Lithium Spectrum in an Electric Field.

By

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After an investigation of the effect of an electric field on the spectrum lines of lithium had been made by Stark[1], Howell[2] attacked the problem by the method first employed by Lo Surdo.[3] Their results were in agreement; but, as they were confined to a certain definite electric field, the relation between the displacements of the components of the lithium lines and the intensity of the electric field was not clearly brought out. In the course of the investigations carried out by T. Takamine and the writer[4], it was shown that Lo Surdo's method was adapted to a study of this relation; and, therefore, in the present investigation, Lo Surdo's method was again employed.

Experimental Arrangement.

A photographic arrangement essentially as described in one of the papers by T. Takamine and the writer[5] was employed. Four-prism-spectrograph for the line λ 4602, and a three-prism-spectrograph for the lines λ 4132 and λ 4148 were used.

For obtaining the spectrum, the vacuum tube shown in Fig. 1 was taken. A glass bulb, in volume about 2 litres, had four side tubes. A glass tube E, containing the cathode, was inserted in the side tube A, and the anode was sealed in the side tube B. At the end of the side tube C, whose diameter was about 3 cms, a plane parallel glass plate was attached by means of sealing wax, so that a

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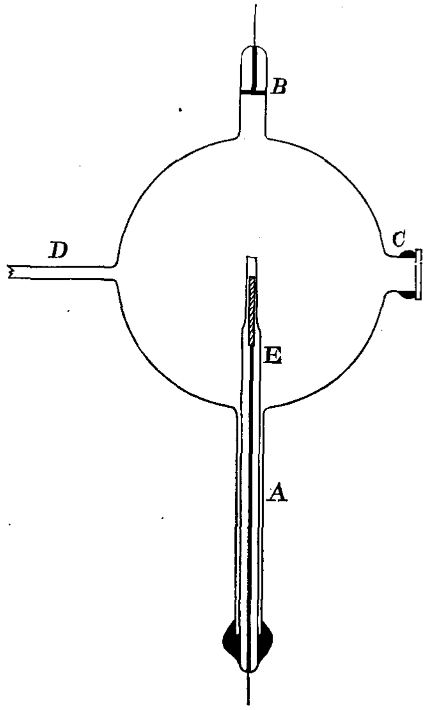
1 Elektrische Spekralanalyse chemischer Atome, (1914).
2 Astrophys. J., **44**, 87, (1916).
3 Rendiconti d. Lincei, **22**, 664, (1913).
4 Mem. Coll. Sci., Kyoto, **2**, 137, 321, 325, (1917).
5 Mem. Coll. Sci., Kyoto, **2**, 137, (1917).

Fig. 1.



fine image of the luminous glow in the Crookes dark space could be projected on the slit of the spectrograph by means of a projection-lens. For this a Cooke's chinematographic lens of two inches focal length was used. Lastly, the side tube D served to connect the bulb to a Gaede pump. The upper portion of the tube E, in which the cathode was inserted, was a capillary tube. Many capillary tubes of various diameters ranging from 2 mm. to 4 mm. were used. In the side of the capillary tube just opposite to the plane parallel plate window and at the upper part, a slit of about 1 mm. wide and 6 mm. long was cut parallel to the axis of the tube. This slit extended down to the level of the top surface of the cathode. This form of tube was first employed by J. A. Anderson.[1]

In order to obtain the lithium spectrum, metallic lithium was used as the cathode. Sometimes it was attached to an aluminium rod, and sometimes deposited at the end of an aluminium rod by electrolysis. The lithium-cathode thus prepared was of such a size that it completely filled the upper capillary portion of the tube E. When the top surface of the lithium-cathode was a very little below the level of the lower end of the slit, the end of the Crookes' dark space, whose length was in most cases of the order of the diameter

1 Astrophys. J., **46**, 104, (1917).

of the capillary tube, was well marked, and comparatively fine components of hydrogen and lithium spectra were obtained.

For the excitation of the discharge in the vacuum tube, an induction coil whose maximum spark-length was 15 cms. was employed. The current in the secondary circuit of the coil was rectified by a valve tube and a spark gap connected in series. The mean current thus rectified was of various intensities, ranging from 0.5 m.A. to 1 m.A.

The intensity of the lithium spectrum was much stronger when air was used as residual gas than when hydrogen was employed, as was observed by J. A. Anderson[1] in the case of some other metals. For this reason, the writer used air as residual gas. The hydrogen lines which were needed for the determination of the electric field were always evidenced with a tolerable intensity by the presence of moisture.

Results.

The spectrum lines of lithium examined in the present experiment were λ6103.8, λ4602.4, λ4132.4 and λ4148.2. Among these, λ6103.8 sufferred no marked influence in the electric field whose intensity was estimated to be about 30000 volt per centimeter. This result agrees well with that of Stark who states that the effect was small in the electric field of 38000 volts per centimeter.

λ4602.4. With a four-prism-spectrograph, the dispersion at this line was 11.1 Å.U. per mm. on the photographic plate. As the intensities of the parallel components were much more reduced than those of the perpendicular components, it was difficult to obtain a good impression fit for the measurement of both components on the same photographic plate. Consequently, the writer was compelled to measure the components separately on different plates. The photograph reproduced in Fig. 2, Plate 1, was used for the perpendicular components, that in Fig. 3, Plate 1, for the parallel components. For the determination of the field-strength, the separation of H_β was used, because, for this line, the proportionality between the separation and the field-strength had been established by Stark and Kirschbaum, and Wilsar on the parallel and perpendicular components respectively. For the separations of this β line the values 3.0 Å.U. per 10000 volts/cm. for p-components, and 1.4 Å.U. per 10000 volt/cm. for

1 Astrophys. J. **46**, 104, (1917).

s-components, given by Stark, were employed. The results of measurements are tabulated in Table 1, and the curve drawn in Fig. 5, Plate II, represents the manner of decomposition of the line λ 4602 in several electric fields. The mark *S represents the value observed by Stark, and the mark *H that by Howell.

Table 1, λ 4602.

p-component.

E in 10^4 volt/cm	2·40	2·13	1·89	1·56	1·44	1·24	1·02	0·85	0·65	0·46
displacement of the v-comp. in Å.U.	−2·9	−2·6	−2·5	−2·3	−2·1	−1·7	−1·5	−1·3	−1·1	−1·1
displacement of the r-comp. in Å.U.	+1·4	+1·3	+1·1	+1·0	+0·8	+0·8	+0·7	+0·6	+0·4	+0·3

s-component.

E in 10^4 volt/cm	3·61	2·87	2·48	1·78	1·28	0·82				
displacement of the v-comp. in Å.U.	−3·1	−2·7	−2·4	−2·1	−1·8	−1·5				
displacement of the r-comp. in Å.U.	+1·5	+1·3	+1·1	+0·7	+0·6	+0·4				

In the present experiment, only two components were observed both in the parallel and perpendicular components respectively. The component which corresponds to the central one observed by Stark did not make its appearance. It is not, of course, clearly decided by the present experiment whether or not there is a very weak central component. With regard to the existence of this central component, Stark also was in doubt. Further study is needed to decide this point.

As the undisplaced component did not really appear in the photograph, the position of this line was determined indirectly. Measuring the distance between the two unaffected spectrum lines which were in the neighbourhood of the line λ 4602, it was seen that the distance was the same at different hights along the lines. One of these lines was taken as a reference-line, and the distance between this line and the line λ 4602 was measured in the region where no electric effect was observed. From this distance the undisplaced position of the line λ 4602 was determined in the electric field. Such a method of determining the undisplaced position of an affected line was applied to the case of λ 4132 and λ 4148.2 also.

As is clearly seen from the curve, the displacement of the red component is proportional to the electric field both in the parallel and perpendicular component. With regard to the violet component-line, although the linear relation between its displacement and the electric force is established, yet its continuation does not pass through the origin. Moreover, the intensity of this component decreases more rapidly than that of the red component, as we pass from a stronger part of electric field to a weaker one, and at last vanishes in a field weaker than about 5000 volt per centimeter. As it is highly important to decide whether or not this component is really an isolated one of the line the writer made further minute examination. Making the condition of excitation nearly equal, three photographs were taken; first with an exposure of 40 minutes, the second with an exposure of two hours and a half, and the third with an exposure of six hours and a half. In all these photographs, the violet component made its appearance up to the field of about 5000 volt per centimeter, and no trace of its continuation was detected in the weaker field. Of course, this phenomenon was observed especially on the perpendicular component. Judging from this, it seems natural to consider that the violet component appears in an electric field stronger than 5000 volt per centimeter. The mark ⊙ drawn at the upper ends of the violet components represents roughly this critical electric field.

Generally speaking, the separation of the parallel components is somewhat greater than that of the perpendicular ones. And the displacement of the violet components is greater than that of the red ones. These facts agree well with the results obtained by Stark and Howell. But with regard to the amount of displacements of the components, the values obtained by Stark are smaller than that got by the present writer. As the intensity of the components was increased, the image of the components appeared much broadened; and consequently, the measurement was made from plates on which the image of the component appeared comparatively weak but sharp.

The spectrum line λ 4602 is of special interest. Kayser[1] regards

1 Handbuch d. Spektroskopie, Vol. II, p. 366.

this as a line easily reversed and much broadened toward the red side. Saunders[1] examined it more closely. He took a set of several photographs of this line on a film, varying exposures and amounts of vapor in the arc so as to furnish wide differences among the set. From the constancy of the distance between the points of maximum density in the image on either side of the "reversal", he concluded that this image, which was considered by Kayser as due to "reversal", is due to the presence of two neighboring lines; namely, a stronger one at λ 4603.2 much broadened toward the red, and a weaker one at λ 4601.6 broadened toward the violet side.

With regard to the broadening of a spectrum line in virtue of a great vapour or current density, Stark[2] considered that it might be accounted for as the effect of an electric field, due to the neighbouring molecules or atoms, on the spectrum lines emitted by the source. In fact the correspondency between the broadening of spectrum lines and their behavior in an electric field was found by Stark and Kirschbaum,[3] and Wendt[4] to hold good of the spectrum lines of certain elements examined. Especially on the spectrum lines of Li, similarity of the two phenomena was noted by Stark and Kirschbaum.

Now, returning to our problem, the fact that the line λ 4602 is a double line seems to be accounted for by the view mentioned above. The facts that the violet component is isolated and that the distance between the violet and the red components is always greater than ca. 1 Å.U. both in the parallel and the perpendicular component, agree well with Saunders' results that the line λ 4602 is double and the distance between the two lines is 1.6 Å.U. Again the intensity of the violet component is weaker than that of the red one both in the parallel and perpendicular component. This assymmetry of the intensities of the two components was also noted by Saunders in the case of the double lines of λ 4602. Lastly the fact observed by Saunders that both of the double line were diffused toward the outer sides seems to be accounted for by the fact that the displacements of both the components observed in the present experiment increased more and more on both sides respectively as the field-strength was increased.

1 Astrophys. J., **20**, 188, (1904).
2 Elektrische Spektralanalyse chemischer Atome, (1914).
3 Ibid.
4 Ibid.

λ4132. With a three-prism-spectrograph, the dispersion at this line was 29.5 Å.U. per mm. on the photographic plate. The photograph reproduced in Fig. 4, Plate I, represents the manner of decomposition of this line in a heterogeneous electric field. For the determination of the electric field, the separations of Hγ and Hδ were used. Using Stark's data, the field strength calculated from the separations of these two lines was found to agree fairly well, and consequently the mean value of these two were employed.

The numerical data obtained are tabulated in Table 2, and graphically represented in Fig. 6, Plate II.

Table 2, λ4132.

p-component.

E in 10^4 volt/cm.	3·37	2·78	2·21	1·78	1·38	0·99		
δλ of the v-comp. in Å.U.	−5·4	−4·1	−3·5	−2·9	−2·0	−1·4		
δλ of the middle comp. in Å.U.	−0·5	−0·3	−0·2	−0·2	−0·1	−0·1		
δλ of the r-comp. in Å.U.	+4·5	+3·8	+3·2	+2·8	+1·9	+1·4		

s-component.

E in 10^4 volt/cm.	3·76	3·19	2·55	2·09	1·84	1·54	1·24	1·13
δλ of the v-comp. in Å.U.	−5·0	−4·0	−3·3	−2·6	−2·2	−2·2	−1·7	−1·3
δλ of the middle comp. in Å.U.	−0·3	−0·2	0	0	0	0	0	0
δλ of the r-comp. in Å.U.	+4·5	+3·9	+3·2	+2·6	+2·1	+1·9	+1·7	+1·3

Both in the parallel and the perpendicular components, three components were obtained respectively. Generally speaking, the behavior of the perpendicular components is similar to that of the parallel ones. The only difference is that the displacements of the former are somewhat slighter than those of the latter. The displacements of the outer two components are proportional to the field-strength, the displacement of the violet component being a little slighter than that of the other. The slight displacement of the central component is toward the violet side. These facts were of course ascertained in the parallel and the perpendicular components respectively. As to the amount of separation, the values observed in the present experiment were somewhat different from those obtained by Stark, but they agreed fairly well with those of Howell.

λ 4148.2 This line was first discovered by Konen and Hagenbach,[1] confirmed by Saunders,[2] and is a member of a combination series of lithium. They observed many spectrum lines belonging to this series in an arc; and found all weak in comparison with the lines belonging to the other series. All were diffused toward the red side.

In the present experiment, a weak line in the neighbourhood of λ 4147 was found to displace toward the red when the field strength was increased. The result of measurement is given in Table 3, and graphically represented in Fig. 7, Plate II.

Table 3, λ 4148.2

p-component.

E in 10^4 volt/cm.	3·37	2·78	2·21
λ in Å.U.	4147·9	4147·9	4147·1

s-component.

E in 10^4 volt/cm.	3·76	3·19	2·55
λ in Å.U.	4148·0	4147·5	4147·0

Here it must be noted that the maximum error in determining the wave length was about 0.5 Å.U. As the line appeared only when a

1 Phys. Z.S., **4**, 801, (1902–1903).

2 Astrophys. J., **20**, 188, (1904).

lithium-cathode was used under various experimental conditions, this may be ascribed to lithium. Moreover, when a lithium cathode was used, a trace of a weak line appeared at λ 4636, which might probably be a member of the same series. If so, the line at λ 4147 might be considered as the same line found by Konen and Hagenbach at 4149.1 Å.U., and by Saunders at 4148.2 Å.U.

The intensity of this line diminished as the field-strength was decreased, and at last vanished in a field weaker than about 15000 volt per centimeter.

The wave length of the line increased linearly with the field-strength, both in the parallel and the perpendicular component, and surpassed 4148 Å.U. at 40000 volt per centimeter. Taking into consideration the explanation of the broadening of a spectral line given by Stark, the fact that this line appears diffused toward the red seems to be easily accounted for by the behavior of this line in an electric field.

Comparison with those of He. Corresponding lines of the diffuse series of He and Li are represented in Table 4.

Table 4.

Corresponding lines of the diffuse series of He and Li

Term number	2	3	4	5
He	5875·9	4471·7	4026·3	3819·8
Li	6103·8	4602·4	4132·4	3915·4

Similar behavior of the corresponding lines of these two elements in an electric field was noticed by Stark. In addition to the similarity mentioned by Stark, we may here add certain new points observed later. Of the line λ 4472 of He, Stark observed 3 p- and 3 s-components, of which the central ones are marked questionable. By further investigation, carried out by T. Takamine and the writer[1], 7 p- and 5 s-components were obtained, of which the central ones are, of course, questionable, as the rectification of the secondary current of the induction coil might not have been perfect.

1 Mem. Coll. Sci., Kyoto, **2**, 325, (1917).

In the case of λ 4602 of lithium, only two p- and two s-components have been hitherto clearly observed, and so many components as in the case of λ 4472 of He have not been obtained. Whether both p- and s-components of λ 4602 decompose themselves into others or not can be decided only by future investigation; but, so far as the "Grobzerlegung" is concerned, the number of components of λ 4472 may be said to be two both in p- and s-components respectively. In a former investigation on He, it was stated that the three violet components of λ 4472 were isolated both on p- and s-components. Considering this from the standpoint of "Grobzerlegung", we may say that both p- and s-components of λ 4472 have one isolated violet component respectively. The same phenomenon was observed in the case of λ 4602 of lithium, as was stated before.

For the line λ 4026 of He, Stark observed 3 p- and 3 s-components. T. Takamine and N. Kokubu[1] give 5 p- and 5 s-components. But, from the standpoint of "Grobzerlegung", it may be considered as 3 p- and 3 s-components, of which the central ones displace a little toward the violet, both in parallel and perpendicular components respectively. T. Takamine and N. Kokubu also noticed that the violet two components were isolated both in the parallel and perpendicular components, but they remarked that the appearance of the isolated components was not well defined. Moreover the displacements of the violet p- and s-components of this line seems to increase nearly proportional to the field-strength. Considering these facts, we may say that the isolation of the two violet p- and s-components of 4026 is not definitely proven.

In the case of λ 4132 of lithium, two outer p- and s-components whose displacements were proportional to the field-strength, and a central p- and s-component which displaced a little toward the violet, were found. But no trace of the isolation of the components of this line was detected in the present experiment. Disregarding the somewhat ambiguous isolation of the violet components of λ 4026 of He, λ 4132 of lithium seems to decompose similarly, so far as "Grobzerlegung" is concerned, as λ 4026 of helium, which corresponds to λ 4132 of lithium.

Isolated components. Many isolated components have been hitherto observed on the spectrum lines of He, Ne, and Li by T. Takamine

1 Mem. Coll. Sci., Kyoto, **3**, 81, (1918).

and the writer,[1] Nyquist,[2] T. Takamine and N. Kokubu[3] and the writer. As all these isolated components appeared similarly on the violet sides of the original lines in their immediate neighbourhood, the view naturally arises that they may be due to a similar cause.

The present investigation on the isolated component of 4602 of lithium shows that no plolongation of this component into the region of smaller field-strength occurs, however the intensity of the line be increased. Taking these facts into consideration, it seems natural to consider that electronic vibration corresponding to an isolated component becomes possible in a given electric field, and thence this electric vibration increases in intensity as the electric field is increased.

Lastly, concerning the relation between an isolated component and the original spectrum line, Nyquist states that they are closely related, and that it is perhaps best to treat the former as a component of the latter. Considering the fact that all isolated components hitherto found appeared similarly on the violet sides of the original spectrum lines, in their immediate neighbourhood, the suggestion given by Nyquist seems to be probable.

Summary.

1. The effect of an electric field on certain spectrum lines of lithium has been studied by Lo Surdo's method.

2. The peculiarity of lines 4602 and 4148.2 in an arc has been explained as the effect of an electric field on these lines.

3. Certain similarity between the corresponding lines of He and Li has been mentioned.

In conclusion, the writer's sincere thanks are due to Profs. T. Mizuno and M. Kimura for the interest they have taken in the research. The writer's thanks are also due to Prof. M. Fukui of Kyoto Higher Technical School for the loan of a Krüss spectrometer.

1 Mem. Coll. Sci., Kyoto, **2**, 325, (1917).
2 Phys. R., **10**. 226, (1917).
3 Mem. Coll. Sci., Kyoto, **3**, 81, (1918).

Plate I

Fig. 2.

Magnification : 5

Fig. 3.

Magnification : 4·8

Fig. 4

Magnification : 7·1

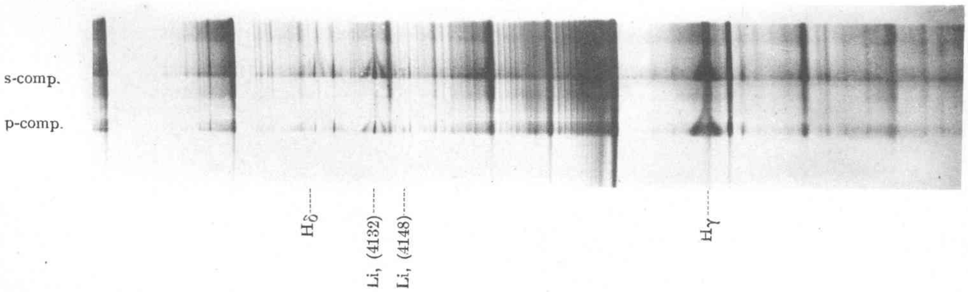


Plate II.

Fig. 5. λ: 4602 — Fig. 6. λ: 4132 — Fig. 7. λ: 4148