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ON THE EFFECT OF MAGNETIC AND  
ELECTRIC FIELDS ON THE MERCURY  
SPECTRUM

BY

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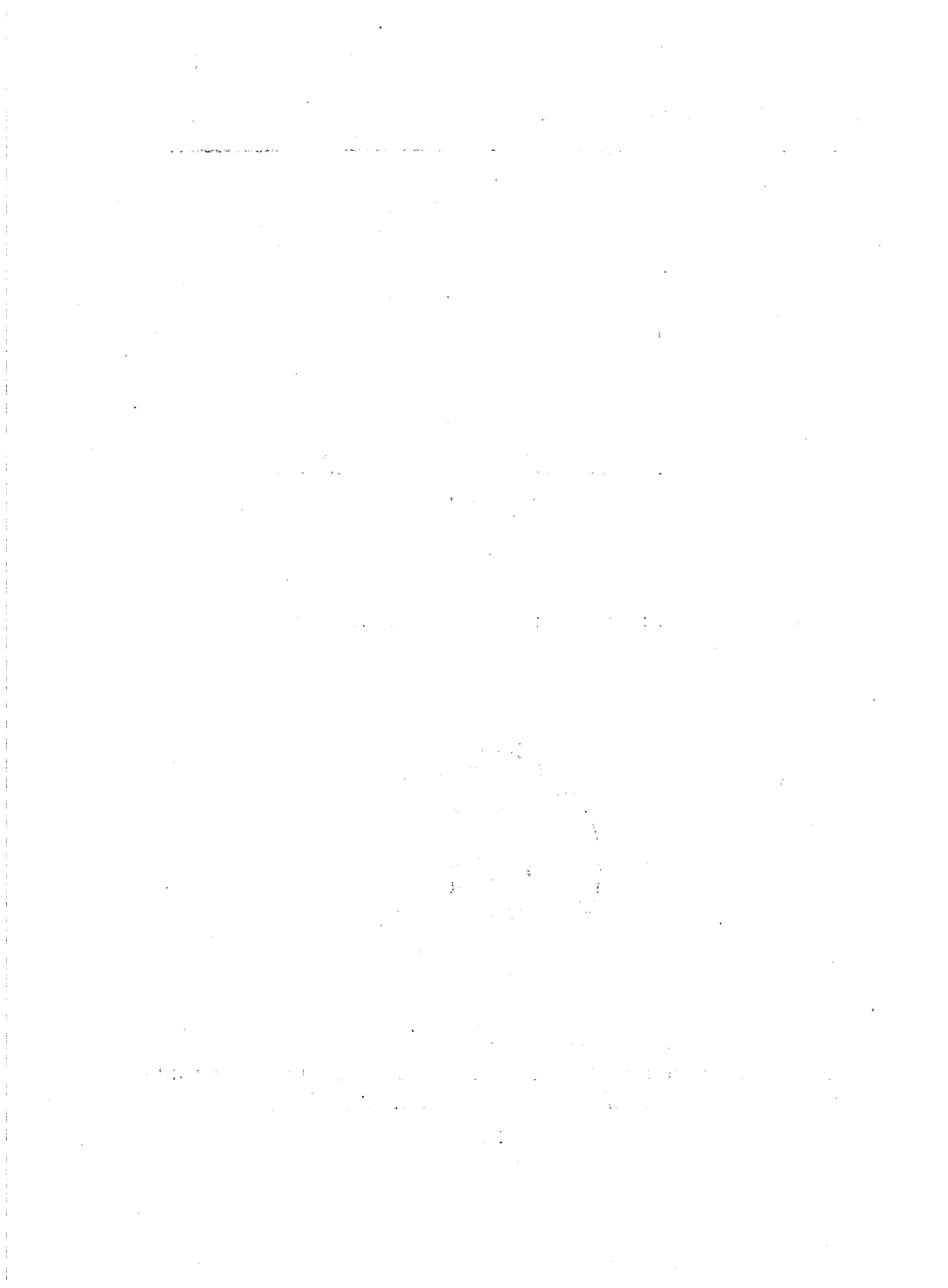
WITH TWO PLATES AND FIGURES IN THE TEXT



KØBENHAVN

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BIANCO LUNOS BOGTRYKKERI

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## § 1. Introduction.

The quantum theory of spectra which has been developed by BOHR, SOMMERFELD and others in recent years on the basis of the BOHR theory of atomic structure has created a renewed interest in investigations of the influence of magnetic and electric fields on spectral lines. Primarily this applies to the hydrogen spectrum and to spectra of the hydrogen type. During the development of the theory of these spectra, which is now fully mastered, the greatest support has been yielded by investigations of this kind.

At present, however, investigation of the more complicated spectra claims the major interest. Already the theory can show some important results, such as the explanation of the appearance of new lines under the influence of magnetic and electric fields. But the theory of these spectra is not yet of a completed character, especially as regards the problem of the origin of the complex structure of series lines, which shows itself in the appearance of doublets and triplets etc. in the spectra of many elements. The solution of these problems will claim new research, and it is to be expected that investigations of the influence of magnetic and electric fields on the spectra will give valuable information.

Not only the purely optical research has supported the theory, but information of the highest value has been rendered to the theory through the work, commenced by FRANCK and HERTZ, on the excitation of spectral lines and

ionisation by impacts of slow electrons on atoms. As is well known, some of their first results were obtained just in mercury vapour and led to a close agreement between measured values of the energy loss of the impacting electrons and the values for the energy claimed on the quantum theory for the excitation of certain prominent lines in the mercury spectrum. Later FRANCK and EINSPORN<sup>1</sup> undertook a more detailed examination by which they succeeded in discovering a far greater number of energy losses. While already in former experiments energy differences were observed corresponding to the transitions  $1S-2p_2$  and  $1S-2P$ ,<sup>2</sup> which give rise to the two most intense mercury absorption lines: 2537 Å and 1850 Å, the later measurements ascertained the existence of energy losses corresponding to the transitions  $1S-2p_1$  and  $1S-2p_3$ . The record of these two transitions is of importance, since no corresponding lines have been observed in the mercury spectrum, although special research has been made.<sup>3</sup>

Professor N. BOHR suggested to us (in April 1921) that we test experimentally whether an external magnetic field were able to render these transitions possible, so as to observe the excited lines optically. This was the beginning of the following investigation on the disturbances in the mercury spectrum caused by external fields. Through experiments in transverse magnetic fields we succeeded in getting the line  $1S-2p_1$  (2270 Å) with a considerable intensity, but no trace of the line  $1S-2p_3$  (2656 Å). Our experimental arrangement did not allow us to state whether the occurrence of the line 2270 was due to a direct action of

<sup>1</sup> J. FRANCK & E. EINSPORN, Zs. f. Phys., 2. p. 18 (1920).

<sup>2</sup> Compare, concerning the notation, table I, p. 6.

<sup>3</sup> A. SOMMERFELD, Atombau und Spektrallinien, 2. Auflage, p. XIV, Braunschweig 1921.

the magnetic field on the radiating atoms or to a secondary effect, originating in an increased action of either the electric field of the discharge or of neighbouring ions. Therefore the investigation was extended to examinations of the action of condensed discharge on the mercury spectrum and of the effect of pure magnetic and electric fields separately. The method used in the latter experiments allowed us to add to the work a detailed investigation of the Stark-effect in the mercury spectrum, of which only a few measurements of WENDT and WETZEL<sup>1</sup> had been previously published.

The first part of the investigations, with the single exception of the experiments in longitudinal magnetic fields, as well as the greater part of the Stark-effect experiments was made by all of us. Due to his return to Japan, Dr. T. TAKAMINE was unfortunately prevented from taking part in the completion of the work and the final discussion of the results.

## § 2. The mercury spectrum.

The arc spectrum of mercury (the *Hg I* spectrum) consists of a triplet and a singlet system. As well known, it is possible to represent each spectral line in the series spectra as the difference between two spectral terms. These terms are arranged in sequences, in the triplet systems denoted by  $ms$ ;  $mp_1$ ,  $mp_2$ ,  $mp_3$ ;  $md_1$ ,  $md_2$ ,  $md_3$ ;  $mb$  etc. and in the singlet system by  $mS$ ;  $mP$ ;  $mD$ ;  $mB$  etc., where  $m$  is an integer characterizing the different terms within the various sequences. The following table gives the values of the mercury terms, as found in FOWLER, Report on Series in Line Spectra, London 1922. In the following, as in

<sup>1</sup> G. WENDT & A. R. WETZEL, Ann. d. Phys., 50. p. 419 (1916).

FOWLER's book, all the wave lengths are measured in international Ångström units and in air, while the frequencies and spectral terms are calculated for vacuum.

The notation used in the table for the spectral terms is not the same as used by FOWLER, but the one adopted by SOMMERFELD in the 3rd edition of »Atombau und Spektrallinien«. This notation differs only from PASCHEN's original one in the use of whole numbers in the S-sequences instead of 1,5 S, 2,5 S etc.

Table I.  
The Hg I Spectrum.

$m =$	1	2	3	4	5	6	7	$j$	$k$
$s$	...	21831	10220	5965	3913	2765	2058	2	1
$S$	84179	20253	9777	5777	3816	...	...	1	
$p_3$	...	46536	14665	7735	4806	3280	2381	1	2
$p_2$	...	44769	14519	7714	4769	3265	2374	2	
$p_1$	...	40138	12974	7358	4570 <sup>1</sup>	3158	2307	3	
$P$	...	30113	12886	5368	4217	3027	2238	1	
$D$	...	...	12848	7118	4521	3124	2288	2	3
$d_3$	...	...	12845	7097	4503	3110	2279	2	
$d_2$	...	...	12785	7073	4491	3105	2273	3	
$d_1$	...	...	12750	7052	4479	3096	2270	4	
$b$	...	...	...	6940	4434	3073*	2254*	3, 4, 5	4
$e$	...	...	...	...	4395*	3053*	2243*	4, 5, 6	5
$f$	...	...	...	...	...	(3038)* <sup>2</sup>	(2237)* <sup>2</sup>	5, 6, 7	6
$g$	...	...	...	...	...	...	(2216)* <sup>2</sup>	6, 7, 8	7
H.T.	109738	27434	12193	6859	4390	3048	2240		

H.T. denotes »hydrogen terms« as calculated by means of the RYDBERG constant for mercury 109738.

\* Newly measured terms (error about three units).

<sup>1</sup> FOWLER gives 4605 (comp. p. 30).

<sup>2</sup> Strongly affected by electric fields, therefore very unaccurate (error more than three units). The terms are measured at the point where the corresponding lines are first seen in the field.

On the quantum theory, a spectrum of this type is assumed to be emitted by transitions between pairs among a multitude of stationary states of the atom, in which one electron moves in an orbit, the dimensions of which are large compared with the orbits of the other electrons. This orbit may be described as a plane periodic orbit, on which is superposed partly a uniform rotation in its plane, partly a precession of this plane of motion around the invariable axis of the atom. The stationary states corresponding to such motions are fixed by three quantum numbers, which may be denoted by  $n$ ,  $k$  and  $j$ . The first of these may be denoted as the principal quantum number, and refers to the periodic motion mentioned, in that sense that in the limit where the precession of the orbital plane as well as the rotation in this plane vanishes,  $n$  remains as the only quantum number describing the stationary states. This number, which in the case of the hydrogen spectrum is identical with the integer number involved in the empirical expression for the spectral terms, is in the other series spectra related to the number  $m$  which fixes the position of the terms within the series, in such a way that it increases by one unit when, within such a series, we pass from one term to the next.

The introduction of the second quantum number  $k$  is necessitated by the rotation of the orbit in its plane and, together with  $n$ ,  $k$  describes the motion in the stationary states in the limit where the precession of this plane vanishes, in which case  $k \frac{h}{2\pi}$  is equal to the angular momentum of the electron around the centre of the orbit. For the  $S$ - and  $s$ -terms  $k = 1$ , for the  $P$ - and  $p_i$ -terms  $k = 2$ , for the  $D$ - and  $d_i$ -terms  $k = 3$  etc.

The third quantum number  $j$ , the appearance of which

is connected with the precession of the orbital plane, fixes the orientation of this plane relative to the rest of the atom by the condition that the resultant angular momentum of the whole atom is equal to  $j \frac{h}{2\pi}$ . This quantum number discriminates between spectral terms which differ only by the indices which in the above notation are fixed to the letters  $p$ ,  $d$  etc.

As regards the possible transitions between the stationary states, the correspondence principle claims that for the undisturbed atom only those transitions are possible for which  $k$  increases or decreases by one unit, and  $j$  either changes by one unit or remains unaltered. These rules are fulfilled by the spectral lines under ordinary conditions, if we ascribe to the spectral terms the values for  $k$  and  $j$  which are given in the table. In the series where  $k > 3$ , several values for  $j$  are stated; this means that the energy of the atom in states where the orbital plane has different orientations with regard to the inner system, does not differ materially.

For a spectrum of the type under consideration a further complication lies on the fact that the spectral terms are naturally divided into two different classes, the so-called singlet terms and the triplet terms, which may be ascribed to stationary states for which the configuration formed by the orbits of the inner electrons is different. We shall not enter more closely on these points here for which the reader may be referred to a recent paper by Professor BOHR, which contains a general theoretical discussion of the appearance of series spectra, and where also the peculiar rules of combinations between singlet and triplet terms are discussed.<sup>1</sup>

The effect of external fields on series spectra is according

<sup>1</sup> N. BOHR, Ann. d. Phys., 71. p. 228 (1923).



to the theory directly related to the change in the motion of the outer electron as a consequence of the action of the external forces. As shown by BOHR the effect of an electric field will in the first place consist in the appearance of new combination lines, which, in case of the undisturbed atom, were excluded in consequence of the above mentioned rules governing the possible variations of the quantum numbers  $k$  and  $j$ .<sup>1</sup> Such new lines are, as is well known, for many spectra of simpler structure, as the alkali spectra, found by STARK and his collaborators in experiments on the influence of electric fields on these spectra and are in full conformity with the theoretical expectations. For the more complicated spectra of the type of the mercury spectrum no systematic investigation has been published regarding the influence of electric fields.

On the other hand, PASCHEN and BACK<sup>2</sup> have recently published an important investigation on the influence of a magnetic field on triplets in the spectra of various elements by which a number of new components appeared. The existence of these is also in conformity with the principle of correspondence, when regard is had to the anomalous Zeeman-effect shown by these lines.

As mentioned in the introduction the object of the present investigation is to throw light on the problem of

<sup>1</sup> Compare N. BOHR, On the quantum theory of line spectra, Det Kgl. Danske Vidensk. Selsk. Skrifter, Naturv. og Math. Afd., 8. Række, IV, 1. p. 36 (1918). See also H. A. KRAMERS, Intensities of spectral lines, Det Kgl. Danske Vidensk. Selsk. Skrifter, Naturv. og Math. Afd., 8. Række, III, 3, p. 287 (1919), where a quantitative treatment is given of the influence of an electric field on the motion of an electron, which describes a Keplerian orbit performing a uniform precession in its plane, and where especially a detailed discussion is given of the effect of electric fields on the fine structure of the hydrogen lines.

<sup>2</sup> F. PASCHEN & E. BACK, Physica, 1. p. 261 (1921).

the origin of spectra of complex type by investigating the effect of electric and magnetic fields, especially as regards the appearance of new lines.

### § 3. Experiments in magnetic fields and with condensed discharge.

In these primary investigations, the object of which as mentioned was to see, if the lines  $1S-2p_1$  and  $1S-2p_3$  appeared in a magnetic field, a discharge tube of a construction shown in fig. 1 was employed. The electrodes were two

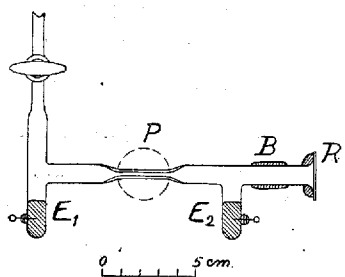


Fig. 1.

mercury cups  $E_1$  and  $E_2$  with fused-in platinum wires. The electrodes were kept warm by a small alcohol flame. To the tube, which was made of Jena glass, a quartz-window  $R$  was sealed on with sealing wax. The seal was kept cool by the moist cotton at  $B$ . The capillary

was about 2 cm long, with an internal diameter of about 2 mm. The tube was evacuated through the stop-cock, the final regulation of the pressure being made by the heating of the electrodes. It was only necessary sometimes, when the spectrum became too impure, to evacuate the discharge tube again. The capillary of the discharge tube was placed transversally between the poles of a WEISS magnet. The pole-ends of this magnet, one of which is indicated at fig. 1 by  $P$ , had a diameter of 1.8 cm. The intensity of the magnetic field was measured by a bismuth spiral and was about 15000 Gauss. The discharge tube was run by a large induction coil. To measure the potential between the two electrodes, a variable spark gap was inserted parallel

to the tube. The light from the capillary was projected, by means of two quartz-fluorite achromates from ZEISS, on the slit of a HILGER quartz spectrograph (Model E 2). To obtain the best possible definition of the spectral lines, the spectrograph was at the more intense exposures cut down to half the aperture. Both WRATTEN and WAINWRIGHT Double Instantaneous Plates and plates made by SCHUMANN'S procedure<sup>1</sup> were used. Although the latter were somewhat more sensitive below 2300 Å, they were only used very little on account of their large grain. The time of exposure was from 10 to 30 minutes. At most of our plates a mercury spectrum without magnetic field was placed immediately besides the spectrum with magnetic field. For more accurate measurements an iron- or copper-arc comparison spectrum was placed above and beneath the mercury spectrum.

When the tube was highly evacuated, and the mercury electrodes were still at low temperature, the discharge was of a spark character; but when the mercury in  $E_2$  was distilling into the capillary (i. e. the temperature of  $E_2$  about 100° and of  $E_1$  about 60°), then the discharge without magnetic field was very intensive and arc-like. With the magnetic field transversal to the capillary, the discharge was constricted and pressed against the side of the capillary by the magnetic field. To maintain the discharge through the tubes it was then necessary to force the potential very considerably. The best results were obtained with about 15000 volts across the tube.

The arc-like discharge without magnetic field showed the ordinary mercury arc spectrum (the  $HgI$  spectrum). Since the tube was run with the rather high potential of the induction coil, there appeared, in addition to the or-

<sup>1</sup> V. SCHUMANN, Ann. d. Phys., 5, p. 349 (1901).

dinary arc lines, some of the lines which are first excited in electric fields. Thus some weak lines of the type  $2p_i - mb$  were seen, corresponding to a variation in  $k$  of 2. Further several strong non-series lines were present, probably lines belonging to the still unanalyzed spark spectrum of mercury (the *HgII* spectrum).

In the magnetic field on the other hand, numerous new lines appeared in the spectrum. Besides the *HgI* spectrum and the lines assigned to the *HgII* spectrum, which were intense, a very great number of new lines was observed. It is a probable assumption, that these last lines belong to the *HgIII* spectrum (the super spark spectrum of mercury). It is to be expected that this spectrum is extremely complicated. It is worth noting that these lines were seen particularly strong in the constricted part of the discharge.

In this constricted discharge the line  $1S - 2p_1$  (2270 Å) from the *HgI* spectrum was easily excited. With a proper vapour pressure in the discharge tube, and a potential of about 15000 volts, the line was fairly intense. One of the best records is reproduced in fig. 2 (plate I). In the figure, two spectra are seen, the upper is without field, the lower with a transverse magnetic field of about 15000 Gauss. Most of the lines are seen in both cases; the numerous lines of the *HgIII* spectrum are too weak in this exposure to be seen in the reproduction. The marked line is  $1S - 2p_1$  and is only seen in the field-exposure. A determination of the wave length of the line, both by means of known mercury lines and compared with an iron spectrum rendered the wave length  $\lambda = 2269.9 \pm 0.1$  Å. From the very accurately known spectral terms  $1S$  and  $2p_1$  the calculated value of  $1S - 2p_1$  is  $\lambda = 2269.97 \pm 0.15$  Å. That the line is not due to some impurity seems to be beyond doubt, especi-

ally since in many of our plates, made under slightly different conditions, the impurity lines are clearly recognized. There is of course always the possibility that the observed line is a mercury spark line, but the chances are small and in our photographs the 2270 seems, to a certain degree, to behave independently of the spark lines.

The line  $1S-2p_3$  is situated very near to the strong arc line 2655.13 Å. Our plates show that  $1S-2p_3$  can not be present with as great an intensity as  $1S-2p_1$ ; with the spectrograph used, it is impossible to decide if it is present with small intensity.

In this connection it is to be borne in mind that the lines in question must be expected to come out fairly intense, if there exists but a small probability for the corresponding transitions. In fact, as no spontaneous transitions from the  $2p_1$ - and  $2p_3$ -states to states of lower energy are possible, we must expect an accumulation of atoms in these meta-stable states in mercury vapour, through which a discharge is passing. Just this circumstance might be expected to make the lines in question a rather delicate means of testing the possible effect of magnetic or electric fields in producing such a probability.

The presence of the magnetic field must, however, be expected to influence the radiation of the atom, not only by the direct action of the magnetic forces, but by effects of a more indirect character. First, the higher potential necessary to force the discharge through the magnetic field, will tend essentially to increase the electric field present in the capillary, and next, the constriction of the discharge against the side of the capillary will cause an enlarged influence on the radiating atom of the forces from neighbouring ions which carry the discharge.

In order to know something about these secondary effects of the magnetic field, a helium discharge tube was arranged in a similar way between the poles of the magnet. The discharge was pressed in exactly the same manner against the side of the capillary, and the spectrum of the constricted part of the discharge showed, besides the ordinary helium spectrum, several of the new series observed by KOCH<sup>1</sup>, LIEBERT<sup>2</sup> and others in electric fields. These series ( $2S-mD$ ,  $2s-md$ ,  $2P-mP$  and  $2p-mp$ ) show, as is allowed in electric fields by the correspondence principle, a variation in  $k$  of 0 and 2. In our helium spectra the series were followed further than by LIEBERT, e. g. the  $2p-mp$  series to the 12th member. Contrary to LIEBERT, whose source of light was faint, and who accordingly had to expose several hours, our plates were only exposed about 30 minutes.

The object of these investigations was the examination of the mercury spectrum in a pure magnetic field. By the arrangement adopted we did not succeed, in so far as we got an indirect action of the magnetic field, but this action did produce the line  $1S-2p_1$ . This action must be of a complex character. To study the problem somewhat more closely we then tried the effect of electric fields on the mercury spectrum; this will be described in § 4. The investigation of the effect of a pure magnetic field was accomplished after several failures by means of the mercury lamp shown in fig. 3. The apparatus, which is made of fused silica, is arranged between the two poles of a large HARTMANN and BRAUN magnet, in such a way that a strong magnetic field is produced longitudinal to a part of the

<sup>1</sup> J. KOCH, Ann. d. Phys., 48. p. 98 (1915).

<sup>2</sup> G. LIEBERT, Ann. d. Phys., 56. p. 589 (1918).

discharge tube. The advantage of the longitudinal field is that there is no possibility for a constriction of the discharge as in the transversal arrangement. The two electrodes are introduced at *E* through the glass tubes *G*, which again are sealed with sealing wax to the quartz tube *Q*. The water jackets *K* keep the sealings cool. The two mercury cups *C* and the free part of the tube between the poles were heated by small gas flames to keep the vapour pressure sufficiently high. The discharge tube was driven

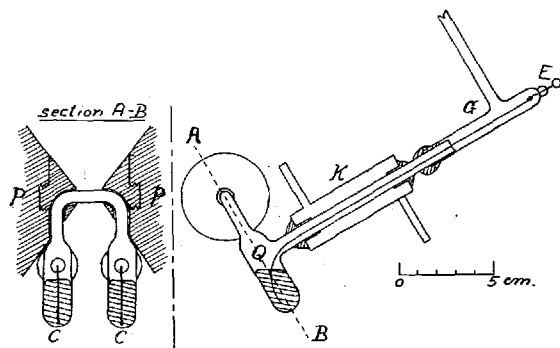


Fig. 3.

by a medium sized induction coil. The magnetic field was measured by a bismuth spiral and found to be about 19000 Gauss. A HILGER quartz spectrograph (Model E 2) was used, and in about 90 min. a very intense mercury spectrum was obtained.

Under these conditions it was found that the line  $1S-2p_1$  did not appear with an intensity the least comparable to that with which it appeared in the transverse magnetic field. The decision as to whether  $1S-2p_1$  was on our plate or not, was made difficult, since the plate was very fully exposed. Therefore even the high members of the series  $2p_2-ms$  were present. Now there is the unfortunate

coincidence, that the wave length of the line  $2p_2-12s$  is 2269.9 Å (calculated), so that with our dispersion (10 Å = 1.8 mm) it is impossible to separate this line and  $1S-2p_1$ . On our plate we found a very weak line at 2269.9 Å, but a comparison of the intensity of this line with the other lines in the same series (especially  $2p_2-11s$  and  $2p_2-13s$ ) showed, that the  $2p_2-12s$  was a little stronger than was to be expected from the decrease of intensity along the series. We therefore concluded that the line 2269.9 Å, obtained in the pure magnetic field, was due mostly to  $2p_2-12s$  and only to a very small degree to  $1S-2p_1$ .

The effect of condensed discharge was tried in a tube of the same construction as shown in fig. 1. One or two Leyden jars (about 3000 cm) were inserted parallel to the discharge tube and a small spark gap in series with the tube. A short spark gap and high vapour pressure, i. e. too high temperature, will produce in the tube a less condensed discharge, while a low temperature gives only a very faint light. By a suitable and not too high temperature and a spark gap of 3—10 mm it was possible to get an intense condensed discharge. Since the conditions were easily kept constant for a considerable time, and the source was very intense, we made the exposures by a large HILGER quartz spectrograph (Model E 1). The maximum time of exposure was 45 minutes. The spectrum of the condensed discharge was of the same complex character as the spectrum of the constricted discharge in the transverse magnetic field. The lines of the *Hg I* spectrum were weaker, the lines of the *Hg II* and *Hg III* spectrum very strong.

The line  $1S-2p_1$  is always excited in a condensed discharge with great intensity. The line  $1S-2p_3$  is not seen.



Near this line (calc.  $\lambda = 2655.7 \pm 0.1 \text{ \AA}$ ) is seen a weak line ( $\lambda = 2655.94 \pm 0.03 \text{ \AA}$ ), but only coming in the strongest condensed discharge, while the  $1S-2p_1$  is seen with the same intensity both in less and in heavy condensed discharge. It is therefore supposed, that this line is not the desired arc line, but may have its origin in the *Hg III* spectrum.

Through our investigations of the Stark-effect (comp. p. 34) we can obtain information as regards the intensities of the electric field required to produce different new lines. From the non-appearance in the condensed discharge of several  $2p_i-mp_j$  combination lines, which appear even in weak electric fields, it is concluded that an effect of a homogeneous electric field stronger than about 1500 volt/cm is not active in the condensed discharge examined. A greater intensity of the electric field must be expected to cause the emission of a number of  $p-p$  combinations, not observed in our condensed spectra. In the condensed discharge the main action is therefore supposed to be the influence of the rapidly changing and very inhomogeneous fields from the neighbouring atoms and ions, and no regular field effect of considerable intensity is active even in the capillary.

As a result we can consequently state, that  $1S-2p_1$  is emitted in the so-called constricted and in the condensed discharge. Since the line was observed in the condensed discharge, we see that an external magnetic field is not necessary for the emission of  $1S-2p_1$ . That the line is observed in the transverse magnetic field (constricted discharge) seems accounted for by the obvious assumption, that the constricted discharge is of the same type as the condensed discharge. Certainly the  $1S-2p_1$  was present in

the longitudinal magnetic field as a faint line, but this is easily explained by considering that it is impossible to avoid totally the action of near atomic fields on the radiating atoms. This action could be described as the condensed action. It seems therefore a justifiable conclusion; that a magnetic field (of intensity as high as 19000 Gauss) can not directly give rise to the emission of  $1S-2p_1$  (and  $1S-2p_3$ ). The condensed action, however, will cause the emission of  $1S-2p_1$  and not of  $1S-2p_3$ . In full accord with this is the interesting fact that LYMAN<sup>1</sup>, in mercury spark, finds a line at  $1404.3 \text{ \AA}$ , which most probably is the  $1S-3p_1$ ,  $\lambda_{\text{vac}} = 1404.4 \text{ \AA}$  (calc.), while no line is found at the place of  $1S-3p_3$ . WOLFF<sup>2</sup> has found in an arc the  $1S-3p_2$ ,  $\lambda_{\text{vac}} = 1435.6 \text{ \AA}$ . The relative behaviour of the  $1S-3p_i$  seems then to be exactly like that of the  $1S-2p_i$ .

#### § 4. Investigations in homogeneous electric fields.

##### a. Experiments.

The investigation in pure electric fields was made by the LO SURDO method<sup>3</sup>, which could be applied to mercury in a very convenient manner. By this method the electric field in the cathode dark space is utilized. As the cathode is simply used a mercury surface in a narrow silica tube. The arrangement is shown in fig. 4. *BC* is a tube 20 cm long made of transparent fused silica with an inner diameter of 5–8 mm. At *B* the tube is sealed with sealing wax to the glass tube *AB* with the mercury anode *A* and the side tube *E* leading to the pump and a

<sup>1</sup> TH. LYMAN, Spectroscopy of the Extreme Ultraviolet, p. 118, London 1914.

<sup>2</sup> K. WOLFF, Phys. Zeitschr., 6. p. 438 (1905).

<sup>3</sup> A. LO SURDO, Lincei Rend., 22. p. 664 (1913).

helium arrangement, which is described below. At *C* the tube is sealed to a narrow barometer tube, which ends in the mercury container *D*. The mercury surface, which acts as the cathode, is at *K*. In the tube was a helium atmosphere of 1—2 mm pressure. The discharge was excited by 6000—10000 volt direct-current. The part of the discharge just over the surface *K*, including the dark space, was projected on the slit of a HILGER quartz spectrograph (Model E 2) by means of two double quartz-fluorite achromates from ZEISS. In the exposures where the polarization components of the Stark-effect were to be recorded, we made use of a quartz WOLLASTON prism (a double-image prism) with glycerine between the prisms instead of canada-balsam, which absorbs in the ultraviolet. This prism could not be placed in the parallel light between the two quartz-fluorite achromates, but had to be arranged in front of the lenses on account of their rotatory power.

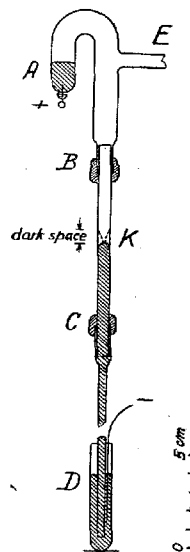


Fig. 4.

Investigations have been carried out by YOSHIDA<sup>1</sup> and in great detail by BROSE<sup>2</sup> with regard to the factors determining the distribution and maximal intensity of the electric force in the dark space. It was found that the narrower the tube the greater was the maximum intensity of the field. The pressure was of only slight influence on the intensity of the field, but the length of the dark space was very sensitive to pressure variations; a high pressure means a short dark space, a low pressure

<sup>1</sup> U. YOSHIDA, Mem. Coll. Sci. Kyoto, 3. p. 183 (1918).

<sup>2</sup> E. BROSE, Ann. d. Phys., 58. p. 731 (1919).

a long dark space. A high pressure was needed to get a great intensity of the discharge, but when the dark space became shorter than 4—5 mm, the details in the spectrograms disappeared. In our final experiments we used a tube of 6 mm diameter and the helium pressure was such that the dark space usually was about 7 mm long.

Just after the discharge was started, only the helium spectrum was seen, but in a short time (about  $\frac{1}{2}$  min.) the surface of the mercury cathode *K* assumed its stationary state, so that the partial pressure of the mercury vapour in the space just over the cathode also reached its stationary value. At the same time the discharge constricted over the cathode on account of static charges on the silica tube, and the discharge took the shape of a cone, as shown in dotted lines in fig. 4. By this constriction there was a considerable gain in intensity of light. Furthermore it was observed that the curvature of the mercury surface was changed by the discharge.

When the tube was operated under normal conditions, the pressure was controlled by the length of the dark space. This length was measured in a telescope with an eyepiece micrometer. The telescope, which was very solidly placed, served also to keep the surface of the mercury constant, undisturbed by the alterations in the pressure of the outer atmosphere. Due to the barometer-like arrangement of the cathode, this was of course very sensitive to changes in the barometer height. It is most important to keep the surface very constant, so that it is always projected at the same point of the slit of the spectrograph. The adjustment of the mercury surface was made by means of a rack and pinion mechanism operated from near the telescope. In this way, by keeping the mercury surface

and the length of dark space constant within a fraction of a millimeter, it was possible to reproduce the same conditions day after day and continue the exposure through several days.

Besides the small adjustments which changes in the height of the barometer necessitated, it was usually necessary, after about 6 hours exposure to shift the tube relative to the surface, because at the sides of the tube in the dark space a black deposit was formed, which, in addition to the screening of the light, also brought out the disturbing flashes, later to be mentioned. Since the mercury surface had to keep its position relative to the spectrograph, the tube was moved. To facilitate this movement, the tube *ABCE* was also mounted on a rack and pinion arrangement, and the connection between *E* and the pump etc. was made through a number of bent glass tubes with GAEDE normal joints. A charcoal tube was inserted near *E*, which together with a thermos bottle with liquid air, followed the movements of the discharge tube. The black deposit could, however, be removed without taking down the whole arrangement by merely heating the silica tube with a small blow pipe to an incipient red glow.

The tube was run, as mentioned above, with high-tension direct-current supplied from two 3 KW 6000 volt direct-current dynamos, which were connected in series. The cathode *K* was connected to earth, the anode *A* at a potential from 6—9000 volts. The occurrence of »flashes« in the discharge tube caused great difficulty in the beginning. At first when we only had a comparatively low resistance in series with the tube, the flashes were very strong and had a tendency to form a real arc discharge of great intensity. Usually they stopped after a few seconds,

but their intense light would spoil the exposures. The probable reason for these flashes seemed to be minute contaminations on the mercury surface or at the tube, acting as WEHNELT cathodes. Therefore it was possible by cleaning the tube and the mercury most carefully to diminish the flashing considerably. When the pressure is low, it is easy to avoid the flashes, but at the pressures where the luminosity of the tube is fairly good, the flashing begins to give trouble.

As a high-tension resistance we used at first a number of 220 volt. 10 C. P. metal filament lamps connected in series. They were found to be, on account of their characteristics, especially convenient for this purpose. With a weak current they have only a small resistance, so that the tube will receive nearly the full tension of the dynamos; but when in the case of a short circuit by a flash the current rises in the tube, then the resistance of the lamps increases and the shock is stopped. The number of lamps was regulated so that for the total tension of the dynamos they allowed only a current of about 30 milli-amperes to pass. Under this condition there was no danger to the tube on account of the flashes, but yet they were too disturbing. The best way of suppressing them was by means of a very large resistance (2—5 meg-ohm), so that the current, even by short-circuiting of the tube did not exceed 3 milliamperes. The flashes were then very short and did not affect the exposure. When the discharge was going on normally, the current was below  $\frac{1}{2}$  milliampere, and the drop of potential in the resistance was smaller than 2000 volts. This very high resistance was made of pencil lines on a ground glass plate. Though we succeeded in avoiding the flashes to some extent, they still determi-

ned a limit above which we could not force the current and therefore the intensity of light.

To get intense spectra we were therefore compelled to prolong the exposures very much which of course made them rather fatiguing, as they demanded constant attendance in order to look after the flashes and the adjustments of the mercury surface and the tube. The longest exposure

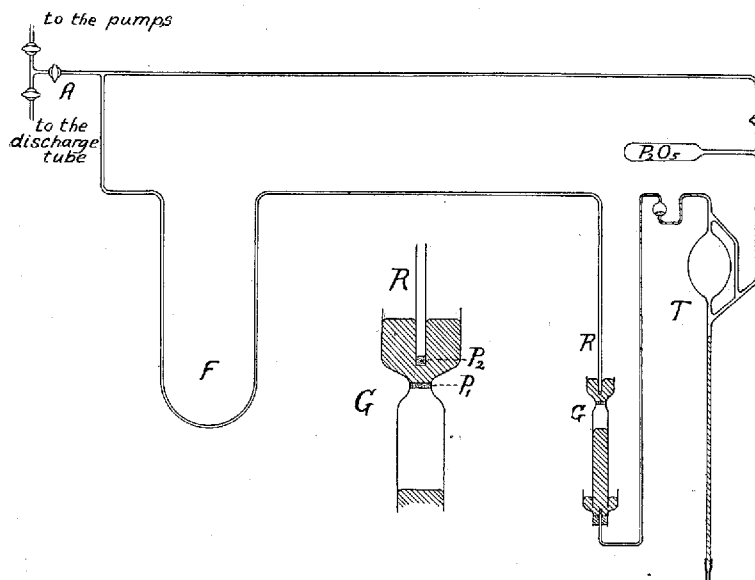


Fig. 5.

was 47 hours divided on 5 days. During the long exposures two quartz spectrographs were sometimes exposed at the same time (HILGER's model E 1 and E 2). However, it is seen from the following reproductions, that in spite of the long duration of the exposure, the definition of the lines was very satisfying. It is to be mentioned, that the temperature in the room where the experiments took place was kept nearly constant during an exposure.

The helium arrangement we used was very convenient and has been used in several other investigations, but has never been described. It affords an example of the very ingenious porous contact by K. PRYTZ<sup>1</sup>. Fig. 5 shows the arrangement schematically. The helium is kept in the gasometer *G* over mercury. The upper part of *G* is shown in greater detail. *P*<sub>1</sub> is a porous plate of the material used by STOCK<sup>2</sup>, which can be fused into glass. In the mercury above *P*<sub>1</sub> is the tube *R* which ends in a similar porous plug *P*<sub>2</sub>. The long connection from *R* to *A* is bent at *F*, so as to be flexible. When *R* is lowered so much that *P*<sub>1</sub> and *P*<sub>2</sub> touche, then the helium can diffuse from *P*<sub>1</sub> to *P*<sub>2</sub>. The great advantage of this arrangement is that it is easy by a short contact between *P*<sub>1</sub> and *P*<sub>2</sub> to take very small amounts of helium into the apparatus. After the experiment the helium is taken back to the gasometer again with the mercury pump *T*.

#### b. Results.

In figs. 6 (plate I) and 7 (plate II) are reproduced some of our records of the Stark-effect in mercury. In fig. 6 is shown a part of the mercury spectrum between 2700 Å and 2250 Å. Since we have projected the image of the vertical discharge tube on the slit of the spectograph, then every point of a spectral line will correspond to a point in the discharge tube. The lower end of a spectral line, as shown in the reproductions, corresponds to points in the dark space near the mercury surface, while the other end of the lines correspond to points in the negative glow, i. e. a little higher than the end of the dark space. The intensity

<sup>1</sup> K. PRYTZ, Ann. d. Phys., 18. p. 617 (1905).

<sup>2</sup> A. STOCK, Chem. Ztg. (1908).



of the electric field will be a maximum very near the mercury surface, and here the spectral lines will also be most affected. The electric field in the dark space decreases gradually by increasing the distance from the cathode, and when the negative glow is reached, the intensity of the field is very small, and accordingly the spectrum is here of a normal appearance. The advantage of the *LO SURDO* method is that a spectrum is thus obtained in which we have the spectral lines, both as they are emitted normally and in all strengths of the field up to the maximum field. It is then very easy to follow the development of the Stark-effect with increasing field. The maximum field in fig. 6 was about 35000 volt/cm. Most of the spectral lines seen on the reproductions are lines which are excited by transitions from large orbits to one of the three  $2p_1$ -,  $2p_2$ - and  $2p_3$ -orbits. The lines may then be represented by the formula  $2p_i - mq$ , where  $i = 1, 2, 3$  and  $mq$  is written for  $ms$ ,  $mp_i$ ,  $md_j$ ,  $mb$ , etc.

The exposures revealed a number of facts which allow of an immediate interpretation on the basis of the theory. According to the theory the effect on the lines is directly related to the change of the orbit of the outer electron under the influence of the electric forces. Now the character and magnitude of this change depends in the first place on the deviation of the orbit from a simple Keplerian orbit. In fact, if the orbit of the outer electron as in hydrogen were of the latter periodic type, the deformation produced by the force would so to speak accumulate from one revolution to the next, resulting, even for small intensity of the force, in a considerable change in the shape and orientation of the orbit. If on the other hand, the orbit under the influence of the inner electrons undergoes rapid varia-

tions in orientation, the effect of the external forces will only be allowed to accumulate within time intervals of the same order of magnitude as the period of these variations. We shall therefore expect that the effect of the electric field on a spectral line will be smaller the larger the difference between the spectral terms under consideration and the hydrogen terms with the same principal quantum numbers. In fact, this difference gives a measure for the frequency with which these variations in the orientation of the outer orbit take place.<sup>1</sup>

Therefore in our exposures we do not observe a Stark-effect of the first lines in the different series, and in the sharp series no influence is observed even in the higher members (e. g.  $m = 10$ ).

On the contrary in fig. 6 it is seen, that the diffuse series from  $m = 5$  exhibit a distinct Stark-effect, increasing by increasing term number. In fig. 6 are seen the three diffuse series:  $2p_1-md_j$ ,  $2p_2-md_j$  and  $2p_3-md_j$ . These three series only differ in that the series electron jumps from the same orbits ( $md$ ) to the three different  $2p$ -orbits and since these latter orbits are unaffected by the field, we can expect that the magnitude of the Stark-effect will be the same in the three series. In our measurements the shift of, for instance, the spectral line  $2p_i-mq$  in the field will only originate in the alteration of the term  $mq$ . Further it is seen in fig. 6 and better in fig. 7, that near each of the diffuse lines is a number of new lines appearing in the field.

<sup>1</sup> These considerations, which already are to be found in BOHR's paper on the effect of electric and magnetic field, Phil. Mag., 27, p. 506 (1914), (see also Phil. Mag., 30, p. 394 (1915)) have received general confirmation through the later extended experimental investigations by STARK and others on the effect of electric fields on series spectra.

In fig. 7 is shown on a larger scale the series  $2p_1-md$  as obtained through the double-image prism. The upper spectrum consists of the normal components, the lower of the parallel components (vibrations resp. normal and parallel to the electric force). In order to explain fig. 7, most of this figure is shown schematically in fig. 8.

Since the experimental arrangement did not allow us to separate the different  $d$ -combinations ( $d_1$ ,  $d_2$ ,  $d_3$  and  $D$ ) in the higher members of the series (when  $m > 5$ ), the diffuse triplets appear only as one line, e. g.  $2p_1-7d$ . For smaller  $m$  the different components are separated, and in figs. 7 and 8 are seen the  $2p_2-4q'$ ,  $q' = d_2, d_3$  and  $D$ .<sup>1</sup>

None of these latter lines or the other  $2p_2$ -combinations and the four  $2p_1-ms$  sharp series lines are shifted by the field. Near  $2p_2-4d_i$  two lines are seen in the field, that is the  $2p_2-4p_1$  and  $2p_2-4b$ . As the correspondence principle prescribes, because they correspond to transitions, where  $k$  changes resp. 0 and 2, their emission is only possible in the electric field of the dark space. The line  $2p_2-4p_1$  is only vibrating normal to the field, while for the  $2p_2-4b$  the parallel component is the stronger. The rules determining the polarization will be discussed later in the paper.

It is of interest to follow in figs. 7 and 8 the character of the Stark-effect with increasing term number in the series  $2p_1-md$ . The first line of this series seen in the figures is the  $2p_1-6d$ . This line is only a little displaced, but grouping around the line are seen several new lines appearing in the field. To the right of  $2p_1-6d$  is found the line  $2p_1-6p_1$ . It appears already in the upper end of the dark space, where the electric force is small, and by increasing field the line becomes more intense and shifts

<sup>1</sup> As far as our results go, only such  $p-d$ -combinations occur in the electric field as are already present in the undisturbed spectrum.

towards red. Still farther away is seen the line  $2p_1-6p_2$ , and it is to be noted that for the emission of this line a much more intense field is needed, and that the displacement of the line is smaller than that of  $2p_1-6p_1$ . That the observed lines really are these combination lines, is proved by a measurement of the wave lengths to which the lines converge in decreasing fields. From the series diagram the terms  $6p_1$  and  $6p_2$  are known, and the calculation of the wave length gives a full agreement between observations and calculations. No terms were known for the higher members in the series, but the lines were easily recognized from their behaviour in the field. Between the  $2p_1-6d$  and  $2p_1-6p_2$  are seen some non-affected lines, which do not belong to the *Hg I*, but probably to the *Hg II* spectrum.

On the more refrangible side of  $2p_1-6d$  is found first the combination  $2p_1-6b$ , which is already excited in a weak field. By greater intensities of the field two more lines are seen, which we will denote by  $2p_1-6e$  and  $2p_1-6f$ . While the lines  $2p_1-6b$  and  $2p_1-6e$  exhibit almost no shift in the field, the  $2p_1-6f$  is shifted towards violet.

Near the next line  $2p_1-7d$  are again seen on the long wave length side the lines  $2p_1-7p_1$  and  $2p_1-7p_2$  and on the short wave length side the lines  $2p_1-7b$ ,  $2p_1-7e$ ,  $2p_1-7f$  and one more line called  $2p_1-7g$ . All the terms  $7p_2$ ,  $7p_1$ ,  $7d$  and  $7b$  show greater displacements than the corresponding 6-terms, but in their appearance in the field the same features are recognized in the 7- as in the 6-combinations.

In the combination  $2p_1-8d$  is observed a line which is not affected by the field and therefore traverses the Stark-effect complex of  $2p_1-8d$ . From our plates by greater dispersion in condensed discharge it was seen that this

line was a spark line, situated  $0.1 \text{ \AA}$  from the  $2p_1-8d$ , and accordingly screening this line by smaller dispersion. Nevertheless the greater part of the Stark-effect is recorded. First the two  $2p_1-8p_2$ ,  $2p_1-8p_1$ , then  $2p_1-8d$  and  $2p_1-8b$  both strongly shifted towards red. The line  $2p_1-8e$  is hidden, while the  $2p_1-8f$  and  $2p_1-8g$  and the new combination  $2p_1-8h$  are seen. The  $8f$ - and  $8g$ -terms are shifted less to the violet than the 7-terms and in the higher members  $m = 9$  and  $10$  this movement of all the components towards the red and the appearance of new combinations is continued. Thus we observe for  $m = 9$  a new line  $2p_1-9i$  and for  $m = 10$ , besides the  $2p_1-10i$  also the  $2p_1-10j$ .

Little can be said about the convergence wave lengths of the new lines, since all the lines which come into the field are very weak near the end, and therefore difficult to follow, and besides that, most of the lines make their first appearance in a field which is strong enough to have already given the lines a considerable displacement. At the lower members ( $m = 4, 5, 6$  and  $7$ ) some measurements of the undisturbed position have been made, the results of which have been included in the table I. The terms have been determined in such a way that the frequency of the uppermost end of a line was measured relative to a known line, usually a  $p-b$  or a  $p-p$  combination; in this way the distance between two terms in a vertical column in the table I was obtained. The new terms are therefore only measured relative to terms in the same column. These measurements are of course not very accurate, but are only given to show that the origin of the new lines is most probably transitions to the three  $2p_i$ -orbits from orbits, which in an undisturbed atom will be near the hydrogen orbits.

The detailed measurements of the plate, of which fig. 7 is only a part, are given in the table II. Besides the  $2p_1$ -series, just discussed, the  $2p_2$ - and  $2p_3$ -series have been measured.

The numbers in the table represent the difference between the mercury terms<sup>1</sup> and the corresponding hydrogen terms in the usual unit of frequency ( $cm^{-1}$ ). This difference affords a very convenient way of measuring and describing the Stark-effect. In the second column are given these differences for the ordinary undisturbed mercury spectrum, as they can be calculated from table I. From the measurements of the displacement of the lines in an electric field we can calculate the values of the corresponding "displaced" terms. In the last six columns of table II are given the difference between these disturbed terms and the hydrogen terms as derived respectively from measurements of the  $2p_1$ -,  $2p_2$ - and  $2p_3$ -combinations in the maximum field, i. e. 20000 volt/cm. The number in parentheses is the approximate intensity at maximum field.

In fig. 9 the result of the measurement is shown schematically. As in the table, the terms are given by the difference from the corresponding hydrogen terms, which in the figure are arranged on the dotted line  $H-H$ . First is given the normal situation of the terms. Because in the undisturbed atom only the  $2p_i$ -terms combine with the  $md$ -term, the other terms ( $mp_i$  and  $mb$ ) are dotted. Connected with the undisturbed terms by the inclined lines are the perturbed terms, as they are measured from both parallel and normal components of the combinations with

<sup>1</sup> When measuring our plates we have always confirmed the values of the spectral terms given by PASCHEN and FOWLER a. o. Only from the two combinations  $2p_i-5p_1$  ( $i = 1$  and  $2$ ) do we find, that the term  $5p_1$  must have the value 4570 instead of 4605, proposed by PASCHEN.

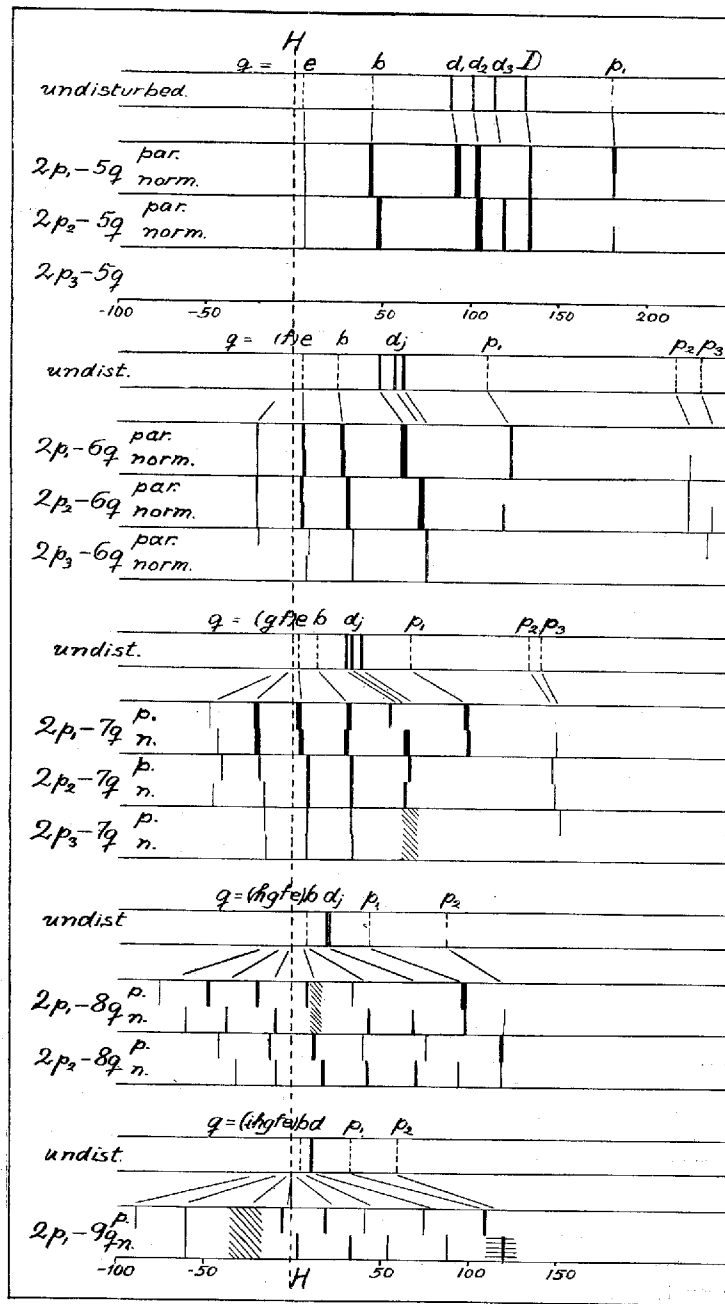


Fig. 9.

**Table II.**  
 Values of mercury terms less hydrogen terms.

<i>m</i> q	Undisturbed	In an electric field of about 20 000 volt/cm.					
		$2p_1$ -combinations		$2p_2$ -combinations		$2p_3$ -combinations	
		parallel	normal	parallel	normal	parallel	normal
$5p_3$	416	—	—	—	417 ( $\frac{1}{2}$ )	—	—
$5p_2$	379	—	—	379 (1)	379 (1)	—	—
$5p_1$	180	182 (4)	182 (3)	—	181 (2)	—	—
$5D$	131	134 (3)	132 (3)	134 (4)	134 (4)	—	—
$5d_3$	113	faint		119 (3)	119 (3)	113 (6)	113 (6)
$5d_2$	101	104 (4)	104 (4)	105 (6)	105 (6)	—	—
$5d_1$	89	92 (6)	92 (6)	—	—	—	—
$5b$	44	43 (4)	44 (4)	48 (4)	48 (4)	44 (3)	44 (3)
$5e$	5	5 (1)	6 (1)	6 (1)	6 (1)	—	—
Hydrogen term 4890							
$6p_3$	232	—	—	—	237 ( $\frac{1}{2}$ )	235 ( $\frac{1}{2}$ )	—
$6p_2$	217	—	225 (1)	224 (2)	224 ( $\frac{1}{2}$ )	—	—
$6p_1$	110	124 (3)	124 (3)	—	119 (2)	—	—
$6d_3$	62	—	—	} 73 (5)	73 (5)	76 (3)	76 (3)
$6d_2$	57	} 63 (6)	63 (6)			—	—
$6d_1$	48		—			—	—
$6b$	25	28 (4)	29 (4)	31 (4)	31 (4)	34 (2)	36 (2)
$6e$	5	5 (3)	6 (3)	4 (3)	5 (3)	9 (1)	7 (1)
$6f$	(-10?)	-21 ( $1\frac{1}{2}$ )	-20 (1)	-21 (2)	-20 (1)	-19 ( $\frac{1}{2}$ )	—
Hydrogen term 3048							
$7p_3$	141	—	—	—	—	152 ( $\frac{1}{2}$ )	—
$7p_2$	134	—	150 (1)	147 (2)	149 (1)	—	—
$7p_1$	67	99 (4)	100 (3)	—	93 (2)	—	—
$7d_3$	39	—	—	} 66 (3)	63 (3)	screened	
$7d_2$	33	} 55 ( $1\frac{1}{2}$ )	65 (4)			—	—
$7d_1$	30		—			—	—
$7b$	14	32 (4)	30 (4)	33 (3)	33 (3)	33 (2)	34 (2)
$7e$	3	4 (4)	6 (4)	9 (3)	9 (3)	8 (2)	7 (2)
$7f$	(-3?)	-20 (3)	-19 (3)	-18 (2)	-16 (2)	-16 ( $\frac{1}{2}$ )	-15 ( $\frac{1}{2}$ )
$7g$	(-24?)	-47 (1)	-43 (1)	-40 ( $\frac{1}{2}$ )	-45 ( $\frac{1}{2}$ )	—	—
Hydrogen term 2240							



Table II. Continued.

<i>m</i> q	Undisturbed	In an electric field of about 20 000 volt/cm.					
		$2p_1$ -combinations		$2p_2$ -combinations		$2p_3$ -combinations	
		parallel	normal	parallel	normal	parallel	normal
$8p_3$		—	—	—	—	—	—
$8p_2$	87	—	120 (1)	119 (3)	119 (1)	—	—
$8p_1$	44	97 (4)	98 (2)	—	94 (1)	—	—
$8d_2$	21	} —	68 (2)	76 ( $\frac{1}{2}$ )	70 (2)	—	—
$8d_1$	20						
$8b$	8	34 ( $\frac{1}{2}$ )	44 (2)	40 (1)	43 (2)	—	—
$8e$		7 (2)	screened	12 (3)	17 (3)	—	—
$8f$		—20 (3)	—9 (3)	—13 (2)	—9 (2)	—	—
$8g$		—47 (3)	—37 (2)	—42 (1)	—32 (1)	—	—
$8h$		—75 ( $\frac{1}{2}$ )	—60 (1)	too weak	—	—	—
Hydrogen term 1715							
$9p_2$	60	—	120 (2)	—	—	—	—
$9p_1$	33	110 (2)	{ very diffuse	—	—	—	—
$9d$	11	75 (1)	87 (1)	—	—	—	—
$9b$	5	42 ( $\frac{1}{2}$ )	55 (1)	—	—	—	—
$9e$		20 (2)	34 (2)	—	—	—	—
$9f$		—5 (2)	+4 (2)	—	—	—	—
$9g$		screened		—	—	—	—
$9h$		—60 ( $\frac{1}{2}$ )	—60 ( $\frac{1}{2}$ )	—	—	—	—
$9i$		—88 ( $\frac{1}{2}$ )	—	—	—	—	—
Hydrogen term 1355							

The error in the measurements is for the stronger lines about 4, for the weaker lines about 8  $\text{cm}^{-1}$ .

Dispersion: 1 mm = 110—140  $\text{cm}^{-1}$ .

the three  $2p_i$ -terms. The approximate intensity in the field is represented by the broadness of the lines. Several of the lines in 8- and 9-combinations are very weak and the errors in the measurement on that account comparatively large.

It is difficult to describe in detail all the changes occurring in the field, but attention may be drawn to some

interesting points, especially to the  $p-p$  combinations, which can be very completely discussed from our different plates. The result can best be summed up in the diagram in fig. 10.

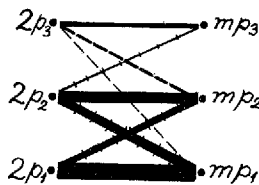


Fig. 10.

All the  $p-p$  lines are first excited in the electric field but by different intensities of the field.

Most of the observations are on combinations where  $m = 5, 6$  and  $7$ . In the figure is given approximately the relative facility with which the combinations appear. The broad lines mean emission even in weak fields, the thin lines only emission in the strongest fields. Furthermore the polarization of the lines is shown. The full lines mean partial parallel vibrations, the crossed lines a total normal and the polarization of the dotted lines has not been determined.

The details are:

$2p_1-mp_1$  appear already below 3000 volt/cm. By increasing term number the parallel component grows stronger than the normal component.

$2p_1-mp_2$  seen by 10000 volt/cm. Only normal components.

$2p_1-mp_3$  not observed.

$2p_2-mp_1$  easily excited from about 5000 volt/cm. Only normal component.

$2p_2-mp_2$  emitted by 5000 volt/cm. Particularly in the higher members more intense than  $2p_2-mp_1$ . Normal components stronger than parallel components.

$2p_2-mp_3$  faint and appear first in strong fields, when the force is 20000 volt/cm. Only normal components (a little doubtful).

$2p_3—mp_1$  very faint and only in the fields higher than 25000 volt/cm. Since these combinations are very difficult to excite we could not observe the polarisation.

$2p_3—mp_2$  faint, observed in strong fields by 15000 volt/cm.

$2p_3—mp_3$  faint, but are emitted more easily than  $2p_3—mp_2$ , by 10000 volt/cm. Only parallel components have been observed.

By the calculation of the minimum excitation voltages it has been supposed that the shift in the field is approximately proportional to the electric force. But these voltages are only to be taken as a rough estimation of the lower voltage, by which the lines are observed on our plates.

While mentioning the  $p—p$  lines we can add that of  $2P—mP$  combinations the two:  $2P—4P$  and  $2P—5P$  were observed, the first even in weak fields, while the latter appears only in stronger fields and is far more faint. No trace of series  $2P—mp_i$  was observed. Of the  $2p_i—mP$  series we have recorded the lines:  $2p_1—3P$  and  $2p_1—4P$ ;  $2p_2—3P$ ;  $2p_3—3P$  (doubtful) and  $2p_3—4P$ , while  $2p_2—4P$  is hidden by the line 2536.7. All these lines were very faint and only emitted in the strongest fields (above 25000 volt/cm). As in the  $2P—mP$  series the intensity in the  $2p_i—mP$  series decreases rapidly with increasing term number. Through the presence of these combinations the values of some of the very abnormal  $mP$  terms have been confirmed.

The  $2p_i—md$  lines, as well as the  $2p—p$  and  $2p—b$  lines, exhibit an increasing displacement with increasing term number. The displacement is for  $5d$  about  $5\text{ cm}^{-1}$ , for  $6d$  about  $15\text{ cm}^{-1}$ ,  $7d$  about  $30\text{ cm}^{-1}$ ,  $8d$  about  $50\text{ cm}^{-1}$ ,  $9d$  about  $70\text{ cm}^{-1}$  with a field of about 20000 volt/cm.

By comparing the  $mp$  terms with the  $md$ 's and the  $mb$ 's it is clearly seen that the greater the distance of a spectral term is from a hydrogen term, the smaller is the influence of the external field. Thus  $mp_3$  and  $mp_2$  are less perturbed than  $mp_1$  and these again less than the  $md$  terms, etc.

As mentioned in the introduction it is claimed by the correspondence principle that in the electric field lines are emitted corresponding to transitions in which  $k$  may change by other values than one. We know that for  $mp$ ,  $md$  and  $mb$   $k$  is respectively 2, 3 and 4. It is therefore very tempting to assign to the new observed terms  $me$ ,  $mf$ ,  $mg$ ,  $mh$ ,  $mi$ , and  $mj$  the values 5, 6, 7, 8, 9, and 10 for  $k$  resp. According to its definition, the rotational quantum number  $k$  is smaller than or equal to the principal quantum number. It is now interesting to see, that, if for the principal quantum number we take  $m$ , the rule  $k \leq m$  really determines the number of the new lines observed in the Stark-effect; for instance, the  $me$ -terms ( $k = 5$ ) are first observed, when  $m = 5$ , and when  $m = 9$  we observe all the terms up to  $9i$ , where  $k = 9$ . Even the line  $2p_1-10j$  corresponding to a jump of  $k$  from 10 to 2 was observed. How far this fixation of the values of  $k$  is allowed from a theoretical point of view is perhaps somewhat doubtful, but it seems, as if at least the greater part of the intensity of the lines originates in transitions from the terms (i. e. orbits), with which we have related the lines.

With increasing term numbers we recognize an evident evolution towards a Stark-effect of the hydrogen type, symmetrically arranged about the normal hydrogen terms. In addition, it is remarkable that while in the terms up to  $m = 7$  there is a coincidence within the experimental error in the displacements observed both in parallel and normal

components of the three  $2p_i$ -combinations, yet for  $m = 8$  and 9 there seems to be no such agreement. Probably this points to the presence of a fine structure of the Stark-effect unresolved in our experiments.

The polarization of the lines, with the exception of the  $2p_i - mp_j$ , is not very marked in the terms of  $m$  smaller than 7. But when  $m$  is greater than 7 it is seen in figs. 7 and 8 that in the  $2p_1 - mq$  series for the lines which are displaced to the red, the normal component is the stronger, while for lines which exhibit a shift to the more refrangible side the parallel component is the stronger. This polarization is more pronounced the higher the terms are in the series. The series of  $2p_2$ -combinations are apparently not polarized, while the  $2p_3$ -combinations are only observed to  $m = 7$ , where no polarization is observed. That this series is not recorded farther is accounted for by the rapid decrease in the sensibility of the ordinary photographic plate in this region ( $\lambda$  about 2250 Å).

Further, the  $2P$ -combinations have also been investigated. Our material is not so large as for the  $2p_i$ -lines. The features of the Stark-effect were nearly the same, but a number of new lines appeared around the  $2P - mD$  lines in the field. Of these the  $2P - mP$  have been discussed. The others were only of small interest, and the corresponding terms  $mB$ ,  $mE$  and  $mF$  were of nearly the same value as the terms in the  $2p_i$ -combinations.

The line  $2P - 5D$  was very little shifted in the field. At  $2P - 6D$  there was a displacement to the red and a distinct resolution of the line into two components in the field, in contrast to the  $2p_i - 6d_j$  and  $2p_i - 6D$  lines, where only a shift was observed. Both of the two components are diffuse, and their mean displacements are, with 35000 volt/cm,

32  $\text{cm}^{-1}$  and 19  $\text{cm}^{-1}$  towards the red. The deviations of the  $2p_i-6d_j$  lines are, with the same field,  $22 \pm 4 \text{ cm}^{-1}$ . An attempt was made to investigate the polarization of the two components, but on account of their small intensity it was very difficult to obtain a reliable result. It seems as if the most shifted component vibrates normal and the other parallel to the field. Also for the next member of the series  $2P-7D$  there was some evidence of a similar splitting up in the field, but this was too faint for any measurements. In the investigations of this question we have enjoyed the help of the late Dr. C. D. UDDEN.

In the very faint series  $2p_i-mD$  ( $i = 1$  and  $2$ ) no analogous splitting-up in the field is observed. It should be mentioned, however, that while the line  $2p_1-6D$  is not polarized in the field, the line  $2p_2-6D$  seems with increasing field to show an increasing polarization, and above 10000 volt/cm it seems only to vibrate normal to the field.

In the table III are summarized all the lines belonging to the  $HgI$  spectrum, which have been observed in the field besides the ordinary lines corresponding to a change in  $k$  of  $\pm 1$ .

Table III.

$m$	$2p_3$ -combinations with	$2p_2$ -combinations with	$2p_1$ -combinations with	$2P$ -comb. with
3	$P$	$P p_1$	$P p_1$	—
4	$P b$	$p_1 b$	$P p_1 b$	$PB$
5	$p_3 p_2 p_1 b e$	$p_3 p_2 p_1 b e$	$p_2 p_1 b e$	$PB$
6	$p_3 p_2 b e f$	$p_3 p_2 p_1 b e f$	$p_2 p_1 b e f$	$BE(FP)^*$
7	$(p_3 p_2)^* b e f g$	$p_2 p_1 b e f g$	$p_2 p_1 b e f g$	$BEF [= f]$
8	$(p_3 p_2)^* b e$	$p_2 p_1 b e f g h$	$p_2 p_1 b e f g h$	
9		$(p_2 p_1)^* b f g h i$	$p_2 p_1 b e f h i$	
10			$(p_2 p_1)^* b e f g i j$	

\* Not separated.

The original intention with the experiments in the electric field was to solve the question of the occurrence of the line  $1S-2p_1$  in electric fields. Only in one of our plates (fig. 6), the most intense, did we get the line  $1S-2p_1$ , very faintly in the field (too faint to be seen in the figure). As was the case in the experiments with the longitudinal magnetic field, we had to expose the plate so much that the series  $2p_2-ms$  was well developed. This series is, as our plate shows, especially strong just over the dark space in the negative glow, while it is faint in the dark space, where the electric field is. By careful examination of our plate we find that the line  $2p_2-12s$  is a little stronger than would correspond to the other lines in the series, and we can follow from this line a very faint line down through the dark space, where none of the  $2p_2-11s$  or  $2p_2-13s$  are seen. We conclude therefore, that in the full length of the dark space and even in the negative glow the line  $1S-2p_1$  is present, but very weak. The remarkable fact is, that the line is seen in such a length. If the line were ordinarily excited by the influence of the electric field, we would expect an appearance of the line like one of the many observed electrically affected lines, which are clearly seen coming in the field. The only natural explanation for the presence of the line in the Stark-effect experiment is therefore, that in the Lo Surdo tube we cannot avoid a condensed action, and that it is this action, which so easily excites the  $1S-2p_1$ , that brings this line faintly to emission. Our result is then, that homogeneous electric fields cannot produce the line  $1S-2p_1$  (and  $1S-2p_3$ ).

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## SUMMARY.

1) This paper brings a detailed investigation of the effect of electric fields (the Stark-effect) on the mercury spectrum up to a field intensity of 35000 volt/cm. The experiments were carried out by the LO SURDO method, using a mercury surface as the cathode. The effect of the electric field consists mainly in the production of new combination lines. For these their relative intensities, state of polarization and displacements in the field were examined. The general feature of the observed effects is in close agreement with the quantum theory of spectra; a more detailed theoretical discussion of our results will shortly be published by Dr. W. PAULI.

2) Further we have endeavoured to find out to what extent transitions from the two meta-stable states,  $2p_1$  and  $2p_3$ , to the normal state of the mercury atom become possible by the presence of external fields, giving rise to an emission of the corresponding lines  $1S-2p_1$  (2270 Å) and  $1S-2p_3$  (2656 Å). As in luminous mercury vapour we may expect a considerable accumulation of atoms in these meta-stable states, the appearance of the mentioned lines should afford a delicate means of examining the effect of external fields. Our results show, however, no detectable effect of homogeneous magnetic or electric fields. On the other hand the line  $1S-2p_1$  is excited in considerable intensity by condensed discharge, whereas the line  $1S-2p_3$  has not been detected at all. The action of the condensed discharge is supposed to consist of forces from neighbouring atoms and ions, constituting a rapidly changing and very inhomogeneous field.

In conclusion the authors wish to express their best thanks and indebtedness to Professor N. BOHR for his kind interest and valuable advice during the work.

Copenhagen, Universitetets Institut for teoretisk Fysik, October 1922.



HgI-spectrum

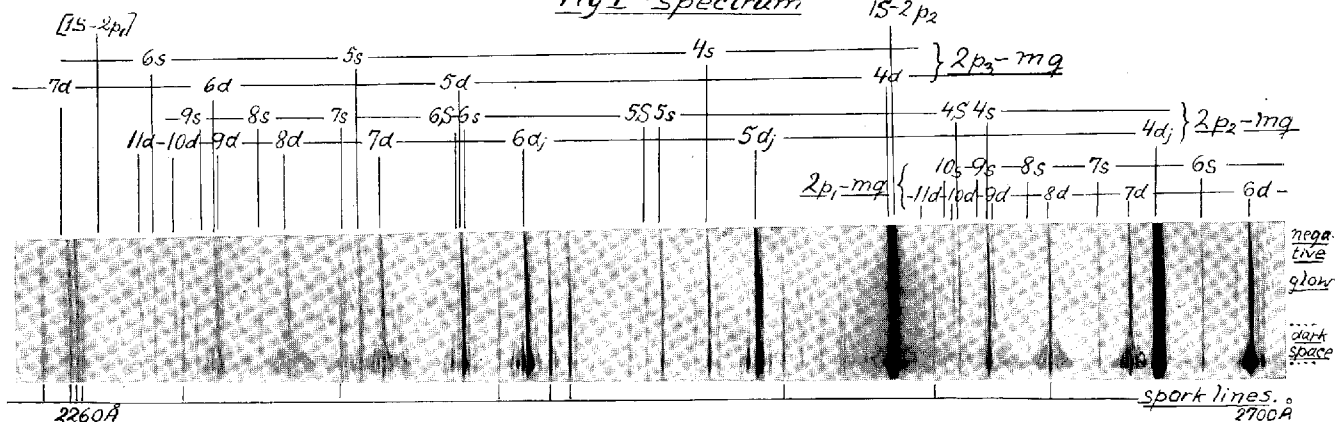


Fig. 6.

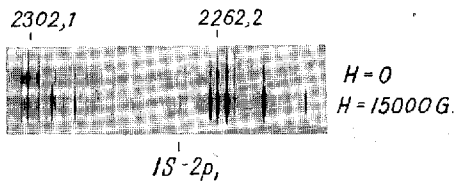


Fig. 2.



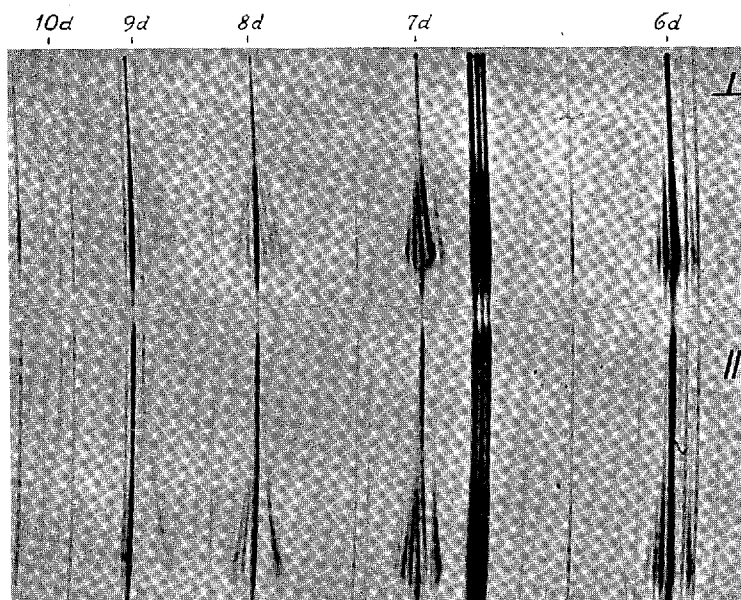


Fig. 7.

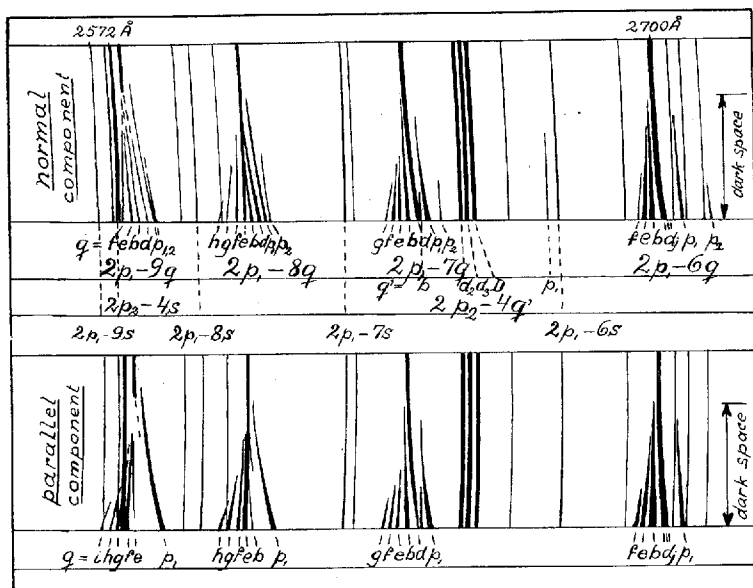


Fig. 8.

