theory of the isotope shift in the light elements is complete, the agreement between calculation and experimental observation should improve as more adequate wave functions are used in the specific mass calculations. As pointed out by Mack *et al.*,[9] such studies of the specific mass effect should prove to be useful in checking the accuracy of the wave functions adopted for the light elements.

Gailer[10] reports that three lines in the lithium spectrum, at 3303 A, 3650 A, and 3720 A, remain to be classified. We believe all three lines to be spurious. A probable explanation for at least two of these lines lies in the list of the persistent lines of the elements. The second member of the principal series of sodium lies at 3303 A and the ultimate line of Fe I (iron was present in Gailer's system), at 3720 A. The other line, at 3650 A, could possibly be from Hg I.

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[9] Bernarda, Burke, Burnett, Hughes, and Mack, Rydberg Conference, Lunds University Årsskrift 50:21, 1954 (unpublished), p. 88.

[10] K. Gailer, Ann. Physik. **126**, 583 (1949).

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Isotope Shift in the First Three Spectra of Boron*

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Isotope shifts have been observed in the first three spectra of boron, with separated isotopes. On the assumption that the total observed shift consists only of the (exactly calculable) normal mass effect and a specific mass effect, the results are as follows (a positive sign indicating a shift of B^{11} toward the violet relative to B^{10}):

	Total shift	$\dfrac{\Delta\sigma_{s,\,\mathrm{obs}}}{\Delta\sigma_{s,\,\mathrm{calc}}}$ (approx)
B I $1s^22s^22p\ ^2P_{\frac{1}{2},\frac{3}{2}}-1s^22s^23s\ ^2S_{\frac{1}{2}}$	$\left\{\begin{matrix}-137\pm12\ \mathrm{mK}\\ -139\pm\ 6\ \mathrm{mK}\end{matrix}\right\}$	1.0 or 0.9,
B II $1s^22s2p\ ^1P_1-1s^22p^2\ ^1D_2$	$+867\pm26$ mK	1.3,
B III $1s^22s\ ^2S_{\frac{1}{2}}-1s^22p\ ^2P_{\frac{1}{2},\frac{3}{2}}$	$\left\{\begin{matrix}+1170\pm120\ \mathrm{mK}\\ +1210\pm\ 90\ \mathrm{mK}\end{matrix}\right\}$	1.4,

where the calculated specific shift, $\Delta\sigma_{s,\,\mathrm{calc}}$ is based on hydrogen-like wave functions of the Hughes-Eckart type.

I. INTRODUCTION

HUGHES and Eckart[1] inaugarated the theoretical study of the isotope shift in light polyelectronic atoms in 1930. Hughes[2] at the same time made an experimental determination for lithium, but the work was done without the benefit of separated isotopes and the experimental results were not sufficient for a close check with theory. The conclusion was that the agreement was reasonable. Hughes[3] has recently investigated the isotope shift in neutral lithium with separated isotopes and found that observations give specific shifts larger than the calculated values.

The current investigation of boron was initiated to consider another three-electron system, B III. The only lines available are those of the resonance doublet at 48 392/58 K (kaysers, 1 K = 1 cm^{-1} = 10^3 mK), 2066/7 A, $1s^22s\ ^2S_{\frac{1}{2}}-1s^22p\ ^2P_{\frac{3}{2},\frac{1}{2}}$. The studies have been extended to repeat Mrozowski's[4] measurements, which he made with unseparated isotopes, on the B II line 28 966 K (3451 A), $1s^22s2p\ ^1P_1-1s^22p^2\ ^1D_2$, and the B I doublet at 40 040/24 K (2497/8 A), $1s^22s^22p\ ^2P_{\frac{1}{2},\frac{3}{2}}-1s^22s^23s\ ^2S_{\frac{1}{2}}$. The B II $1s^22p^2\ ^1D_2-1s^22s3p\ ^1P_1$ line was not excited in our sources. Calculations have been made for the B I lines by Opechowski and Devries[5] and by Vinti.[6] A calculation for the B II line has been made by Vinti.[6] Hughes' paper[3] contains a brief outline of the theory.

II. EXPERIMENTAL

For excitation of the B III spectrum a special high-excitation, sharp-line source was required. The resonance doublet has been previously observed only in the hot spark, but high voltages in a highly condensed discharge could not be used since that would have produced broadened lines. A compromise was effected with a condensed-hollow-cathode source. The tube itself was

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[1] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930); the last equation on page 697 should be labeled "(13)".

[2] D. S. Hughes, Phys. Rev. **38**, 857 (1931).

[3] R. H. Hughes, preceding paper [Phys. Rev. **99**, 1837 (1955)].

[4] S. Mrozowski, Z. Physik **112**, 223 (1939).

[5] W. Opechowski and D. A. Devries, Physica **6**, 913 (1939).

[6] J. P. Vinti, Phys. Rev. **58**, 879 (1940).

TABLE I. Isotope shifts in the spectra of boron (values in mK except where noted).

Line							$\Delta\sigma_{s,\mathrm{calc}}$			$\Delta\sigma_{s,\mathrm{obs}}{}^{a}$
λ(A)	σ(K)	$\sigma_{\mathrm{obs}}-\sigma_{\mathrm{tab}}$(K)	Classification	$\Delta\sigma_{\mathrm{obs}}{}^{b,c}$	$\Delta\sigma_n$	$\Delta\sigma_{s,\mathrm{obs}}$	Lower level	Upper level	Line	$\Delta\sigma_{s,\mathrm{calc}}$
2065.783	48 392.33	−0.3	B III $1s^22s\ {}^2S_{\frac{1}{2}}-1s^22p\ {}^2P_{\frac{3}{2}}{}^{\circ}$	$+121_0\pm 9_0$	+240	$+97_0\pm 9_0$	0	−671	+671	1.45±0.14
2067.238	48 358.28	−0.2	B III $^2S_{\frac{1}{2}}-\ {}^2P_{\frac{1}{2}}{}^{\circ}$	$+117_0\pm 12_0$	+240	$+93_0\pm 12_0$	0	−671	+671	1.39±0.18
2496.8	40 040		B I $1s^22s^22p\ {}^2P_{\frac{1}{2}}{}^{\circ}-1s^22s^23s\ {}^2S_{\frac{1}{2}}$	−137 ±12	+199	−336± 12	$-33_0{}^{d}$ -367^{e}	0 0	$-33_0{}^{d}$ -367^{e}	1.02 ± 0.04^{d} 0.92 ± 0.03^{e}
2497.7	40 024		B I $^2P_{\frac{3}{2}}{}^{\circ}-\ {}^2S_{\frac{1}{2}}$	−139 ± 6	+198	−337± 6	$-33_0{}^{d}$ -367^{e}	0 0	$-33_0{}^{d}$ -367^{e}	1.02 ± 0.02^{d} 0.92 ± 0.02^{e}
3451.298	28 966.39	+1.0	B II $1s^22s2p\ {}^1P_1{}^{\circ}-1s^22p^2\ {}^1D_2$	+867 ±26	+144	+723± 26	-305^{e}	-872^{e}	$+567^{e}$	1.28±0.05

[a] The uncertainty shown does not include that of the calculation.
[b] Positive (negative) shift means, direction the same as (opposite to) that of the normal mass shift, i.e., B^{11} shifted to the violet (red) from B^{10}.
[c] The ± values are estimated limit (i.e., high-confidence) errors.
[d] See reference 5.
[e] See reference 6.

similar to one described by Tolansky[7] as a hot hollow cathode. A somewhat similar discharge has been used by Paschen[8] in 1923 and by Gartlein and Gibbs[9] in 1931, and more recently by Edlén and Glad,[10] and others. A condensed pulsating voltage was applied to the tube. Capacitances varying from $\frac{1}{8}$ to 1 μf were used. The condenser was charged to the desired voltage with a power supply and allowed to discharge through the tube with a mechanical interrupter consisting of a four-pronged wheel, rotating at about 75 rpm, making contacts with spring-brass strips. The discharge appeared steady and was concentrated mainly inside the cathode. Small sparks appeared within the cathode during operation. Optimum operation for the excitation of the B III resonance lines used a $\frac{1}{2}$-μf condenser at 1200 volts. Exposure times of ten minutes were sufficient with a 21-foot grating at f:42.

The vacuum system for the B III lines was small, simple and static. The single vessel contained two cathodes so prepared that the two separated isotopes of boron could be used alternately. When a forepump and an efficient charcoal trap had produced a black vacuum, helium was allowed to enter through a three-valve system until the brightest hollow cathode discharge was observed. The condensed spark could then be started.

Although the B II 28 966 K line and the B I 40 040/24 K lines could be excited in the above-described tube operating without the condensed spark, these lines with their small isotope shifts could not be studied in the hot hollow cathode because of Doppler broadening, so an Arroe-Mack tube[11] was employed. Two such tubes were mounted in parallel so that the separated isotopes could be photographed simply by switching, without otherwise changing the operating conditions. The vacuum, which again was static, was obtained as it was with the condensed hollow-cathode discharge system.

A Fabry-Perot interferometer in series with a quartz E-1 Littrow spectrograph was employed for the study of the shift in the B I 40 040/24 K doublet. All other studies were made with the 21-foot Rowland mount grating spectrograph.

The photographing of radiation above 47 000 K required special emulsions. Two were used in this study. The Eastman SWR plate proved satisfactory; however, the Eastman IIa-Ouv proved to be more convenient to handle and slightly more sensitive in that region. Eastman 103-0 plates were satisfactory for all the lines to the red of 47 000 K.

III. RESULTS

The results of this investigation may be most readily seen from Table I. Here σ_{tab} refers to the Moore-Sitterly[12] atomic energy level tables. The lines listed in the $(\sigma_{\mathrm{obs}}-\sigma_{\mathrm{tab}})$ column have been carefully remeasured, the B III lines at concentrations 96 percent B^{10} and 97 percent B^{11} respectively, in the fifth grating order against third-order iron lines with precautions in alignment to minimize the errors inherent in this method, and the B II lines in the third order against third-order iron lines. The normal mass shifts, $\Delta\sigma_n$, have been recalculated with modern values for the constants.[13,14] According to our sign convention, which is that of most investigations of the isotope shift in the spectra of light atoms, the normal shift in a line is positive, and for a level, positive shift means the relative depression of the heavier isotope, the matching point being a common series limit. The column labeled $\Delta\sigma_{s,\mathrm{obs}}$ is simply the difference between the previous two columns, and carries the implied assumption that the total shift arises only from the normal and the specific mass shifts of the levels. In the $\Delta\sigma_{s,\mathrm{calc}}$ columns, the value without a reference number is from our own calculations, made with the aid of Hughes and Eckart's[1] Eq. (13), with the values $Z_1=4.68$, $Z_2=3.19$ after Morse, Young, and Haurwitz.[15]

The isotope shift itself in the B III lines was measured

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[7] S. Tolansky, *High Resolution Spectroscopy* (Pitman Publishing Corporation, New York, 1947), p. 50.
[8] F. Paschen, Ann. Physik **71**, 142 (1923).
[9] C. W. Gartlein and R. G. Gibbs, Phys. Rev. **38**, 1907 (1931).
[10] B. Edlén (private communication to J. E. Mack).
[11] O. H. Arroe and J. E. Mack, J. Opt. Soc. Am. **40**, 386 (1950).
[12] Charlotte E. Moore, Atomic energy levels, National Bureau of Standards Circular 467, 1949, Vol. 1.
[13] E. R. Cohen, Phys. Rev. **88**, 353 (1952).
[14] J. E. Drummond, Phys. Rev. **97**, 1004 (1955).
[15] Morse, Young, and Haurwitz, Phys. Rev. **48**, 948 (1935).

relative to neighboring aluminum lines on 15 plates; although the lines were much sharper than could be obtained from a hot spark, still they had an average half-intensity width of about 1300 mK, and were not easy to measure. The ratio of about 1.4 between observed and calculated values shows a need for restudy of the theory.

The B II $2s2p\,{}^1P_1-2p^2\,{}^1D_2$ line shift was completely resolved with natural boron, which has a B^{11}/B^{10} abundance ratio of about 4.3 or 4.4; however, better exposures for measurement were made by mixing the isotopes so that the concentrations were approximately equal. The value of $+867\pm26$ mK agrees with Mrozowski's[3] earlier value of $+877\pm4$. The error in our determination is a limit (high confidence) error obtained from 15 readings on each of two similarly exposed plates. In part of Mrozowski's paper the ± stands for twice the greatest departure of any measurement from the mean, but it is unlikely that the readings on this line could be so consistent. Here the ratio of almost 1.3 between the observed and the calculated specific shift again indicates rather poor agreement.

Fabry-Perot fringe systems were compared for the B I 40 040/24 K doublet, taken with separated isotopes at the concentrations used for the B III investigation. The values for the isotope shift of these lines are -137 ± 12 and -139 ± 6 mK, respectively. These values are believed to be better than Mrozowski's[4] earlier values of -175 ± 12 and -168 ± 10 mK taken from microphotometer traces of asymmetries in Fabry-Perot fringes from natural-abundance samples, with Doppler half-intensity breadths about equal to the line separation. Excellent agreement exists between the observed shift and the specific shift of -330 mK calculated for these lines by Opechowski and Devries[5] with Hartree radial functions. Vinti's[6] recalculation, using Morse, Young, and Haurwitz[15] wave functions yielded -366 mK, appreciably higher than the value reported here and in close agreement with Mrozowski's values, which with the use of our value for the normal shift, come to -373 ± 12 mK.

IV. CONCLUSIONS

In B III the great practical advantage of having an extraordinarily large specific isotope shift is largely offset by the considerable line width occasioned by the necessity of exciting the third spectrum. It is unusual to find a specific mass shift so large compared with the normal mass shift as occurs in our B III and B II lines. The considerable disagreement in a ratio of about 1.4 between the observed and the calculated values in the B III resonance lines indicates that the wave functions without interconfiguration interaction, used thus far in the calculations, are inadequate. Hughes'[3] values for the same transition ($1s^22s-1s^22p$) in Li I show almost as high a ratio (1.32 ± 0.04) between the observed and the calculated values; moreover, he was able to show that there must be a positive isotope shift in the ground level. It appears reasonable to assume a corresponding shift in the B III ground level. This can be understood if an admixture with $1s2p^2$ is assumed in the ground level. The more complicated configurations in B II and B I show successively smaller disagreement.

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