Physics. — *The Structure of the Calcium Fluoride Band* λ 6087. By S. GOUDSMIT. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of February 26, 1927).

The most accurate investigation of the structure of the calcium fluoride bands is that by DANJON [1]), who observed that these bands seem to show an entirely different structure from that of most of the other bands hitherto known. He could examine band λ 6087 most accurately, because this band is more easily resolvable than the other bands from this spectrum and is more simply constructed.

On cursory examination this band has the appearance of an ordinary group of bands, the band edges of which form a regular series. DANJON was, however, of the opinion that this could not be the case. For it appears that the bands do not overlap, as in an ordinary group of bands, but that every band seems to stop at the very place where the following band begins. Further DANJON particularly pointed out that the frequencies of the lines of the whole band can be represented by a single formula, with one parameter. According to DANJON we have to do here with one band which presents remarkable intensity anomalies. From the first band edge the intensity decreases regularly, till suddenly an intense line makes its appearance, after which the intensity again slowly diminishes. This is repeated a few times, the mutual distance of the lines at the same time becoming greater.

The purpose of our investigation was to examine whether DANJON's view still appeared to be correct, if measurements were made with greater dispersion than was used by him.

The spectrum was photographed in the second and the third order of a concave grating with a radius of curvature of 6 meters and with 14438 rulings to the inch. The arrangement was that of EAGLE. In the region examined the dispersion in the second order amounted to about 12 Å per cm. and in the third order to about 8 Å per cm.

The greatest difficulty was to find a suitable source of light, and this has not been entirely overcome. The most satisfactory arrangement was an arc, the two carbons of which had a vertical position, the lower (positive) carbon having a perforation filled with calcium fluoride. Use was successfully made of a magnet in the well-known way to "blow" the arc in a definite direction, and to promote in this way the regular

[1]) A. DANJON, Diplôme d'Etudes sup. Paris (1914).

consumption of the calcium fluoride filling. The arc was operated with a direct current arc, which had to be continually regulated by the hand. Other sources gave the band to be investigated, which is one of the faintest of the spectrum, with too small intensity. The source used had, however, the very great drawback that the lines were fairly diffuse: it is to be regretted that our attempts to overcome this difficulty have not succeeded. The consequence of this was that the resolving power of the grating could not be entirely used; the limit for the resolution was defined by the diffuseness of the lines. In consequence of this the measurements in the third order have no advantages at all over those in the second, on the contrary, they required a longer time of exposure without giving better resolution.

With the times of exposure at which the band under investigation gave the best blackening, varying from 30 to 80 minutes, the neighbouring group of bands λ 6064 was already greatly over-exposed, and clearly showed reversals on most photographs.

Fig. 1 shows the intensities of the band as given by DANJON. This sketch is in conformity with his conception that the whole is one band with regular intensity anomalies. This conception finds expression in the figure: leaving the anomalies out of consideration, the intensity decreases regularly towards the tail of the band. This decrease is, however, not real; the appearance is caused by the fact that the lines towards the tail of the band lie further apart with diminishing wave-length, and that owing to this the blackening on the plate seems less. The real course of the intensity is represented by fig. 2. This is an intensity curve of one of the photographs in the second order of the grating made with a Moll-photometer [1]). Roughly a curve would be obtained about as in fig. 3. The most striking feature is that in the first apparent band the intensity seems to decrease most rapidly, in the following bands this diminution proceeds more and more slowly and at the end all the lines have even about equal intensity so that it is not possible to define there the apparent edges with certainty, as in the beginning. When observing this it should, however, be taken into consideration that in the successive bands the lines lie farther and farther apart, and in consequence of this a seemingly slower decrease of the intensity is caused. As a matter of fact the number of lines in the bands should be taken into account in this comparison.

In view of what precedes it is improbable that DANJON's view should be correct. Nor does it seem that we have to do here with a number of bands each of which stops exactly where the next begins. Probably

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1) The description of the arrangement for the application of the scale on the photogram, which was also used very successfully in this investigation, is found in KOK and ZEEMAN, These Proc. **27**, 884, 1924.

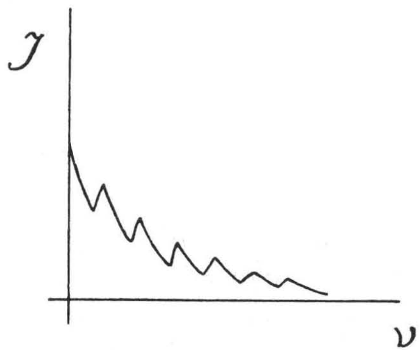

Fig. 1.

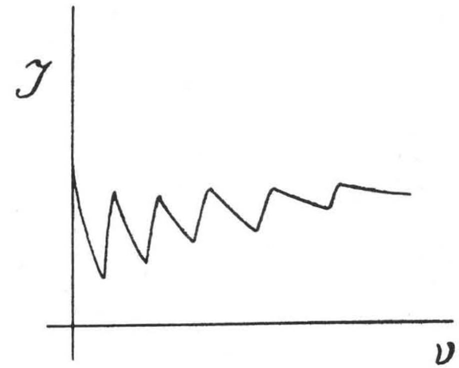

Fig. 3.

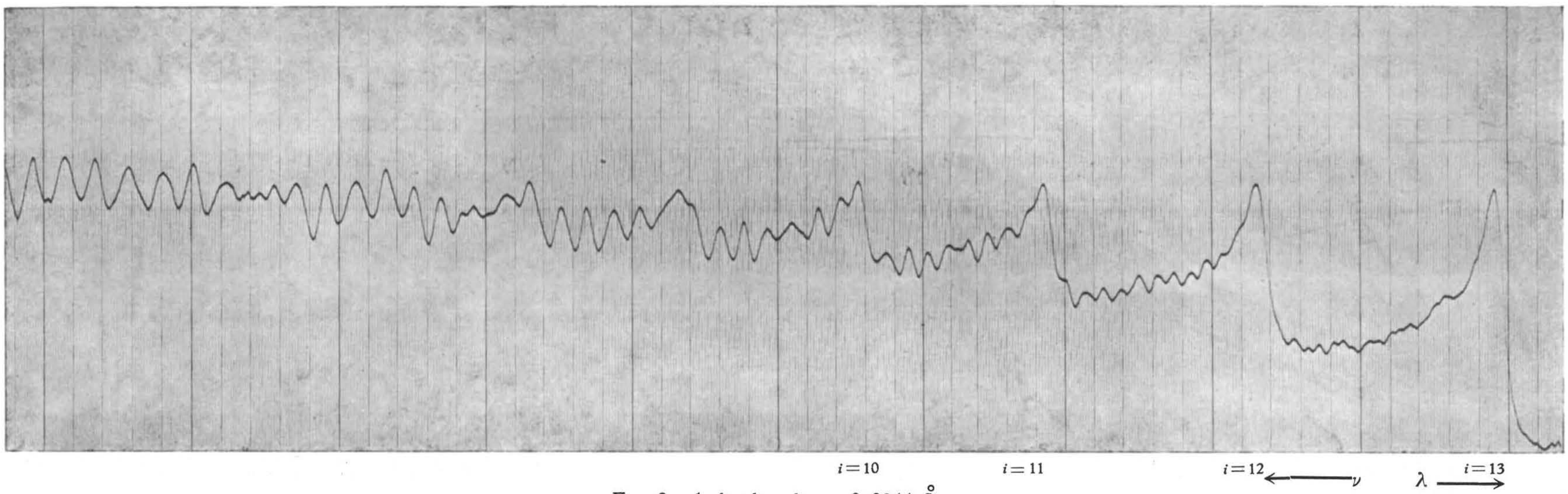

Fig. 2. 1 dividing line = 0.0244 Å

we have to do here with a group of bands of which the successive bands are superposed, but that in this case the lines from the different bands happen to coincide and consequently present the appearance of one continuous band. When this is assumed, it may be understood why the intensity in the successive bands diminishes more and more slowly. This is due to the superposition of lines from the different bands; in the first band the normal intensities are found, in the second the last lines of the first band coincide with those really belonging to the second band, changing their apparent intensities, in the third band lines from the second band produce the same effect, those of the first probably having no longer any influence, and so on. This superposition has not yet much influence for the second band, because the lines in question from the first band have a high number, greater than 33; in the third band, however, it is already very pronounced, because the overlapping extreme lines of the second band start already with the number 13 and are hence rather intense.

There is another reason indicating that probably we are not dealing here with one band. A close examination of the photographs and of the photometer curve reveals certain irregularities, which always become more and more pronounced towards the end of the band. It appears as if the coincidence of lines from the different bands does not take place so accurately as might be supposed at first sight. At different places the lines are diffuse, which seems to suggest "interference" of the lines from the different bands. Near the end of the group of bands this has such a great disturbing effect that it is no longer possible there to identify the lines with certainty.

Even if the conception of the structure of these bands given here, in contrast with that of DANJON, is correct, these bands do not present a normal structure, as will appear in the discussion of the band-formula to be given later. Inasmuch as this is the only known example of bands from this kind of a tri-atomic molecule, it is not yet possible to decide with certainty which interpretation is the correct one.

Before discussing the numerical data, we wish to point out that in consequence of the diffuseness of the lines their measurement could be made much better with the photometer than with the comparator. The edges, however, presented a difficulty. In consequence of there being a region of slight blackening on one side and a region of intense blackening on the other side, the maximum of the curve of intensity for the edges was always slightly displaced towards the latter region, especially at the beginning. The accuracy that could be reached, was no greater than about 0.015 Å.

According to DANJON all the lines of the group of bands can be represented by one formula, an ordinary zero-branch formula:

$$\nu = 16428{,}24 + 0{,}004497\, n^2 + 0{,}0000010\, n^3 \quad . \quad . \quad . \quad . \quad (1)$$

In accordance with what precedes, our opinion is, however, that this fact is more or less accidental, and that in reality we have to do here with a number of different bands. Each band must then have a formula of its own. From the preceding formula we expect for these bands:

$$\nu = 16428{,}24 + 0{,}004497\,(m+p)^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this p is evidently the number that the first line from each band has in DANJON's formula. Hence p is equal to zero for the first band, and the ordinary zero-branch formula is obtained. The other bands seem to be zero-branch formulae of which the first $p-1$ lines are absent. They may, of course, also be taken as positive branches, but then an explanation is required why the negative branches are not present. The values of p are: 0, 34, 47, 56, 63, 69, 74.

Formula (2), however, still rests on the supposition that the lines from the different bands accurately coincide. It would not be easy to interprete the strange series of p-values. It seems more probable to us that for the derivation of the band formula another fact observed by FABRY [1]) should be utilized. The band edges, the first lines of every band, themselves satisfy again a quadratic formula, namely: [2])

$$\nu_i = 16428{,}24 + 0{,}208.58\,(13^2 - i^2) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Remarkable is here the appearance of the integer 13 in this formula. It might be held to be accidental, if the values 13.5, 14 and 14.5 did not occur in other groups of bands in this spectrum. If it is now assumed that formula (1) is valid approximately, and if this is combined with formula (3), we find for the bands:

$$\left.\begin{aligned} \nu = 16428{,}24 + 0{,}004497\,(m + 6{,}807\sqrt{13^2 - i^2})^2 + \\ + 0.0000010\,(m + 6{,}807\sqrt{13^2 - i^2})^3 \end{aligned}\right\} . \quad (4)$$

The coinciding of the different bands arises through the fact that the values p obtained as solutions of the equations

$$0{,}004497\,p^2 + 0{,}0000010\,p^3 = 0{,}20858\,(13^2 - i^2),$$

come pretty near to whole numbers, especially in the beginning. As the deviation from a whole number must be pretty great to have a disturbing influence, this may very well be only accidental.

It should still be pointed out that the structure of the bands renders it probable that the values of m must be integers, also the numbering of the values i is integral in this band.

The table gives the wave-lengths in the first part of the band from new measurements in the region where the measurement is still pretty

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1) Journ. de Phys. **4**, 245, 1905.

2) In this formula i passes through the values 13, 12 etc. to 0. If it is desired to have the numbering in inverse order, $(13-i)$ should be substituted for i.

n	m		n	m	
0	$i=13$ 0	λ 6087.08 Å	43	$i=12$ 9	λ 6083.98 Å
—	—		44	10	.83
—	—		45	11	.67
29	29	5.71	46	12	.52
30	30	.62	47	$i=11$ 0	.37
31	31	.51	48	1	.21
32	32	.39	49	2	.05
33	33	.27	50	3	2.86
34	$i=12$ 0	.16	51	4	.70
35	1	—	52	5	.52
36	2	—	53	6	.34
37	3	4.80	54	7	.16
38	4	.66	55	8	1.98
39	5	.55	56	$i=10$ 0	.78
40	6	.41	57	1	.60
41	7	.27	58	2	.41
42	8	.12	59	3	.20

certain. The lines between $n = 0$ and $n = 29$ could not be resolved. In DANJON the resolution into lines did not begin before $n = 47$.

Let us finally consider the other bands investigated by DANJON. According to a communication by DANJON he has succeeded in resolving another group of bands, viz. λ 6051, also into lines. For the lines he gives the probable formula:

$$\nu = 16526{,}1 + 0{,}006233\, n^2 + 0{,}0000083\, n^3.$$

For the edges the formula is:

$$\nu_i = 16526{,}1 + 0{,}2030\, (14^2 - i^2).$$

According to our conception the following formula would be written for this groups of bands:

$$\nu = 16526{,}1 + 0{,}006233\, (m + 5{,}707 \sqrt{14^2 - i^2})^3$$
$$+ 0{,}0000083\, (m + 5{,}707 \sqrt{14^2 - i^2})^3.$$

For the other groups of bands only the edges have been measured. The formulae for these are:

$$\lambda\, 6064{,}61: \quad \nu_i = 16489{,}1 + 0{,}1895\, (15{,}5^2 - i^2)$$
$$\lambda\, 6037{,}17: \quad \nu_i = 16564{,}1 + 0{,}2279\, (13{,}5^2 - i^2).$$

If the formula (4) given here renders the correct conception of the bands, it would be probable that we have to do here with two moments of momentum, one with a quantum number m and one with the quantum number 13, of which the projection normal to m is equal to i, the projection along m is then $\sqrt{13^2 - i^2}$. Neither the theory nor the experiments are, however, sufficient to give, with certainty, a theoretical interpretation. Probably an electron moment of momentum also plays a part here, for, as is known, these bands, in contrast with most others, show a large ZEEMAN-effect.

I am greatly indebted to Prof. R. FORTRAT (Grenoble) for suggesting this investigation to me, and to Prof. P. ZEEMAN for his encouragement, advice, and for the necessary instruments which he placed at my disposal.

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