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**Physics.** — “*On the structure of the absorption lines  $D_1$  and  $D_2$* ”.

By Dr. G. J. ELIAS. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 24, 1914).

Some time ago Prof. H. A. LORENTZ drew my attention to the results of an investigation by Miss G. v. UBISCH<sup>1)</sup>. From phenomena observed by the writer during the investigation of the polarisation state of light emitted by a sodium flame in a magnetic field after it had passed through a tube filled with absorbing sodium vapour, she infers that the wave length for which the absorption of the vapour is a maximum, depends on its temperature, and in such a way too that on rise of temperature a displacement towards the red takes place. The amount of this at 270° would be about 0.17 Å.U. with respect to the emission line. It seemed worth while to ascertain this result by direct observation. During the summer months of last year Dr. W. J. DE HAAS and myself occupied ourselves with this question.

At first we intended to use an échelon-spectroscope for these researches, observe by the aid of this the spectrum of a monochromatic source of light, and then superpose the absorption lines of sodium vapour on this. This vapour was in an iron tube, closed on both ends by plates of selected plate glass, and provided with water cooling; in the middle the tube, which contained there a vessel of metallic sodium, could be heated. Such tubes were used by R. W. WOOD for the investigation of fluorescence of sodium vapour. First a blow-flame served as monochromatic source of light, which was blown by means of air in which a very finely divided solution (mist) of soda was suspended. Afterwards the flame of a Méker-burner was preferred, burning in an atmosphere in which a mist of soda was also suspended. This was reached by placing the flame inside an iron exit tube, at the bottom of which a reservoir was attached, which was in communication with the air, and into which the soda-mist was blown by means of an aspirator. This method appeared very efficient to obtain a sodium flame of constant intensity, which is moreover easy to regulate.

The lines obtained by means of this source of light, were too broad for the investigation with the échelon-spectroscope when the intensity of the light was sufficient for the observation, the self-reversal moreover being very troublesome then. If on the other hand, the light intensity was diminished till the lines were narrow enough, the intensity was again too slight for the observation.

<sup>1)</sup> G. v. UBISCH. Inaug. Diss. Strassburg. 1911. Ann. d. Phys. 35. p. 790; 1911.

We have therefore then tried to see the phenomenon directly by means of the spectrometer, which served for provisional dispersion in the experiments with the échelon spectroscope. We were of opinion that, the dissolving power of the prism system amounting to 60.000, it must be possible to observe in this way a displacement of the above given amount. Nothing was to be detected of this, however. It is true that the at first narrow absorption line (which has originated by self-reversal in the sodium flame) widened considerably on the heating of the WOOD tube up to about half the distance of the two  $D$ -lines, but a displacement could not be perceived.

On account of Dr. DE HAAS' return to Berlin we had to stop our joint observations at this point, and I continued the research alone.

First I tried to obtain comparatively narrow emission lines, which should be intensive enough to superpose the absorption lines on them in the investigation with the échelon spectroscope by electric discharges in a heated evacuated WOOD tube with sodium. This, however, appeared impossible, the width remained considerable, and the self-reversal troublesome.

Then I took another course, and used an arclamp as source of light. To obtain monochromatic light I used the above mentioned spectrometer as monochromator, diminishing the widths of the slits so that the issuing light comprised a range of only about 0,5 Å. U., for some observations 0,4 Å. U. In this case the adjacent spectra will overlap only for a small part, as the distance between two successive orders amounts to 0,39 Å. U. The dissolving power of the échelon spectroscope, which consists of 30 plates of 14,45 m.m., amounts to 450.000<sup>1)</sup> for  $D$ -light.

The absorption lines of the arc of light, which are caused by the sodium vapour present in it, appear, observed in this way, to be double. Both for  $D_1$  and for  $D_2$  there are two maxima of absorption, which are somewhat sharper for  $D_1$  than for  $D_2$ , and the distance of which is smaller for  $D_1$  than for  $D_2$ , under for the rest the same circumstances. These distances are, however, variable. The lamp burning normally, the distance generally amounted to 0.053 Å. U. for  $D_1$ , to 0.078 Å. U. for  $D_2$ , for a point lying in the middle of the arc, when SIEMENS' S A-carbons were used. It sometimes occurred, however, for a certain pair of carbons that the distance was much smaller, down to half the value; sometimes too that it was much larger, up to almost double the said amount. When new

<sup>1)</sup> The results of the observations made about the components of the mercury lines by the aid of this échelon spectroscope, were in agreement with those of most of the other observers.

carbons are set burning, the distance is also much larger than the normal one, when the arc hisses, the reverse takes place: the lines grow fainter, and the distance grows smaller, in case of very decided hissing they can even become entirely invisible. Also in different places of the arc the distance is different, for the negative carbon the distance is much larger — about twice as large as a rule — than for the positive carbon.

Between the two absorption maxima lies also a region of absorption, which on the whole is of only little greater intensity than the maxima of absorption. Now and then it makes the impression that there are still more feeble maxima of absorption in this region; I have, however, not been able to ascertain this with perfect certainty.

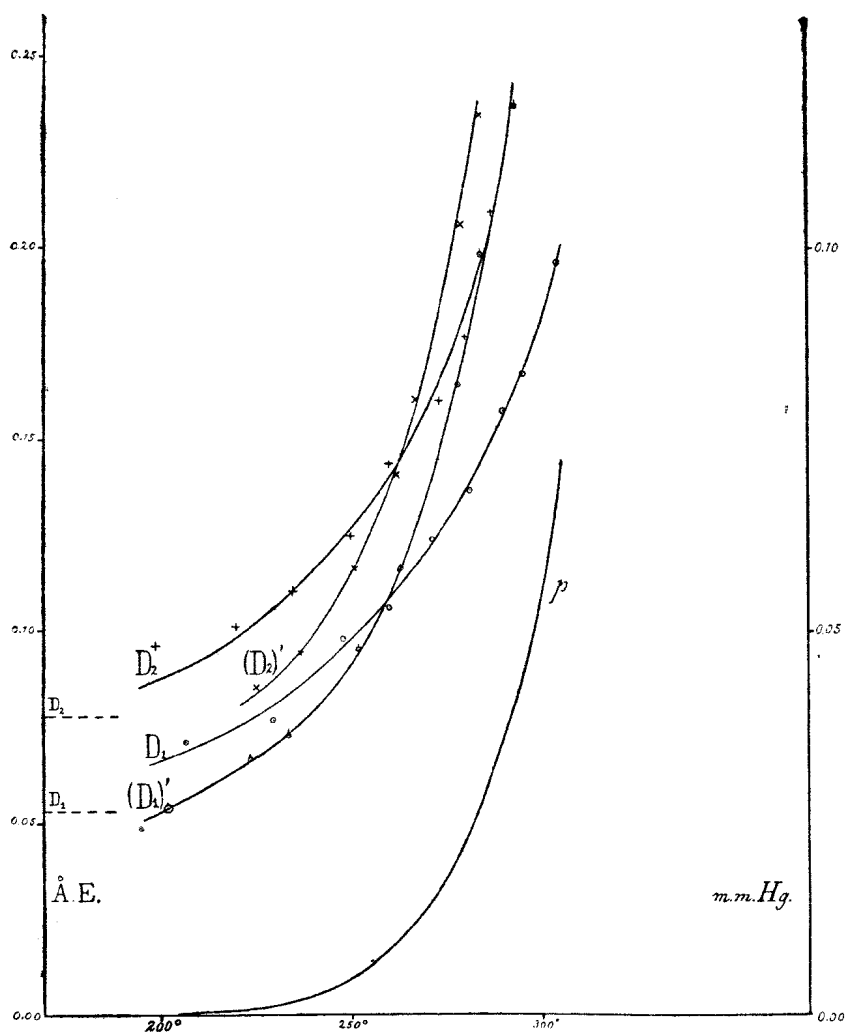
I could artificially modify the aspect of the absorption lines very considerably by blowing a little soda mist into the arc by means of a tube placed parallel to the positive carbon, which lies horizontal; in order not to disturb the equilibrium of the arc the blown in air current had to be only very weak, while the quantity of sodium could be modified by varying the concentration of the sodium solution. It then appeared that always when soda was blown into the arc the distance of the components of the two *D*-lines increased, these becoming vaguer at the same time. The greater the quantity was of the soda that was blown in, the further the components were split up, and the less sharp they became. This splitting up could even reach an amount of about  $0,3 \text{ \AA. U.}$ , in which case they were, however, very vague. The splitting was always perfectly symmetrical with respect to the original double absorption line. The maxima of absorption were — for so far as perceptible — of equal intensity, the sharpness of the two components also seeming pretty well equal. I have not undertaken further quantitative measurements about this, since it would have been impossible to determine the quantity of sodium in the arc, even when the velocity of supply was known; at most this quantity could be very roughly estimated; nor was the phenomenon perfectly constant. Similar phenomena, still less constant, however, were observed when carbons were used which were soaked in a diluted solution of soda.

When the Wood tube is placed in the way of the rays of light so that it follows the spectrometer, which cuts a small portion out of the spectrum, so e.g. between object glass and eye-glass of the reading glass, the absorption lines of the sodium vapour appear also to be double, in which the distance of the components increases as the temperature rises. At the same time, however, distinct phenomena of anomalous dispersion are perceptible, as soon as the heating of

the tube takes place in a somewhat unsymmetrical way. For this reason, and at the same time on account of the large differences of temperature which must necessarily exist in the Wood tube, at which there can be no question of saturate vapour, I did not undertake quantitative measurements.

Finally in order to be able to carry out measurements which should be liable to interpretation, I have generated the sodium vapour in a vertical glass tube, which was first provided with some pieces of sodium, then evacuated down to about 0.001 m.m. of mercury, and sealed to. This tube was uniformly heated all over its length by an electrical way, so that the temperature may be assumed to be the same at all places, and accordingly the sodium vapour to be saturate. In the enclosure there were made two apertures, through which the light fell in horizontal direction. As the glass gradually clouded somewhat at these places, I later on applied side tubes which were also electrically heated, while a wider glass tube was also used. The bore of the tube, with which I carried out my final measurements, amounted to 28 mm. For a reason to be stated later, this tube was placed between object glass and eyeglass of the reading glass. Of course the image suffered by this, but nevertheless it was possible to measure the distances of the components.

The phenomena which I observed in this way were qualitatively in perfect harmony with what I had seen by means of Wood's tube, and during the blowing in of the soda mist into the arc. On rise of temperature the distance of the components increases, while they become less sharp at the same time. Up to almost  $300^{\circ}$  the distance can be very well measured, the results of these measurements have been represented in the curves  $D_1$  and  $D_2$ . At higher temperature the width is too large to be investigated by means of the échelon spectroscope, the phenomenon becoming very vague then, so that the absorption maxima are clearly perceptible on slight magnification only, the light intensity is only little greater than between the absorption maxima than in the maxima themselves. The greatest width measured amounts to about  $0,21 \text{ \AA.U.}$ , as is visible from the figure. The resolution is always greater for  $D_2$  than for  $D_1$ ; the curves indicating the course in the two cases run perfectly parallel. On the whole the components of  $D_1$  are somewhat sharper than those of  $D_2$ ; of  $D_1$  the component lying to the side of the red is the stronger and sharper, of  $D_2$ , that which lies to the side of the violet. I think I have been able to observe with pretty great certainty that the two components of  $D_2$  are each double, so that the absorption region would be bounded here by two absorption maxima on either



side, which can be distinguished from each other with difficulty. I have not been able to observe anything similar for  $D_1$ , there the absorption maxima seemed single to me. At  $274^\circ$  I found about  $0.035 \text{ \AA.U.}$  for the distance of the two absorption maxima, of which each component of  $D_2$  consists, at  $290^\circ$  about  $0.045 \text{ \AA.U.}$  The distances of the components of  $D_2$  indicated in the figure refer to the extreme components. The region lying between the absorption maxima situated on either side is on the whole of uniform intensity, which, chiefly at the higher temperatures, is but very little greater than that of the absorption maxima. Whether there are still more faint maxima in this region, I have not been able to observe with certainty, though I now and then got the impression that such was, indeed, the case.

In the figure I have also indicated the mean amount of the width of the region of the arc absorption by means of short dotted lines. Further the curve indicated by  $p$  denotes the vapour tension of the sodium vapour for the temperature in question. The scale of the ordinates on the right hand side of the figure refers to this curve. For the determination of this curve I made use of KRÖNER's <sup>1)</sup> research on the vapour tension of alkalimetals; for this it was necessary to extrapolate the values found by KRÖNER, for which purpose I used GRÄTZ's <sup>2)</sup> formula, which is formed from DUPRÉ-HERTZ's <sup>3)</sup> formula based on that of CLAPEYRON by assuming the validity of VAN DER WAALS'S law for the vapour instead of that of BOYLE-GAY LUSSAC. GRÄTZ's formula

$$p \cdot e^{-\frac{\alpha p}{T}} = k T^{-m} e^{-\frac{n}{T}}$$

containing four constants, I had to assume four points of the vapour tension curve. I took three points for them, which had been directly determined for sodium by KRÖNER, viz.  $T=693$ ,  $p=2.00$ ;  $T=733$ ,  $p=4.20$ ;  $T=773$ ,  $p=8.64$  (temperatures in absolute scale, pressures in m.m. of mercury). I derived the fourth point, availing myself of RAMSAY and YOUNG'S rule, from KRÖNER'S determinations for potassium and found for it  $T=589$ ,  $p=0.11$ . I found from this for the constants using BRIGG'S logarithms,  $\alpha = 28.877$ ,  $\log k = 164.88$ ,  $m = 48.748$ ,  $n = 18143$ . By the aid of these constants I calculated the values of  $p$  given in the figure.

One might be inclined to ascribe the observed phenomena to anomalous dispersion; the observed dark lines would then be no absorption lines proper, but "dispersion lines". If this were actually the case, the light of the considered wave length would only have changed its direction, without having undergone absorption. As to the absorption lines in the light arc, taking the comparatively small value of the anomalous dispersion at the densities in question into consideration, the point of intersection of the rays of light coming from the arc with the plane of the spectrometer slit could never be far distant from the crater image. When this image is moved over the plane of the slit we should therefore have to see light lines in some positions instead of dark ones. As I have never observed anything like this, not when I placed the arc lamp in other positions

<sup>1)</sup> A. KRÖNER. Ann. der Phys. 40. p. 438. 1913.

<sup>2)</sup> GRÄTZ. Zeitschr. f. Math. u. Phys. 49 p. 289. 1903.

<sup>3)</sup> HERTZ Wied. Ann. 17. p. 177. 1882.

DUPRÉ. Théorie mécanique de la chaleur. p. 69. Paris 1869.

either, so that the direction of the issuing beam of light with respect to the light arc was a quite different one, I think I may conclude that the arc lines are not to be attributed to anomalous dispersion.

Nor can for analogous reasons this be the case with the lines which were observed after the light had passed through sodium vapour in a uniformly heated glass tube. Here too light lines would have to be observed at some distance from the dark ones, of which there was however, no question.

On the other hand — as I already remarked just now — when the unsymmetrically heated Wood tube was used, I saw a sharp light line by the side of the dark region, which latter became blacker then at the same time; in fact besides the absorbed light, also the anomalously dispersed light has vanished from this region.

Everything considered I am therefore of opinion that anomalous dispersion has had no influence on my final results.

I will mention here another phenomenon, which at first made its influence felt in a peculiar way. In my first experiments I had placed the glass tubes in which the sodium vapour was generated, before the entrance slit of the spectrometer, so that the whole beam of white light passed through it. The measurements which I then made of the distances of the components for different tubes, which were distinguished by the thickness of the radiated layer of vapour, were not in harmony; at the same temperature the distance of the components was found larger as the radiated layer was thicker. This peculiar phenomenon must undoubtedly be a consequence of the presence of fluorescence light, which the sodium emits under the influence of the incident white light. According to Wood's researches<sup>1)</sup> it is just the two *D*-lines which are very prominent in the fluorescence light. This light will be the stronger as the traversed layer is thicker. In this way it is explicable that the absorption spectrum can be subjected to a modification which will become greater with increasing thickness of layer.

When, however, the distance of the absorption maxima increases in consequence of the superposition of the fluorescence light over the absorption spectrum, which is greatly the case at higher temperatures (see the curves  $(D_1)'$  and  $(D_2)'$ ), it is easy to see that the maximum, resp. the maxima, of the fluorescence light must be situated between the absorption maxima so that the curve representing the intensity of the fluorescence light, exhibits a rise at the place of the absorption maxima, when we move to a point lying halfway

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<sup>1)</sup> R. W. WOOD. Phys. Opt. p. 444; 1905.



between the two absorption maxima. If the absorption maxima coincided with maxima of fluorescence, the former would either not shift their places, or they would split up. Hence we arrive at the conclusion that at temperatures above about  $260^{\circ}$  the maxima of absorption do not coincide with maxima of fluorescence, but that the latter maxima, resp. maximum, lie between the maxima of absorption.

I have indicated two curves in the figure for which the influence of the fluorescence light is visible, the curves  $(D_1)'$  and  $(D_2)'$ . They represent the distance of the components of  $D_1$  and  $D_2$  for a radiated thickness of layer of 40 m.m., in which the tube of sodium vapour was placed before the entrance slit of the spectrometer: the distance from the tube to the slit was about 10 cm., the opening of the incident beam being about 1 : 10. Under these circumstances it was also possible to observe the fluorescence light by means of a spectroscope.

If the tube with sodium vapour was placed between object glass and eye glass of the reading glass, the fluorescence can only be brought about by the light that belongs to the narrow spectral range, issuing from the spectrometer, instead of through the undivided white light. It is easy to see that the part of the fluorescence light, which in this case is already very faint, the part that finally reaches the retina, will have to be exceedingly small in comparison with the observed light; the influence of the fluorescence light will, therefore, have to be imperceptible then. I have actually convinced myself that when the tube with vapour is placed between object glass and eye glass of the reading glass the distance of the absorption maxima is independent of the thickness of layer traversed by the rays. For this purpose I compared a tube of 50 m.m. bore with the tube of 28 m.m. used for the measurements; in these two cases the distance of the components was the same at the same temperature.

I think myself justified in drawing the conclusion from all that has been observed that the distance of the absorption maxima of the sodium lines is closely connected with the density of the vapour, and that in this way that the splitting up increases with increasing density. That what has been observed is chiefly an effect of density, and not in the first place a temperature effect, is supported by the fact that the influence of the soda mist blown into the arc is for the greater part the same as that of absorbing sodium vapour of much lower temperature. The temperature at which the absorption in the arc takes place, will namely undoubtedly be much higher than that of the vapour in the glass tube. On the other hand the

phenomenon in the arc is dependent in a high degree on the quantity of soda, the temperature varying very little as long as the equilibrium in the light arc is not disturbed.

In my opinion besides the density also the temperature can have influence, though the latter will be slight. If the arc lines were exclusively dependent on the density of the vapour in the arc, the horizontal dotted lines in the figure would have to cut the curves for  $D_1$  and  $D_2$  in points for which the abscissae are equal. As this seems to be almost the case, the influence of the temperature cannot be very large.

Also with regard to the degree of the absorption — so the value of the absorption index — there can very well be difference between higher and lower temperatures; I have, however, not examined this. And at last, the absorption lines of low temperature are somewhat sharper than those in the light arc.

Returning to what Miss v. UBISCH derived from her experiments, viz. a displacement of the absorption maxima of sodium vapour on change of temperature, we may question whether this result can be brought into connection with the observations described just now.

In the experiments under consideration the main point was the absorption to which the components of the two magnetically split sodium lines (briefly called ZEEEMAN-components) were subjected in the WOOD tube filled with sodium vapour.

The measurements were made of the relative intensities of the differently polarized beams of light both normal to the lines of force of the magnetic field (transversal), and in the direction of the lines of force (longitudinal) (in the transversal observations the beams polarized parallel to and normal to the lines of force, in the longitudinal observations both the circularly polarized ones.) These beams of light were emitted by a sodium flame which was placed between the poles of a magnet; the undispersed sodium light was subjected to absorption in a WOOD tube. This tube was every time heated to a definite temperature, and the temperature being kept constant, the magnetic field was varied till the difference of the intensities of the differently polarized beams of light was a maximum; this measurement took place by rotation of a glass plate, which served as a compensator. For every temperature of the WOOD tube the field was determined, in which the difference of the intensities became a maximum. Miss v. UBISCH makes the supposition that this difference will be a maximum when one ZEEEMAN-component coincides with the maximum of absorption, and the other is not absorbed at all. By the aid of this the writer deduces that at  $270^\circ$  the displacement of the

sodium lines would amount to  $0.17 \text{ \AA.U.}$ ; in this case the difference of the intensities was therefore a maximum at a distance of the ZEEMAN-components or on an average  $0.34 \text{ \AA.U.}$

Now on closer consideration it is clear that the correct interpretation of Miss v. UBISCH's observations would be very intricate, and many more data would have to be available for it. In the first place we should have to know the correct distances and intensities of the ZEEMAN-components, before they undergo absorption in the WOOD tube; further the accurate course of the curve that denotes the connection between the intensity of the light transmitted in this tube with the wave length, should be known. The absorption maxima of sodium vapour not being sharply defined lines, much will depend on the intensity and sharpness of these maxima; this is the more obvious when it is borne in mind that the real maximum difference of intensity observed by Miss v. UBISCH, constitutes only a few percentages of the whole amount. With so small a difference we should be sooner inclined to assume a difference in absorption to that amount than as the author does, suppose that one ZEEMAN-component is not weakened at all, the other only a few percentages in the case of a thickness of layer which is at any rate pretty considerable. It is easy to imagine cases in which the absorption maxima are of equal intensity, but difference of intensity of the ZEEMAN-components is a maximum, when they lie outside the absorption maxima.

Everything considered the amount given by the author can only represent the distance of the absorption maxima as far as the order of magnitude is concerned; accordingly I do not think that the result of my observations (distance of the absorption maxima of about  $0.15 \text{ \AA.U.}$  at  $270^\circ$ ) is in contradiction with that of Miss v. UBISCH.

Besides it is possible that the temperature has not been given perfectly accurately. In this respect a WOOD tube presents more sources of errors than the uniformly heated tube which I used. Moreover the difference need not be very great, taking the very rapid increase of the resolution in the neighbourhood of  $300^\circ$  into consideration.

When seeking an explanation of the observed phenomena now that it has appeared that in the first place there is here question of a density effect, we are naturally led to look for a connection with the widening of spectrum lines in general, and with the explanation which STARK has given for it, which comes to this that this widening

would be the consequence of electrical resolutions of the spectrum lines. It is easy to understand that the greater the density of an (emitting or absorbing) gas, the more frequently it will occur that the vibrating electron systems are in the neighbourhood of electrically charged systems, and will therefore perform their vibrations under the influence of the electric field of these charged systems; hence the spectrum lines brought about by these vibrations will be the more perceptible by the side of those which arise from systems which do not vibrate in an electrical field. In this way we shall be able to obtain a great number of lines, which all being superposed, can make the impression of a broad band. It is very well possible that definite groups of these vibrations can be predominant which will give rise to the appearance of maxima of absorption (resp. emission). If we wanted to give further particulars about this, it would be necessary to enter into an examination of the mechanism of the phenomena <sup>1)</sup>.

As to the order of magnitude of the above described phenomena, it is indeed interesting to compare it with the order of magnitude of the electrical resolutions as STARK has observed them. When we assume that a vibrating system is placed in an electrical field originating from an electrical elementary charge at such a distance as the mean distance of the atoms in saturate sodium vapour of about 280° amounts to, the resolution of the *D*-lines, when taken as an electrical resolution, would at this temperature agree — as far as the order of magnitude is concerned — with the resolutions which STARK found in this part of the spectrum, always on the supposition of a linear course of the electrical resolution with the intensity of the field.

Above 260° the observed resolution increases pretty accurately with the power  $\frac{1}{3}$  of the density, the increase being slower at the lower temperatures; therefore what was observed just now about the order of magnitude of the resolution at 280° cannot possibly be of general validity, as this would require an increase not with the power  $\frac{1}{3}$ , but with the power  $\frac{2}{3}$  of the density.

I also observed the *D*-lines in the solar spectrum, which also exhibited two components each. On the whole the phenomenon was in accordance with what is observed for saturate sodium vapour of about 270°. The distance of the components was about 0.15 Å.U.;

<sup>1)</sup> Even without thinking of electrical resolutions, I pronounced the opinion already before that the "own period" of a vibrating system might vary as it was under the influence of neighbouring systems, and that widenings of spectrum lines might be the consequence of this. Cf. G. J. ELIAS, Diss. Utrecht; p. 146 et seq.

I did not however carry out accurate measurements about this. They further seemed to me slightly less sharp than those which were observed for sodium vapour of low temperature, though this difference was not very conspicuous. If the resolution were really only little dependent on the temperature and possible other factors, we might draw the conclusion from this that the density of the sodium vapour in the chromosphere of the sun is as great as that of saturated sodium vapour of about  $270^{\circ}$ .

I further made some observations on the emission lines of sodium vapour. For this purpose I used a glass discharge tube which contained some sodium, and which was heated to  $200^{\circ}$  or  $300^{\circ}$ .

It then appeared that the emission lines, both  $D_1$  and  $D_2$ , were double, and that the distance of the two light lines increased with increasing temperature. It is not impossible that self-reversal plays a part in this; it was, however, peculiar in this that chiefly for  $D_1$ , the two light lines on either side of the dark core differed in intensity, which would not have to be the case for self-reversal.

With regard to the emission lines  $D_1$  and  $D_2$ , MICHELSON<sup>1)</sup> has pronounced the opinion that they would each consist of four components, two intenser ones, and two very faint ones, the distance of the intenser ones amounting to about  $0.15 \text{ \AA.U.}$  FABRY and PÉROT<sup>2)</sup> are, however, of opinion, that reversal phenomena would play the principal part in this.

In conclusion I will still state that already a long time ago I observed for the emission lines of copper when this is in the light arc, resolutions of entirely the same order of magnitude as those which I have now described for the absorption lines  $D_1$  and  $D_2$  of the sodium, also with the aid of the échelon spectroscope. I then observed with a pretty high degree of certainty that these resolutions were greater as the density of the copper in the arc increased. I could not carry out measurements about this, however, as the amount of the resolution was very variable, and besides I had no means to determine the density of the copper in the arc.

*Haarlem, February-April 1914.*

*Physical Laboratory  
of "TEYLER'S Stichting."*

1) A. A. MICHELSON and E. W. MORLEY. Amer. J. (3) 34. p. 427; 1887. Phil. Mag. (5) 24 p. 463. 1887.

A. A. MICHELSON. Rep. Brit. Ass. 1892 p. 170. Phil. Mag. (5) 34 p. 280. 1892.

2) CH. FABRY and A. PÉROT. C. R. 130 p. 653. 1900.