in Tables II and IV. Many new levels were identified; the total number of known levels is increased from 27 to 45. Hyperfine structure separations of levels are given in Tables II, III, and IV; all values previously reported by Zeeman, Back, and Goudsmit for 13 atomic levels were corrected and separations for 28 more levels were determined.

INTRODUCTION

The arc spectrum of bismuth has been the subject of many investigations. The energy level scheme was definitely settled by the classical work on Zeeman effect and hyperfine structure by Goudsmit and Back and by Zeeman, Back, and Goudsmit.[1] There was not much hope that a reinvestigation of this spectrum would yield enough new results to make the work worth while. The present investigation was started in collaboration with Dr. F. Bueso-Sanllehí primarily as a study of the resolving power of the Chicago 30-foot gratings. It was believed that the bismuth hyperfine structure patterns would constitute a very good source for such a study. This expectation was partly fulfilled, since pictures showing an unusually high resolution were obtained. The author, however, found a little later that a mercury hydride spectrum (mercury deuteride for regular 21-foot gratings) excited with high intensity in a mercury arc[2] constitutes in every respect a much more convenient source for such a study. The latter source is operated very easily; it is ready for use at any moment and the spectrum, extending from λ2800 to λ4300, consists of many band lines with a very narrow structure (isotope effect of mercury) of a variable distance.

The closer examination of the first spectrograms obtained of the bismuth spectrum revealed several points of interest. It was evident (especially in the case of the line λ3024) that some of the hyperfine structure separations given by Zeeman, Back, and Goudsmit[1] are not quite correct. Therefore a more extensive study of the spectrum was made by using a source which turned out to be extremely good for this investigation. A few discrepancies between early works of Nagaoka and Mishima[3] and Zeeman, Back, and Goudsmit[1] were found to have an explanation; the hyperfine structure separations reported by Zeeman, Back, and Goudsmit[1] were corrected (13 levels) and separations in 28 more levels were determined. The number of established atomic energy levels of bismuth has been raised from 27 to 45 and their positions determined with high accuracy. A very short account of a part of the results obtained was presented a year ago at the Chicago Physical Society Meeting.[4]

EXPERIMENTAL

In the early part of the experiments a water-cooled hollow cathode discharge tube was used. This type of source causes the inconvenient appearance of both the arc and spark spectra at the

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[1] P. Zeeman, E. Back, and S. Goudsmit, Zeits. f. Physik **66**, 1 (1930) and the references there to previous work.

[2] A description of such a powerful source is contained in the article S. Mrozowski, Zeits. f. Physik **95**, 524 (1935).

[3] H. Nagaoka and T. Mishima, Proc. Imp. Acad. **2**, 249 (1926).

[4] S. Mrozowski and F. Bueso-Sanllehí, Phys. Rev. **61**, 108 (1942).

same time. Because of a low density of bismuth vapor, only the strongest lines can be investigated and even in those lines very weak components often can hardly be detected. A quartz tube containing a piece of metal and filled with helium at few mm pressure excited by a short wave oscillator constitutes a much more satisfactory source for an arc spectrum of a metal with relatively high vapor pressure. Such a source has been studied in detail by the author in the case of the spectrum of lead[5] and the reader is referred to this paper for the description of the experimental arrangement and precautions to be taken in order to avoid the destructive influence of the condensed metal on the walls of the tube. A similar arrangement was adopted in this investigation; the length of the quartz tube was, however, increased to about 25 cm.

An increase of the vapor pressure of bismuth, which is regulated by the temperature of the oven surrounding the tube, has a double effect on the spectrum. First, the average velocity of the electrons is diminished which favors the excitation of the lower energy levels; by a sufficient increase of pressure the first spark spectrum can be completely eliminated. Secondly, the rapidly increasing density of the vapor produces a great increase in the intensity of the weakest lines (or components); the strongest lines (or components) being more and more weakened by reabsorption. This is the reason that, for instance, the weakest components of the line λ2938 could be investigated and gives also an explanation of the presence in the spectrum of many weak lines which have not been recorded previously by other authors.

The spectrum was photographed end-on with the 30-foot grating spectrograph: λ2850–λ6500 in the first, λ2228–λ4722 in the second, and λ2228–λ3067 in the third order. The slit width varied from 12μ (strongest lines) to 25μ (weakest lines). The exposure time ranged from a few minutes to about 48 hours. In the case of long exposures there was no difficulty in picking out a period of time with a sufficiently constant pressure ($\Delta p \leqslant 0.1$ inch); a greater difficulty arose from long period variations of the grating temperature. Although the functioning of the temperature control arrangement was recently improved, there are still slight variations of temperature present which decrease the resolving power in the case of long exposures. Moreover, recently by using a powerful mercury arc[2] as a source, the author has found by very short exposures (2–5 min.) that at the time of switching on of the automatic heating arrangement a heat wave is created which in most of the cases decreases a little the resolving power of the grating for a period of a few minutes. It seems therefore quite certain that the highest resolving power obtained in this work (400,000 in the third and 300,000 in the second order) does not represent the true maximum resolving power of the best 30-foot grating (so called No. 3) in use.

Secondary iron standards were used as a comparison spectrum. Because of the width of the iron lines and the small density of standards (especially in some regions) the wave numbers obtained are less exact than should be expected for such a high dispersion (± 0.02–0.03 cm^{-1}, in some regions even worse).[6] The distances of hyperfine structure components are obtained naturally with a much higher accuracy amounting to around ± 0.003 cm^{-1} in favorable cases (completely resolved structures).

RESULTS

In Table I are given the results of measurements of hyperfine structures for lines corresponding to transitions to the five lowest levels of Bi I belonging to the configuration $6p^3$. Lines observed only in one order are marked by crosses †. The positions of components are given in 10^{-3} cm^{-1} relative to the component corresponding to the transition between h.f.s. levels with highest F quantum numbers (in most cases this is the strongest component). The numbers in parentheses indicate the components in order of decreasing intensity. At low pressures the intensity distribution seems to be in almost all cases in agreement with the theoretical formulas of Hill; one exception will be mentioned below.

Enlarged photographs of several lines are given in Fig. 1. The first picture (a) shows the completely resolved pattern of the line λ2627. This

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[5] S. Mrozowski, Phys. Rev. **58**, 1086 (1940).

[6] See the discussion of this point in the paper S. Mrozowski, Phys. Rev. **60**, 730 (1941).

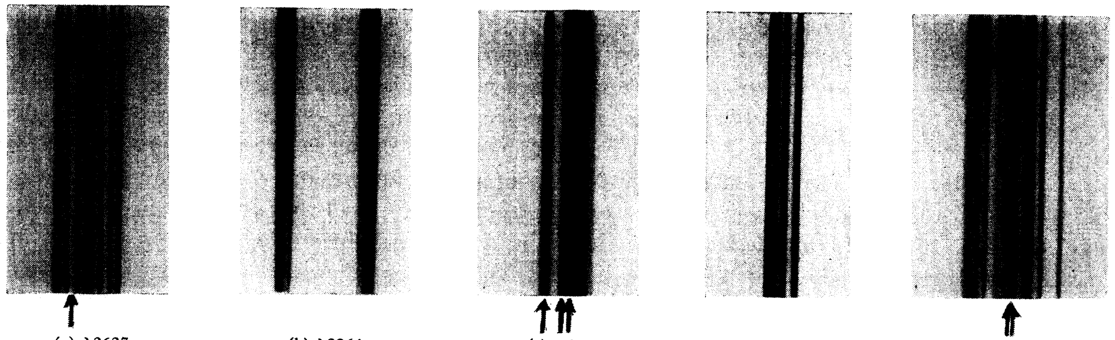

(a) λ2627 (b) λ2864 (c) λ2938 (d) λ2993 (e) λ3024

FIG. 1. Enlargements of photographs of hyperfine structures of lines of bismuth obtained in the third order of the 30-foot grating spectrograph. The picture (e) shows the highest resolution ever obtained with a grating (400,000).

line has been investigated by Zeeman, Back, and Goudsmit[1] in the fifth order of a 21-foot Rowland grating and the structure found by them seemed to agree with the predicted pattern satisfactorily. But the comparison of their predicted pattern with Fig. 1a shows the absence of their fourth component from the left (wide gap after component 3 marked by an arrow in Fig. 1); this is exactly what should be expected, since according to the formulas of Hill this component should appear only with extremely low intensity.

Zeeman, Back, and Gousmit[1] mention a discrepancy between their results and those of Nagaoka and Mishima[3] in the case of the line λ2938. The study of this line at different pressures shows that there is no discord at all. Zeeman, Back, and Goudsmit used a well-cooled source giving an intensity distribution close to the theoretical, and were able to observe only the strongest components, group (1) and group (2)–(3). Nagaoka and Mishima had a source with a higher vapor pressure of bismuth and the strongest components were weakened by reabsorption. This is seen also from the deviations from the theoretical intensity distribution in the case of other lines observed by them. In λ2938 they were able to observe even the weakest components. A picture of this line at conditions corresponding to theirs is given in Fig. 1 (c), where the main components (1) and (2)–(3) weakened by reabsorption are marked with arrows.

The high resolving power of the grating is illustrated also by the pictures of the lines λ2864, λ2993, and λ3024. The sharpness of components in the line λ2993 indicates the extreme smallness of the total hyperfine structure separation in the upper level. The picture of the line λ3024 (1-hour exposure) is especially interesting, since it shows the highest resolution ever obtained with a grating. Until now many spectra have been investigated in higher orders of diffraction gratings, but so far as the author is aware, even with the best gratings available a resolving power of more than 300,000 never was obtained in practice. The distance of the components in the close doublet in the middle of the pattern (fifth and sixth components from the right, marked with arrows) corresponds to a resolving power of 385,000; the nice resolution of this doublet indicates that the resolving power obtained in this case was probably even a little higher, maybe around 400,000. The high resolving power of the grating can be well appreciated by a comparison of the microphotometer tracings obtained for this line from pictures taken in the third order of the Chicago 30-foot grating and in the fifth order of a 21-foot Rowland grating (the last curve was taken from the work of Zeeman, Back, and Gousmit).[1] Both curves are drawn with the same scale in Fig. 2 (a); the contour observed by Zeeman, Back, and Goudsmit is resolved here into 11 components. The structure observed is in a very good agreement with the earlier results of Nagaoka and Mishima,[3] but differs considerably from the pattern predicted by Zeeman, Back, and Goudsmit[1] [their predicted pattern is included in Fig. 2 (a)]. In spite of such an apparently great discrepancy the predicted pattern was brought into agreement with the observed by only a slight adjustment of the separations reported by Zeeman, Back, and Goudsmit for the upper $7_{5/2}$ and the lower ${}^2D^\circ{}_{5/2}$ levels (see Table

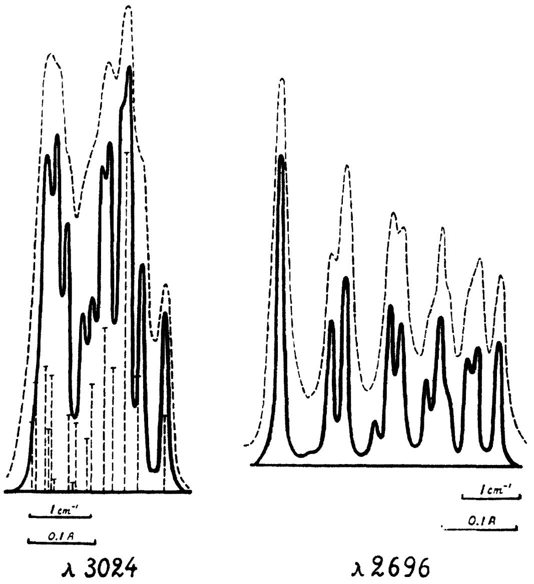
II), since this type of a pattern is very sensitive to a small change in the ratio of separations. In Fig. 2 (b) a comparison of microphotometer traces obtained for the line λ2697 in this work and by Zeeman, Back, and Goudsmit is presented. A very interesting unexplained feature of this line is a too high intensity of the fifth component from the left, which should be weaker than the sixth according to the formulas of Hill.

In general the data agree with those of former investigators very well. The wave-lengths of the components with highest F quantum numbers were determined with the highest accuracy and the results are given in the left part of the Table I. From the corresponding wave numbers obtained from Kayser's Tabelle der Schwingungszahlen the exact term values of the energy levels with highest F quantum numbers were found and are collected in Table II. The terms marked by a star are new terms established in this work; the levels denoted by (Th) were reported only by Thorsen,[7] those by (T) were given only by Toshniwal.[8] All the remaining levels were reported by both of these authors. The numbering of the even terms 1 to 19 adopted by Bacher and Goudsmit[9] has been retained in Table II; a level reported by Thorsen (20) and not included in the tables of Bacher and Goudsmit (they probably regarded it as insufficiently well established) was confirmed by the newly found line λ3038. A new level 23 has been found, which almost coincides with a level reported by Thorsen on the basis of only one line observed (λ2251, no combination principle involved). This line does not fit the level scheme exactly; on the other hand Toshniwal's tables do not include such a wave-length, only a slightly different one λ2249, which was used by him in identifying the level 18. Which of these classifications is the right one cannot be decided without remeasuring the position of the line in question.

In order to make the data collected in Table II as complete as possible the wave-length of all other classified lines which could not be determined in this work but which were reported by Thorsen[7] or Toshniwal[8] are included in Table II and put in parentheses to indicate their lower accuracy. All newly classified lines are marked by stars. Three terms 16, 17, and 18 identified by Toshniwal[8] were added, although several doubts can be raised. The existence of the level 16 is extremely doubtful, since the lines in question for such a low level should show a high intensity; in spite of this none of them was observed in this work. Further, if Toshniwal's line λ3239.7 is identical with a weak line λ3241 observed in this work the classification is incorrect, since the h.f.s. of the latter line (a triplet) is incompatible with the structure expected. For the last level 18 the classification of the line λ2249 is uncertain (see above).

The J quantum number of the level 12 was changed from $\frac{3}{2}$ to $\frac{5}{2}$, since the line λ3093 reported by Toshniwal[8] could not be found on my spectrograms. An uncertainty exists about the J value of the level 19, since the structure found for the line λ2448 seems to fit better with $J=\frac{3}{2}$, but on the other hand the absence of the transition $19\rightarrow{}^2D^\circ{}_{5/2}$ seems to require $J=\frac{1}{2}$.

The exact wave-lengths for the three lines λ2276, λ2230, and λ2228 are also given in Table



(a) (b)

FIG. 2. Comparison of microphotometer tracings obtained from plates taken in the third order of the 30-foot Chicago grating (continuous curve) and in the fifth order of a Rowland 21-foot grating (broken curve; redrawn from the paper by Zeeman, Back, and Goudsmit, reference 1). For the line λ3024 the pattern predicted by Zeeman, Back, and Goudsmit (reference 1) on basis of their measurements of other lines is added.

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[7] V. Thorsen, Zeits. f. Physik **40**, 642 (1927).

[8] G. R. Toshniwal, Phil. Mag. **4**, 774 (1927).

[9] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, New York, 1932), pp. 85–86.

TABLE I. Structures of Bi I lines. Transitions $X\rightarrow 6p^3$.

λ in A	Components in 10^{-3} cm^{-1}‡
2400.965*	−580(10)?, 0(1), 242(9), 892(2), 1049(8), 1569(3), 1704(7), 2143(4), 2273(4), 2659(5), 3013(6)
2448.683*	−670(4), −525(3), weak diffuse (5), −270(2), 0(1)
2496.678*	0(1), 605(2), 1113(3), 1524(4), 1847(5), 2097(6)
2515.619*	−616(4), −466(3), −253(2), 0(1)
2524.470*	−762(4), −575(3), −330(2), 0(1)
2594.771*	0(1), 588(2), 1089(3), 1502(4), 1837(5), 2084(6)
2600.654*	0(1), 585(2), 1084(3), 1489(4), 1814(5), 2067(6)
2627.834	−2020(4), −1880(4), −1640(3), −1292(3), −1027(2), −810(4), −560(3), −262(3), 0(1)
2696.614	−3744(7), −3367(8), −3223(9), −2864(11), −2705(4), −2503(10), −2092(6), −1881(3), −1637(12), −1131(2), −874(5), 0(1)
2730.583*	0(1), 125(2), 2007(2), 2101(1)
2780.450	−779(2), −626(2), −449(2), −250(2), 0(1)
2781.260*	−242(2), 0(3), 1648(4), 1890(1)
2798.724*	0(1), 577(2), 1078(3), 1480(4), 1827(5), 2059(6)
2809.684	0(1), 546(2), 997(3), 1387(4), 1685(5), 1922(6)
2863.863*	0(1), 198(2), 365(6), 2080(5), 2252(4), 2362(3)
2883.642*	0(1), 1886(2)
2897.969	−466(6), −259(2), 0(1), 98(4), 256(3), 448(5)
2926.315*	0(1), 1878(2)
2938.320	0(1), 58(5), 424(3), 640(2), 798(4), 949(6), 1104(7)
2960.918*	0(1), 1857(2)
2988.993	−620(4), −464(3), −258(2), 0(1)
2993.312	−600(4), −460(3), −255(2), 0(1)
3024.577	−1229(6), −1153(7), −1013(2), −863(8), −642(12), −521(10), −376(4), −290(3), −90(5), 0(1), 226(9), 590(11)
3038.740*	0(1), 1911(2)
3067.663	−1000(1), −892(2), −95(2), 0(1)
3076.632	−660(4), −504(3), −277(2), 0(1)
3103.052*	0(1), 1859(2)
3267.686*	0(1), 1877(2)
3397.302	0(1), 592(2), 1102(3), 1519(4), 1837(5), 2107(6)
3402.877*	0(1), 588(2), 1089(3), 1501(4), 1833(5), 2075(6)
3405.326	0(1), 1760(2)
3510.975	0(1), 568(2), 1058(3), 1465(4), 1782(5), 2026(6)
3596.123	−1040(6), −573(2), 0(1), 458(4), 841(3), 1320(5)
3888.166	−179(2), 0(3), 1708(4), 1888(1)
4121.906	0(3), 714(2), 1879(1), 2597(4)
†4271.509*	0(1), diff. 285(2), diff. 490(3)
4308.523	0(1), 1896(2)
4493.005	0(1), 1850(2)
4722.373	−1430(2), −1284(3), −1089(5), −459(6), −260(4), 0(1)
†6134.570*	−1196(4), −910(3), −795(6), −565(5), −384(2), 0(1), 110(7)

‡ The numbers in parentheses give the qualitative intensities: 1 — strongest, 2 — next strongest, and so on.
† Observed only in the first order.
* Structure not investigated before.

II although their structure could not be resolved and only the position of the center of gravity was determined. The very good agreement of the wave numbers obtained and the term values determined from other lines shows that the corrections for the index of refraction of air given by Meggers and Peters and used in the preparation of tables by Kayser are correct within the limits of accuracy of my measurement. The more recently reported formulas for the correction, having a smaller coefficient in the term λ^{-4}, seem to be inadequate for the short wave-length region (λ2500–λ2000).[10] The small difference between the wave numbers and the term values amounting to $+0.03$ cm^{-1} is opposite in direction to the expected shift of the center of gravity caused by the h.f.s. and also to the shift required by the newer formulas. Moreover, the real difference is probably even a little higher, since the wave-lengths were determined from the third order by use of second order Fe standards; the correction introduced for the departure of the temperature and pressure from normal was found for the lines around λ2500 to be rather a little too small than too big.

The h.f.s. collected in Table I gave the h.f.s. separations of levels presented in Tables II and III. In the last table the less certain values are marked by stars. For the ground state the considerable uncertainty is caused by the incomplete

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[10] Cf. the discussion of this point in Rev. Mod. Phys. **14**, 65 (1942).

TABLE II. Even terms and their combinations with the 6p^3 terms.

Even terms	6p^3	$^4S^\circ_{3/2}$ 0	$^2D^\circ_{3/2}$ 11418.77	$^2D^\circ_{5/2}$ 15438.42	$^2P^\circ_{1/2}$ 21661.81	$^2P^\circ_{3/2}$ 33165.01	Over-all h.f.s. Separation in cm^{-1} This work	Z. B. G. (reference 1)
$1_{1/2}$	32588.66	3067.663 32588.66	4722.373 21169.89				0.828	0.830
$2_{3/2}$	43912.43	2276.551 s. 43912.50	3076.632 32493.66	3510.975 28474.01	4493.005 22250.61		0.056	~0.1
$3_{5/2}$	44816.91	2230.605 s. 44816.93	2993.312 33398.13	3402.877 29378.50		(8579.74) 11652.2	≤ ±0.005	<0.1
$4_{3/2}$	44865.13	2228.207 s. 44865.15	2988.993 33446.36	3397.302 29426.71	4308.523 23203.31	(8544.54) 11700.2	−0.020	~ −0.1
$5_{1/2}$	45915.61	(2177.22) 45915.7	2897.969 34496.84		4121.906 24253.80	(7840.33) 12751.1	−0.715	−0.708
$6_{1/2}$	47373.61	(2110.31) 47371.3	2780.450 35954.82		3888.166 25711.80	(7036.15) 14208.4	0.180	0.20
$7_{5/2}$	48491.31	(2061.70) 48488.1	2696.614 37072.56	3024.577 33052.88			3.113	3.166
$8_{3/2}$	49461.59	(2021.21) 49459.3	2627.834 38042.82	2938.320 34023.15	3596.123 27799.78	†6134.570 16296.56	1.430	1.415
$9_{3/2}$	51019.18	(1959.48) 51017.3	2524.470 39600.34	2809.684 35580.73	3405.326 29357.37	(5599.41) 17854.1	0.160	very narrow
$10_{5/2}$	51158.47	(1953.89) 51163.2	2515.619 39739.69	2798.724 35720.06			0.017	
$19_{1/2}$	52244.70	(1913.6) 52241	2448.683 40825.90		3267.686 30593.90		0.060	
$11_{5/2}$(Th)	53878.82	(1855.9) 53865	(2354.49) 42459	2600.654 38440.38	3103.052 * 32217.02		0.025	
$12_{5/2}$	53965.95	(1852.3) 53970	(2349.10) 42556.5	2594.771 38527.53	(3093.58)*T*? 32315.7		≦ ±0.005	
$20_{1/2}$(Th)	54559.64	(1832.3) 54558	(2317.70) 43133.4		3038.740 * 32898.83		~ −0.04	
$21_{3/2}$?	55425.28*			(2499.52)? * 39995.6	2960.918 * 33763.47		~0.04	
$22_{7/2}$	55479.57*			2496.678 * 40041.15			−0.015	
$23_{1/2}$ or $_{3/2}$	55824.51*		(2251.73)Th 44396.6		2926.315 * 34162.70		~0.012	
$24_{1/2}$ or $_{3/2}$	56330.04*				2883.642 * 34668.23	†4315.700? * v.w. 23164.72	≤ ±0.005	
$13_{3/2}$(T)	56569.45		(2214.11) 45150.7	(2430.45) 41132.1	2863.863 34907.64	†4271.509 * 23404.37	−0.477	
$14_{5/2}$(T)	57075.66		(2189.58) 45656.6	2400.965 41637.13		4181.100? * v.w. 23910.44 diff.	−0.930	
$25_{1/2}$	57606.14*		(2164.1)? * 46194.1		2781.260 * 35944.33	4090.310 s. 24441.15	0.242	
$15_{3/2}$(T)	58273.21		(2133.68) 46852.3	(2333.79) 42835.6	2730.583 36611.40		−0.265	
$16_{5/2}$(T)	(43208)?	(2313.8) 43205.6	(3144.6) 31791.4	(3599.9) 27770.4				
$17_{3/2}$(T)	(64020)			(2057.68) 48582.8	(2360.1) 42358.1	(3239.73) 30854.8		
$18_{3/2}$(T)	(66103)			(1973.08) 50665.7	(2249.38) 44442.9	(3035.18) 32937.5		
Over-all h.f.s.	This work	−0.225	−0.606	2.082	1.885	0.250		
Separation in cm^{-1}	Z. B. G. (reference 1)	−0.08	−0.606	2.030	1.875			

s. = single. v.w. = very weak. diff. = diffuse.
† Observed only in the first order.
* New terms and new lines.

resolution of the line λ3067; only the separation of the levels $F=6$ and 5 could be taken directly from the data of Table I and the two others were evaluated approximately. The value of the over-all separation is therefore also uncertain; however, it is clear that the total separation is not smaller than 0.2 cm^{-1} and that consequently Zeeman, Back, and Goudsmit[1] greatly underestimated its value. Two separations in the level 15 were evaluated roughly in a similar manner from the line λ2730. Also for the level 14 only one separation of sublevels could be obtained

TABLE III. Hyperfine structure.

Term	Separation in 10^{-3} cm^{-1}										
	$F=2$		3		4		5		6		7
$^4S^\circ_{3/2}$						−55*		−75*		−95	
$^2D^\circ_{3/2}$						−146		−200		−260	
$^2D^\circ_{5/2}$		245				332		416		500	590
$^2P^\circ_{3/2}$						60*		80*		110	
$7_{5/2}$		375				500		620		748	870
$8_{3/2}$						382		478		570	
$13_{3/2}$						−110		−169		−198	
$14_{5/2}$		−118*				−154*		−190*		−226*	−242
$15_{3/2}$						−60*		−80*		−125	

* Relative to the level with highest F value.

TABLE IV. Odd terms $(6p^2nx)$ and their combinations with the term $1_{1/2}$.

Term		Line λ	Line ν	H.f.s. in 10^{-3} cm^{-1}	Separation in cm$^-$
$1^\circ_{3/2}$(Th)	(41125.3)	(11711.1)	8536.6		
$2^\circ_{3/2}$	(42941)*	(9657) *	10352		
3°	50599.67*	†5550.621 *	18011.01	0(1), 817(2)	∼0.015
$4^\circ_{3/2}$	53468.70*	†4787.928 *	20880.04	0(1), 804(2)	∼0.040
5°	53708.49*	†4733.566 *	21119.83	0(1), 848(2)	∼−0.035
$6^\circ_{1/2}$(T)	53893.70	†4692.417	21305.04	0(3), 560(1), 830(2), 1390(4)	−0.560
$7^\circ_{3/2}$	54570.59?*	†4547.920 *	21981.93	0(1), 1022(2) both very diffuse	∼−0.250
8°	55393.67*	4383.774 *	22805.01	0(1), 825(2)	≦±0.008
9°(T)	56088.38	4254.175	23499.72	0(1), 833(2)	≦±0.010
$10^\circ_{1/2}$	56275.96*	4220.486 *	23687.30	0(3), 306(2), 830(1), 1134(4)	−0.305
11°	56316.47*	4213.280 *	23727.81	0(1), 820(2)	∼0.012
12°	56908.97*	4110.634 *	24320.31	0(1), 835(2)	∼−0.012
13°	57309.64*	†4044.008 *	w. 24720.98	0(1), 820(2)	∼0.012
14°	57593.72*	†3998.064 *	w. 25005.06	0(1), 817(2)	∼0.015
15°	57800.77*	†3965.229 *	v.w. 25212.11	0(1), 870(2)	∼−0.06
16°	64711.14*	3112.185 *	32122.48	0(1), 840(2)	∼−0.020

† Observed only in the first order.
* New terms and new lines.

from the line λ2401; the others were calculated by approximate application of the Landé interval rule (the total separation being known from the over-all width of the line λ2401 minus the over-all separation of the level $^2D^\circ{}_{5/2}$). Finally the two smaller separations in the level $^2P^\circ{}_{3/2}$ were obtained indirectly from only one line (λ6134) and are therefore of a low accuracy.

The high accuracy obtained in the case of the levels $^2D^\circ{}_{3/2}$, $^2D^\circ{}_{5/2}$, $7_{5/2}$, and $8_{3/2}$ makes a study of interval rule deviations possible. However, these deviations have already been studied for the line λ4722 and for several lines of Bi II and Bi III by Schüler and Schmidt[11] with great precision and the quadrupole moment of the nucleus Bi^{209} was calculated. Since the results of the present work for the level $^2D^\circ{}_{3/2}$ almost coincide with theirs, no new determination of the quadrupole moment from the other three levels mentioned above has been attempted.

Of the odd terms corresponding to the excitation of at least one electron ($6p^2nx$), only three were known previously. Thirteen more were detected in the course of this investigation. All these terms combine with the even term $1_{\frac{1}{2}}$ and were easy to identify in view of the wide doublet structure of the term $1_{\frac{1}{2}}$. They are all collected in Table IV. The term 1° was discovered by Thorsen[7] and was denoted by Bacher and Goudsmit[9] as 20°; the term 2° was identified by the author on the basis of combinations. The term 7° and the classification of the line λ4548 are subjected to some doubts in view of the large deviation of the doublet separation from the value 0.828 (term $1_{\frac{1}{2}}$). An unclassified line λ3659.862 was observed with the following structure: −1824(2), −1637(3), −1378(5), −597(6), −333(4), 0(1); the separations of levels involved are: a doublet level ±1045, and a fourfold level ∓187, ∓262, ∓333. However, since the components of λ4548 are very diffuse the doublet separation of the level involved is certainly considerably different from the value 1022 and both these lines certainly do not have a level in common.

TABLE V. Lines not involving $6p^3$ levels.

Line‡ λ	ν	Classification
7335.01*	13629.5	13 −2°
7838.70	12753.7	11 −1°
8210.83	12175.7	9°−2
8761.54*	11410.4	10°−4
8907.81	11223.0	9°−4
9828.8	10172.8	9°−5
10106.1	9892.3	9 −1°
10301.7*	9704.5	7°−4
11073.2	9028.4	6°−4
11555.5*	8651.5	4°−3
11994.5	8334.9	8 −1°
12166.5*	8217.1	10 −2°
22554.2*	4432.6	6°−8

‡ All wave-lengths taken from Toshniwal (reference 8).
* Newly classified.

In Table V are collected all remaining lines classified as transitions not involving one of the $6p^3$ levels. The small number of such lines (Tables IV and V in all 29 lines) indicates that our knowledge of the arc spectrum of bismuth is still fragmentary. It seems that more substantial progress can be expected at present from a study of the spectrum in the infra-red and short ultraviolet regions only.

In the course of this work several forbidden lines emitted from the four metastable levels (configuration $6p^3$) were observed. A closer study of this group of lines is intended in the near future.

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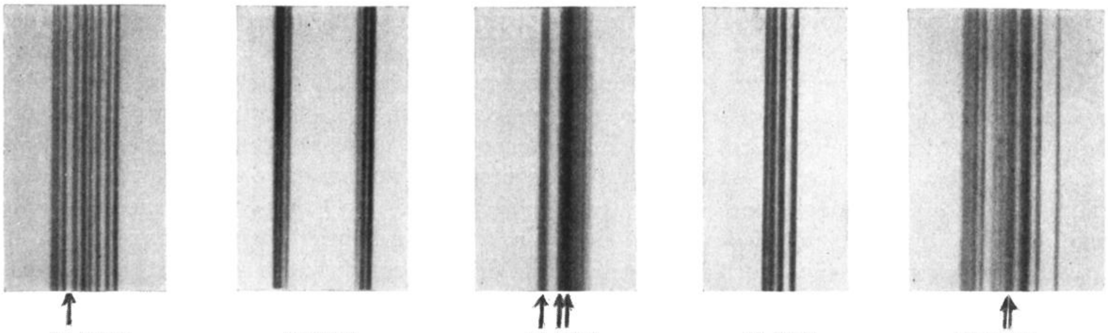
[11] H. Schüler and Th. Schmidt, Zeits. f. Physik **99**, 717 (1936).



(a) λ2627 (b) λ2864 (c) λ2938 (d) λ2993 (e) λ3024

Fig. 1. Enlargements of photographs of hyperfine structures of lines of bismuth obtained in the third order of the 30-foot grating spectrograph. The picture (e) shows the highest resolution ever obtained with a grating (400,000).