Experimental study of quartet transitions in B III

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New experimental results for the doubly excited quartet levels in B III have been obtained using the beam-foil excitation technique. Both wavelengths and lifetimes are reported and the wavelength accuracy is higher than that in most previous investigations. A remeasurement of the $2s\,2p\,^4P^o$–$2p^2\,^4P$ transition yields a wavelength of 1702.1±0.1 Å, which confirms the most accurate theoretical value 1701.8 Å. The important $2s\,3s\,^4S$–$2s\,3p\,^4P^o$ transition has been observed for the first time. The new findings are discussed in relation to recent calculations.

I. INTRODUCTION

The quartet system $(1s\,2snl, 1s\,2pnl\,^4L)$ of Li I and higher members of the isoelectronic sequence has been studied extensively both experimentally and theoretically. Recent progress has been summarized by Andersen and Mannervik.[1] The beam-foil excitation has proven to be an outstanding method for populating these states, and most of the experimental results come from such measurements. While the quartet systems of Li I (Ref. 2) and Be II (Ref. 3) are now quite firmly established, the knowledge about the systems of higher Z along the sequence is more fragmentary.

For B III the first experimental result was reported by Martinson *et al.*,[4] who identified a line at 1701 Å as the lowest quartet transition $1s\,2s\,2p\,^4P^o$–$1s\,2p^2\,^4P$. Later, To *et al.*[5] presented additional data on B III quartets. Their proposed assignments were, however, partly erroneous largely because there were no accurate calculations available to guide the identification work. More recently, three articles[6–8] have presented valuable new information about the B III quartet spectrum. Chung *et al.*[6] performed extensive configuration-interaction calculations of level energies with relativistic effects included within the Breit-Pauli approximation. In addition, Chung *et al.* also reported experimental data for B III quartet lines in the 300–400-Å region. A wealth of experimental data was presented by Agentoft *et al.*[7] who studied the boron spectrum between 300 and 6300 Å. That investigation was combined with some calculations which complement those reported in Ref. 6. As a result a detailed energy-level diagram for the B III quartets was established. Shortly thereafter, Fairley and Laughlin[8] published model-potential calculations on the B III quartets. They also discussed several of the previous assignments.

We have performed thorough studies of the beam-foil spectra of boron between about 400 and 7000 Å in order to study, among other things, the singlet and triplet terms in B II, the inner-shell excited quintets in B II, and the quartets in B III. Many new lines have been found and much analysis is still in progress. However, we have already obtained results on the quartets of B III which are of interest in relation to the recent results and discussions of other authors.[6–8]

II. EXPERIMENTAL TECHNIQUE AND DATA ANALYSIS

The measurements were performed at the 400-kV heavy-ion accelerator at the Research Institute of Physics (Stockholm). To obtain a boron beam BF_3 was introduced in the ion source and a beam of typically 10 μA of $^{11}B^+$ was extracted from the accelerator. Most of the measurements were performed at a beam energy of 250 keV. This is a much lower energy than those used by Chung *et al.*[6] (6 MeV) and Agentoft *et al.*[7] (typically 2.5 MeV). According to the charge state distribution after the foil[9] a beam energy of about 1 MeV would optimize the fraction of B III. A beam energy of 2.5 MeV gives about the same fraction of B III as our energy of 250 keV does. Although we know that the excitation function for (B III)** (quartets) is not equal to that of singly-excited B III levels, we find that our comparatively low beam energy also works very well for studies of the B III quartets. The possible disadvantage with the lower beam energy is the larger contribution from the spectra of B I and B II, of which particularly the latter is complicated and line rich in comparison with the spectra of B III, B IV, and B V which dominate the spectra at the higher beam energies. However, this disadvantage is amply compensated by the fact that we obtain many reference lines in our beam-foil spectra which facilitate the wavelength determination.

The experimental technique for recording spectra and lifetimes have been described earlier.[10] The procedures for the data analyses of line spectra and decay curves have also been discussed.[2,11] The results presented here were obtained either with a Minuteman 310-NIV (1-m normal-incidence) vuv monochromator equipped with an EMR 541F-08-18 photomultiplier with a LiF window or with a Heath EUE 700 monochromator. For the latter we used an EMI 9789 QA photomultiplier for the 2000–5000-Å region and a Hamamatsu R 943-02 IR photomultiplier for

the 5000–7000-Å region. The lines between 1100 and 2000 Å measured with the Minuteman monochromator were recorded in the first, second, and third order. The wavelength uncertainties were between 0.1 and 0.5 Å.

III. RESULTS AND DISCUSSION

In Table I we report our experimental data for transition wavelengths and lifetimes. The wavelengths were determined using accurately measured wavelengths for transitions in singly-excited B II and B III as references.[12]

The wavelength of the lowest transition in the quartet system, $1s\,2s\,2p\,^4P^o-1s\,2p^2\,^4P$ is of particular importance. In their careful theoretical study of this transition Chung *et al.*[6] found that the nonrelativistically calculated term energies would correspond to a wavelength of 1705.5 Å. However, theory also showed that the relativistic contribution to each term is quite substantial, about 1000 cm^{-1}. In the perturbation expansion of Chung *et al.*[6] the main part comes from the first terms (mass correction and Darwin term). The other relativistic terms are about 100 times smaller. When the transition energy is calculated a cancellation occurs which reduces the relativistic contribution to 129 cm^{-1} for the transition energy (this cancellation effect explains why careful nonrelativistic calculations can give fairly good results). By including the mass correction and Darwin terms, Chung *et al.*[6] obtained a transition wavelength of 1702.0 Å. Addition of mass polarization gave 1702.3 Å, and further, by including retardation, the theoretical value finally became 1701.8 Å. This was found to be in agreement with the experimental value of Martinson *et al.*,[4] 1701.4±0.5 Å. In the present work we obtained a wavelength of 1702.1±0.1 Å for the transition $1s\,2s\,2p\,^4P^o-1s\,2p^2\,^4P$. This was determined from measurements in the first, second, and third order. The new value is larger than that of Martinson *et al.*[4] The recent value of Agentoft *et al.*[7] of 1701.3±0.3 is significantly smaller than the present result—our value is almost three standard deviations away. This discrepancy might be caused by the scarcity of reliable calibration lines at higher beam energies, noted above. On the other hand, To[5] in his unpublished work reports a value of 1702.2 Å but unfortunately without including an error estimate.

While the overall agreement between our experimental value and that accurately calculated by Chung *et al.*[6] appears as quite satisfactory, there is still a deviation of 0.3 Å or 10 cm^{-1}, well above the experimental uncertainty. In trying to analyze this problem it is instructive to study another paper by Chung[13] which gives the energies of the terms $1s\,2s\,2p\,^4P^o$ and $1s\,2p^2\,^4P$ for Li I and several other members of the sequence. The calculations are similar to those in Ref. 6. For the lowest quartet of Li I a term energy of 463 046 cm^{-1} (relative to the $1s^2 2s\,^2S$ ground state) was obtained, in very good agreement with the latest experimental result 463 050±5 cm^{-1} (Ref. 2) (also discussed in Ref. 14). To obtain this theoretical value Chung used the nonrelativistic result of Bunge and Bunge[15] to give the zeroth-order contribution to the energy. However, if the nonrelativistic energy obtained by Chung were used the

TABLE I. Wavelengths and lifetimes in the quartet system of B III. Wavelengths above 2000 Å are given in air, while wavelengths below 2000 Å are given in vacuum.

Wavelength (Å)				Lifetime of upper level (ns)		
This work	Other Experiments	Theory	Assignment	This work	Other Experiments	Theory
1702.1±0.1	1701.4±0.5[a]	1701.8[c]	$1s\,2p\,3p\,^4P-1s\,2p\,4d\,^4D^o$		2.1 ±0.2[a]	2.20[c]
	1701.3±0.3[b]				2.6 ±0.2[b]	2.07[d]
					1.45±0.15[e]	
					2.20±0.15[e]	
1727.4±0.4	1726.1±0.8[b]	1728.2[c]	$1s\,2p\,3p\,^4P-1s\,2p\,4d\,^4D^o$	0.14±0.09		0.19[c]
		1735.6[d]				0.20[d]
1753.0±0.2	1753.2±1.0[b]	1754.7[c]	$1s\,2p\,3d\,^4F^o-1s\,2p\,4f\,^4F$	0.74±0.15		0.76[c]
		1756.5[d]				0.77[d]
1764.9±0.1	1765.1±0.5[b]	1765.4[c]	$1s\,2s\,3d\,^4D-1s\,2s\,4f\,^4F^o$	0.75±0.10	1.0 ±0.2[b]	0.75[c]
		1766.1[d]				0.76[d]
1979.6±0.2	1977.3±1.0[b]	1980.0[c]	$1s\,2p\,3d\,^4D^o-1s\,2p\,4f\,^4F$	0.87±0.10		0.76[c]
		1983.9[d]				0.77[d]
2381.4±0.2	2382 ±1[b]	2380.5[c]	$1s\,2s\,3p\,^4P^o-1s\,2p\,3p\,^4P$			0.52[c]
		2363.9[d]				0.53[d]
2926.0±0.5	2931 ±1[b]	2926.6[c]	$1s\,2s\,4f\,^4F^o-1s\,2p\,4f\,^4F$			0.76[c]
		2927.6[d]				0.77[d]
6126.8±0.1		6110.9[c]	$1s\,2s\,3s\,^4S-1s\,2s\,3p\,^4P^o$	18.4 ±0.5		20.6[c]
		6098.5[d]				21.8[d]

[a]Martinson *et al.* (Ref. 4).
[b]Agentoft *et al.* (Ref. 7).
[c]Chung *et al.* (Ref. 6) and Agentoft *et al.* (Ref. 7).
[d]Fairley and Laughlin (Ref. 8).
[e]Träbert *et al.* (Ref. 16). (The shorter value corresponds to the lifetime of $^4P_{1/2}$ and $^4P_{3/2}$, while the larger value is the lifetime of $^4P_{5/2}$.)

total energy would be 24 cm^{-1} higher. This number should be seen in relation to the contributions from mass polarization (-3.4 cm^{-1}) and retardation ($+2.0$ cm^{-1}) which give in total an effect of $-3.4+2.0=-1.4$ cm^{-1}. From this discussion we conclude that it is very valuable that the new calculations[6,7,13] include the relativistic contributions, but in order to make the inclusion of the small terms such as mass polarization and retardation meaningful the nonrelativistic energy has to be very accurate (at least better than 10 cm^{-1} for B III). Considering the nonrelativistic energy which Chung[13] obtained for Li I it is not obvious that this is the case for B III. In fact, their value without both mass polarization and retardation is in better agreement with our value than their final result. We conclude that this reflects that the zeroth-order term does not have a precision high enough to make the contributions from the small effects to be of real significance. However, it must be stressed that the inclusion of the relativistic effects is essential, and it is clear that the final result of Chung *et al.*[6,13] is superior to all nonrelativistic calculations. Träbert *et al.*[16] have recently measured the lifetimes of the fine-structure levels of the $1s2p\,^2P$ term (see Table I). The shorter lifetime of the $J=\frac{3}{2}$ and $J=\frac{1}{2}$ levels compared to that of the $J=\frac{5}{2}$ level reflects mainly the contribution from nonradiative decay due to quartet-doublet mixing. So far, no calculations have been performed which analyze these effects for B III.

Table I also shows that we have observed the $1s2s3s\,^4S-1s2s3p\,^4P^o$ transition at 6126.8±0.1 Å. A section of the spectrum covering this wavelength is shown in Fig. 1. The theoretical result of Chung *et al.*[6] is 6110.9 Å (in air), which thus differs 42 cm^{-1} from our experimental transition energy. We obtained a lifetime of 18.4±0.5 ns for the $1s2s3p\,^4P^o$ term to be compared with the theoretical value of Chung *et al.*[6] 20.6 ns and Fairley and Laughlin[8] 21.8 ns. It is quite probable that the slightly shorter experimental lifetime is influenced by beam divergence after the foil, which would result in an increasing loss of beam particles with the distance from the foil—an effect which would show up mainly for long lifetimes. We have analyzed such effects in detail for lifetime measurements in Cu.[17] For boron which is a much lighter element we expect the effect to be smaller,[18] but still it might be sufficient to explain the present discrepancy.

A problem in the study of the B III quartets is the comparatively low experimental accuracy for the wavelengths below 600 Å. This is a serious limitation when using closed-loop considerations to support the identifications. If we, e.g., would have needed further support in order to establish the assignment of the 6126.8 Å line, the closed loop $1s2s2p\,^4P^o-1s2s3s\,^4S-1s2s3p\,^4P^o-1s2p3p\,^4P-1s2s2p\,^4P^o$ could be considered. If we use the wavelengths of Agentoft *et al.*[7] for the $1s2s2p\,^4P^o-1s2s3s\,^4S$ and $1s2s2p\,^4P^o-1s2p3p\,^4P$ transitions and our own wavelengths for the other two multiplets, we obtain an energy difference of 20±100 cm^{-1} between the $1s2s2p\,^4P^o-1s2p3p\,^4P$ transition and the sum of the $1s2s2p\,^4P^o-1s2s3s\,^4S-1s2s3p\,^4P^o-1s2p3p\,^4P$ transition energies. Thus, the assignments form a consistent set, but the method is not entirely satisfying because of the substantial uncertainty. The latter is due to the large error, typically 70 cm^{-1}, in the determination of the short wavelengths.

For the $1s2p3p\,^4P-1s2p4d\,^4D^o$ transition we obtain a wavelength of 1727.4±0.4 Å, which is slightly closer to the theoretical value than the result of Agentoft *et al.*[7] We also report a lifetime which is in agreement with theory, although our accuracy for this short lifetime is low. For the $1s2p3d\,^4F^o-1s2p4f\,^4F$ transition we determined the wavelength 1753.0±0.2 Å in very good agreement with previous work[7] (see Fig. 2 which shows transitions between the ^4D and ^4F levels). We also report the first lifetime measurement for this transition, which gave a value in good agreement with theory. Agentoft *et al.*[7] reported two additional transitions from the $1s2p4f\,^4F$

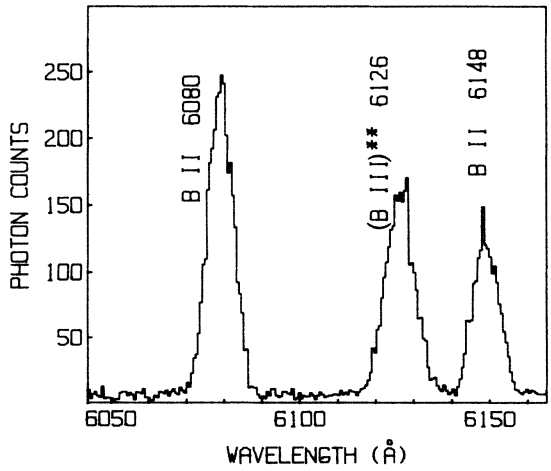

FIG. 1. Part of the beam-foil spectrum of boron recorded at 250 keV. The line at 6126 Å is the $1s2s3s\,^4S-1s2s3p\,^4P^o$ transition in B III.

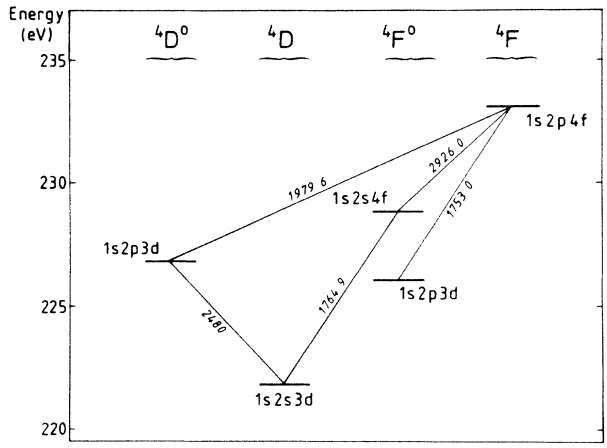

FIG. 2. A partial Grotrian diagram for the quartet system of B III. The transitions between $^4D^o$, ^4D, $^4F^o$, and ^4F levels are indicated. All wavelengths (in Å) are from this work, except for the transition $1s2s3d\,^4D-1s2p3d\,^4D^o$, 2480 Å, which is taken from Agentoft *et al.*[7] The latter paper also contains a more extensive Grotrian diagram. Note that, because of the very long lifetime of $1s2p3d\,^4F^o$, the transition from $1s2p3d\,^4F^o$ to $1s2s3d\,^4D$ has not been observed.

term, i.e., to $1s2p3d\,^4D^o$ and to $1s2s4f\,^4F^o$, for which the agreement with their theoretical values was, however, not so good. Fairley and Laughlin[8] criticized the identification of the 2931 Å line as being the $1s2s4f\,^4F^o - 1s2p4f\,^4F$ transition and found that this transition should be very weak (while the line in Fig. 3 of Ref. 7 is fairly strong). They also point out that the experimental values of Agentoft *et al.* do not result in a correctly closed loop $1s2s4f\,^4F^o - 1s2p4f\,^4F - 1s2p3d\,^4D^o - 1s2s3d\,^4D - 1s2s4f\,^4F^o$ (Fig. 2). They proposed instead that the 2931-Å line is due to a transition in B IV. In our spectra recorded with the Minuteman monochromator, we observe a line at 2931 Å, but this is the B I $2s2p^2\,^4P - 2p^3\,^4S^o$ transition in the second order. This ought not to give problems at the high beam energy used by Agentoft *et al.*, for which the contribution from B I is very small. In the spectra we recorded with the Heath monochromator, for which wavelengths below about 2000 Å are blocked, we observed a very weak line at 2926.0±0.5 Å with an intensity which is of the right order of magnitude according to the transition probabilities calculated by Fairley and Laughlin.

For the $1s2p3d\,^4D^o - 1s2p4f\,^4F$ transition we obtained 1979.6±0.2 Å, which deviates significantly from the experimental result of Agentoft *et al.*[7] but is in much better agreement with theory. Checking the loop discussed by Fairley and Laughlin[8] we find that our values make the loop to close perfectly with a "mismatch" of 0±18 cm^{-1}, while the experimental values of Agentoft *et al.* give a mismatch of 123±37 cm^{-1}. Thus we find our new values convincing.

For the decay curves of the 1979-Å line we had some convergence problems in the fitting procedure. However, requiring a cascade with a lifetime close to 2.5 ns, which is expected for the $1s2p4f\,^4F - 1s2p5g\,^4G^o$ transition, we obtained a value 0.87±0.10 ns in fairly good agreement with theory. The difficulties in the lifetime analysis might indicate a blend, which, however, could not be resolved in any of the first three spectral orders. But since the 1979-Å wavelength fits into the loop of experimental wavelengths and since it is in agreement with theory we consider the value as reliable. As mentioned above the lifetime measurement on another decay branch of the $1s2p4f\,^4F$ term (at 1753 Å) gave a lifetime of 0.74±0.15 ns in agreement with the theoretical result 0.77 ns.[7,8]

Finally, we obtained support to the assignment of the line at 2381.4±0.2 Å as due to the $1s2s3p\,^4P^o - 1s2p3p\,^4P$ transition. Berry and Subtil[19] have identified this line as the B IV transition $4s\,^1S - 5p\,^1P^o$. Fairley and Laughlin[8] seem to agree with this interpretation. From our measurements we conclude that the line present in our spectra at this wavelength can only have a small contribution from B IV. The B IV transition $4s\,^3S - 5p\,^3P^o$ at 2256 Å has in our spectrum an intensity of about 40% of the intensity of the 2381 Å line. Since the singlet transition is weaker than the triplet we think that less than 20% of the line intensity observed at 2381 Å should originate from the B IV transition. At 2.5 MeV, where the B IV fraction is about 20 times higher than at our beam energy of 250 keV,[9] the contribution from B IV at this wavelength might, however, be larger [depending on the excitation function of (B III)**].

IV. SUMMARY

We have presented experimental results on quartet transitions in B III. These have been discussed in relation to recent experimental and theoretical data. The recent calculations by Chung *et al.*[6,7,13] and Fairley and Laughlin[8] are in general very reliable. In particular, the relativistic calculations by Chung *et al.* are quite accurate. For further comparison with theory it would be very interesting if the experimental excitation energies could be related to an absolute scale as was done in Li I earlier.[2] Finally, we conclude that much progress has been made during the last two years in solving the structure of the quartets of B III and a firm basis has now been established to which further investigations can be related.

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