

On the other hand, $4p(^1D)^2P_{1/2}$ is 0.215 too high. A similar situation exists for the $j=\frac{3}{2}$ levels. For $4p(^3P)$ the g -sum is normal within experimental limits. For $5p(^3P)$ the sum is 0.059 too small. But the $5p(^1D)$ sum is 0.062 too large. Here is striking evidence of the sharing of g -values by two configurations.

It is worth noting that perturbations of g -

values caused by configuration interaction seem to be greater the smaller the j -value concerned. This is in general agreement with theory.

Note added in proof: The g -values in Table V indicate that the chlorine atom, like those of the rare gases, exhibits a type of coupling (in the limit) which is represented when the electrostatic interaction is weak compared with the spin-orbit interaction, but strong compared with the spin coupling of the external electron. We have called this type of coupling $[(j_1k_1)s_2]$.

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Forbidden Lines of Bismuth BiI

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A group of forbidden lines of bismuth BiI, namely $\lambda 8755$, 6476 , 5640 , 4615 , 4597 , and 3014 , all belonging to transitions between levels of the configuration $6p^3$ (Fig. 1) was investigated with a spectrograph of high resolving power. The hyperfine structures observed are collected in Table I and the photographs obtained are reproduced in Fig. 2. Predicted patterns with components corresponding only to the change of the quantum number F by 0 or ± 1 and intensities calculated on basis of usual formulas for electric dipole radiation are in best agreement with the observed ones (Fig. 3). The absence of components corresponding to $\Delta F = \pm 2$ shows the predominantly magnetic dipole character of the radiation. All observed separations of components and wave-lengths of the forbidden lines found are in very good agreement with the values predicted on basis of the highly accurate level scheme of the bismuth atom previously determined by the author.

IN a series of papers¹ the author succeeded in showing that the investigation of the isotopic and hyperfine structures of a forbidden line furnishes an easy method for determination of the type of the forbidden radiation, a method which is usually more convenient than the investigation of the Zeeman effect. Not many systematic investigations have been carried out on the electric quadrupole and magnetic dipole lines (the second order radiation) and until now only the case of a p^2 configuration has been more closely studied.² Since the lines of a mixed character present a considerable interest in view of a recently discovered interference effect,³ an extension of the investigations to forbidden

multiplets of the p^3 configuration seemed to be worth while. In this paper the author is presenting the results of corresponding experiments carried out with bismuth vapor. The experiments had to be interrupted before intensity measurements could be done. Since, however, there seems to be no hope they will be performed in the near future, it seemed appropriate to report the results now obtained, that is of the hyperfine structure investigations.

The experimental arrangement was the same as that used in the work on the analysis⁴ of the spectrum of bismuth BiI. A quartz tube with outside electrodes, permanently connected to the pumping system and containing a piece of metal, was filled with helium at about 5-mm pressure and excited by short electric waves (3–4 meter wave-length). For an intense production of forbidden lines, however, higher temperatures of

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¹ For references see the general reports: S. Mrozowski, Bull. Polish Inst. Arts and Sciences America 2, 200 (1943); or S. Mrozowski, Rev. Mod. Phys. 16, 153 (1944).

² S. Mrozowski, Phys. Rev. 58, 1086 (1940).

³ F. A. Jenkins and S. Mrozowski, Phys. Rev. 60, 225 (1941).

⁴ S. Mrozowski, Phys. Rev. 62, 526 (1942).

the furnace (higher pressure of bismuth vapor) and a decreased power of the high frequency oscillator were required. The optimum conditions for excitation of forbidden lines of metals in such an arrangement were previously studied in the case of the spectrum of lead,² and it was shown that such a discharge is a very intense source of forbidden lines. The increase of the partial pressure of bismuth vapor is followed by the appearance of the well-known rich band spectrum of Bi₂ in the region 5000–7000Å. The conditions of excitation of this band spectrum are the same as of the forbidden lines—the power delivered by the oscillator must not be too high, otherwise the molecules are dissociated by the high current and only an atomic spectrum of BiI is emitted. This band spectrum was photographed some time ago by the author in collaboration with Dr. F. Bueso-Sanllehi in the first order of the big Chicago grating No. 3 and it was found that the bands are quite nicely resolved into a multitude of lines. Long series of lines (branches) can be easily picked out; however all bands overlap strongly with each other and this creates such a mixup that no analysis was attempted. The presence of the band spectrum is of some inconvenience only in the case of the line λ5640, which is quite weak and therefore requires long exposures. Fortunately this line originates in the highest metastable level ²P_{3/2} and, therefore, has its maximum intensity at relatively lower vapor

densities of bismuth. The other line in the region of the band spectrum, namely λ6476, is so intense that no traces of the band lines appear even for strongly overexposed photographs of this line.

The level scheme of the lowest group of levels of BiI (6*p*³ configuration) is represented in Fig. 1. Six forbidden lines observed and two other transitions, the presence of which was not but probably could be easily checked with a medium spectrograph (dashed lines), are inserted in this graph. No photograph of the line λ8691 could be obtained with the big grating, although exposures were extended over 60 hours. Evidently this line is much weaker than the neighboring line λ8755. The three strongest forbidden lines, namely λ8755, λ6476, and λ4615, were found in the spectrum of a discharge tube by other investigators some time ago.⁵ In this work at the optimum excitation conditions these lines are belonging to prominent lines of the spectrum. All lines were photographed in the first order of the big grating No. 3, with exception of the lines λ4615 and λ3014 which could be obtained also in the second order. The exposure time ranged from a few hours (λ6476) to 48 hours (λ8755 and λ5640). The infra-red line λ8755 was photographed on Eastman-Kodak M-1 plates, and λ5640 on Ilford panchromatic plates.

The photographs obtained are reproduced in Fig. 2. It is easily noticeable that the lines λ4597 and λ3014 are far from being resolved. In case of the line λ8755 a very wide slit had to be used and therefore the structure is obliterated revealing only a diffuse doublet. The results of the measurements of the hyperfine structures are collected in Table I. Since the separations of the levels involved are well known from the analysis of other lines of bismuth,⁴ a comparison of observed and predicted pattern can be made. In Fig. 3 the predicted structures are inserted for the case of pure magnetic dipole radiation, that is, only components for which Δ*F*=0, ±1 are included with intensities calculated on basis of the usual formulas for hyperfine structure. The applicability of these rules for the electric dipole radiation to the magnetic dipole case of hyperfine structure was demonstrated experi-

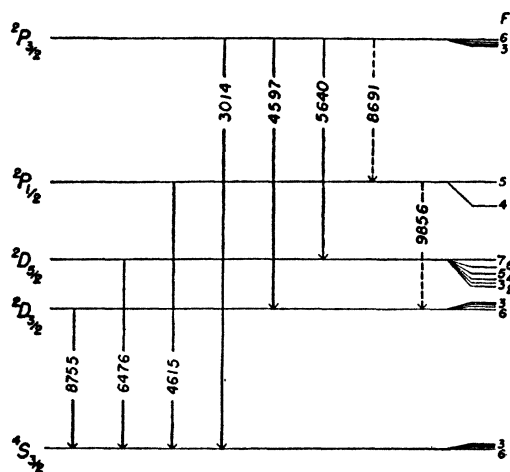


FIG. 1. The lowest levels all belong to the 6*p*³ electronic configuration and the forbidden lines of bismuth BiI. On the right the hyperfine separations of levels, but on a 1000 times larger scale, are given.

⁵ G. R. Toshniwal, Phil. Mag. 4, 774 (1927).

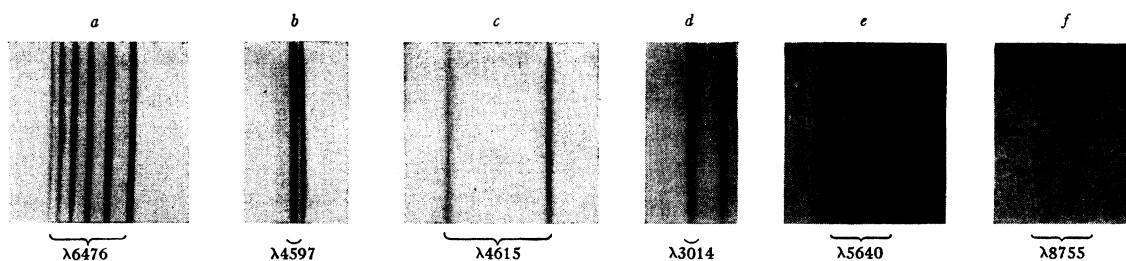


FIG. 2. Hyperfine structure of forbidden lines of bismuth BiI. Photographs *a*, *b*, *e*, and *f* were obtained in the first and *c* and *d* in the second order of a 30-foot grating spectrograph.

mentally by the author² and explained theoretically by Gerjuoy.⁶ The observed structures are represented by curves and the measured positions of the peaks are inserted below in the form of shaded circles. The positions of weak components not quite resolved from neighboring strong ones ($\lambda 4615$ and $\lambda 6476$) were determined visually with the comparator. As it was observed in a similar case by the author,⁷ the results are surprisingly good, our vision being sensitive rather to the rate of the change in density on the plate than to the change of the density itself. For the line $\lambda 5640$ the intensity of the second component on the left seems smaller than (or equal to) that of the third; this is probably because of the partial resolution of the doublet which causes the easily visible widening of the second component and lowers at the same time its peak intensity. The measured total splitting of the line $\lambda 5640$ is a little greater than the predicted value and this seems to indicate that the total splitting of the $^2P_{3/2}$ level reported in the paper⁴ on BiI was a little too high and should probably be around 0.23 cm^{-1} instead of 0.25 cm^{-1} . The separation for the ground level $^4S_{3/2}$, which was found⁴ to be almost three times larger than the value estimated previously by Zeeman, Back,

TABLE I. Hyperfine structure. Components in 10^{-3} cm^{-1} (approx. relative intensity 1—strongest, 2—next strongest, and so on).

8755	0 (1), +380 (1)
6476	-2300 (6), -2030 (5), -1660 (4), -1200 (3), -676 (2), -580 (7), 0 (1)
5640	0 (1), +520 (2), +940 (2), +1310 (3), +1640 (4), +1870 (4)
4615	-2090 (2), -1990 (4), -90 (3), 0 (1)
4597	-760 (2), -502 (2), -255 (3), 0 (1)
3014	-300 (1), 0 (2)

and Goudsmit,⁸ is confirmed by the structures observed for the lines $\lambda 6476$ and $\lambda 4615$.

In Table II the exact wave-lengths and wave numbers for the components corresponding to transitions with highest F quantum numbers are compared with the values expected on basis of the term values previously reported.⁴ Very good agreement is obtained, except in the case of the weak and diffuse line $\lambda 3014$; the discrepancy in the case of the line $\lambda 8755$ does not have to be taken seriously, since the line is very diffuse and the wave-length was determined relative to the second-order iron lines introducing a correction

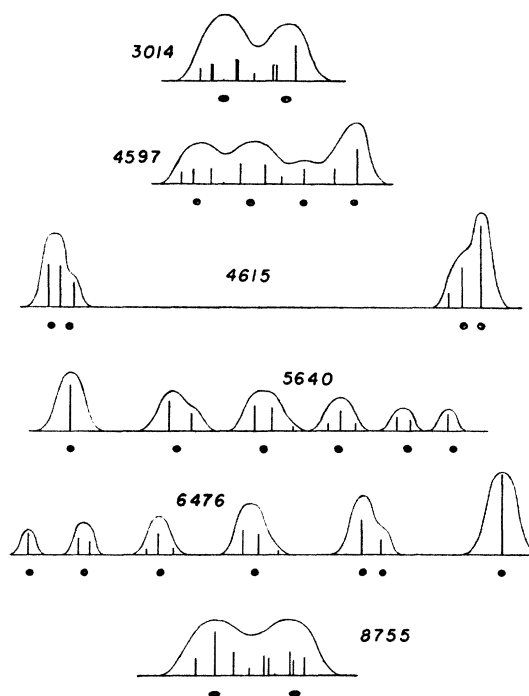


FIG. 3. Predicted and observed structures of forbidden lines of bismuth BiI.

⁶ E. Gerjuoy, Phys. Rev. **60**, 233 (1941).

⁷ S. Mrozowski, Zeits. f. Physik **112**, 223 (1939).

⁸ P. Zeeman, E. Back, and S. Goudsmit, Zeits. f. Physik **66**, 1 (1930).

TABLE II. Measured wave numbers of components with highest F quantum numbers for the forbidden lines of BiI. Deviations from predicted values in parenthesis.

Final level \ Upper level	$^3D_{3/2}$ 11418.77	$^3D_{5/2}$ 15438.42	$^2P_{1/2}$ 21661.81	$^2P_{3/2}$ 33165.01
$^4S_{3/2}$ 0	λ 8754.90 11419.03 (+.26)	λ 6475.535 15438.46 (+.04)	λ 4615.122 21661.85 (+.04)	λ 3014.343 33165.09 (+.08)
$^2D_{3/2}$ 11418.77				λ 4597.216 21746.22 (-.02)
$^2D_{5/2}$ 15438.42				λ 5639.702 11726.53 (-.06)

for the dispersion of the air at the given temperature—a procedure which hardly can give a highly accurate result.

The very good agreement between the predicted and observed structures and the failure to observe any components for which $\Delta F = \pm 2$ are a good evidence for the predominantly magnetic dipole character of the radiation of the whole group of forbidden transitions studied. It is hard to estimate how high the possible admixture of an electric quadrupole radiation may be without performing intensity measurements. However from the appearance of the best resolved line λ 6476 I would expect for this line the admixture to be not higher than 15 percent. Theoretically this percentage could be easily determined by use of tables published not long ago by Shortley, Aller, Baker, and Menzel,⁹ if only an integral involving radial factors of the p -orbital would be known. From the same tables the relative intensities of lines originating from the same upper level can be obtained as functions of the unknown integral. A measurement of the relative intensities of the lines λ 3014, 4597, 5640, and 8691 would therefore lead to a determination of the percentage of the electric quadrupole radiation and would at the same time present a

⁹ G. H. Shortley, L. H. Aller, Y. G. Baker, and D. H. Menzel, *Astrophys. J.* **93**, 178 (1941).

good opportunity for a check of the theoretical predictions (since a ratio for two lines would be sufficient for determination of the percentage). On the other hand the same percentage could be determined from an observation of the interference effect in the magnetic field⁸ furnishing an additional check on the theoretical relations. In the past the effort was made to get such a double check for the case of the spectrum of lead,^{2, 3, 6} but unfortunately the agreement is not good. (See the discussion of this point in the article in *Reviews of Modern Physics*, reference 1.) It seems, therefore, necessary to perform measurements of relative intensities of lines in forbidden spectra with a higher accuracy, preferably for a whole group of spectra like Pb, Bi, Se, Te,¹⁰ and maybe some others, in order to secure more reliable data for comparison with theoretical predictions. At the same time valuable information could be collected about the concentration of metastable atoms in different states and its dependence on different factors. Further experiments with the interference effect in the line λ 7330 of Pb should be repeated⁸ and extended to the longitudinal Zeeman effect, and also the same effect in lines of mixed character for other elements should be investigated.

¹⁰ H. Niewodniczanski and F. Lipinski, *Nature* **142**, 1160 (1938).

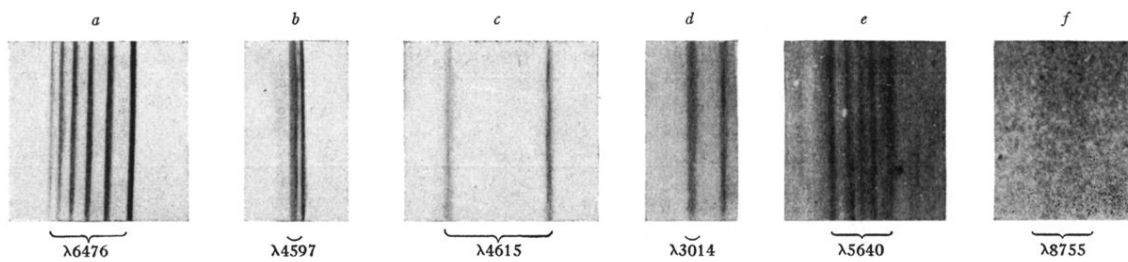


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