

The Effect of Pressure on the Band Spectra of the Fluorides of the Metals of the Alkaline Earths.

By R. ROSSI, B.Sc.

(Physical Laboratories, The University of Manchester.)

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The effect of pressure on arc spectra of several elements has been carefully examined in recent years by Humphreys* and Mohler† in America and by Duffield‡ in this country.

All lines were found to widen out and to shift under pressure towards the less refrangible end of the spectrum, and for a given line this shift was found to be approximately proportional to the pressure of the gas surrounding the arc.

The cyanogen bands were also investigated by Humphreys and Mohler, but were found not to show any pressure-shift. Their heads reverse§ under pressure, and the components in which the bands are resolved widen out but do not show the least trace of shift. I have repeated these experiments up to pressures of 110 atmospheres, but even at that high pressure the centre of the heads of the bands at atmospheric pressure is seen to coincide with the centre of the reversals of the same heads under pressure.

It has been suggested by Humphreys that lines which show a large Zeeman effect ought to show a large pressure-shift effect, but the experimental proof of such a connection is not yet complete.

No evidence that bands showed a Zeeman effect was obtained until Dufour,|| about one year ago, observed that the bands of the fluorides of the metals of the alkaline earths are an exception to this rule. It was therefore thought interesting, on account of Humphreys' hypothesis, to see if these particular bands which show a marked Zeeman effect would also be displaced by pressure. I was fortunate in having the use of the 21½-foot Rowland concave grating of this laboratory, which has been previously carefully mounted by Dr. W. G. Duffield and used by him for similar work.

* W. J. Humphreys, 'Astrophys. Journ.,' vol. 4, p. 249; vol. 3, p. 114; vol. 22, p. 217; vol. 26, p. 18.

† J. F. Mohler, 'Astrophys. Journ.,' vol. 3, p. 114; vol. 4, p. 175.

‡ W. G. Duffield, 'Phil. Trans.,' A, vol. 208, p. 111 (1908); and vol. 209 p. 205 (1908).

§ J. E. Petavel and R. S. Hutton, 'Phil. Mag.' [6], vol. 6, p. 571 (1903).

|| A. Dufour, 'Comptes Rendus,' vol. 146, pp. 118 and 229, 1908; 'Le Radium,' October, 1908.

Both the first and second order spectra were observed, giving on the photographic plate a dispersion of 2.6 and 1.3 Ångström units respectively per millimetre.

The source of light was an electric arc placed inside the pressure cylinder designed by Prof. Petavel.* The fluorides examined were placed in the positive carbon of the arc, which was excited by direct current (about 12 amperes at 100 volts). Wratten and Wainwright panchromatic plates were found to be the most suitable, the maximum exposure being one hour at 40 atmospheres in the second order spectrum.

The comparison spectrum, at atmospheric pressure, was photographed in the central strip of the plate both before and after the one taken under pressure, to show whether any accidental displacement had occurred during the exposure. The spectrum taken under pressure appeared above and below the comparison spectrum. The photographs were measured with Kayser's machine, from 8 to 16 readings being taken for each band.

Each of the components into which a band was resolved was found to shift the same amount towards the red end of the spectrum. Hence measurements were made on as many components as possible, but in some cases where the band was much weakened by pressure, measurements had to be confined to the first and most distinct component, viz., the head of the band.

Owing to the asymmetrical reversal and widening of the components of these bands under pressure it is difficult to make accurate measurements, and in some cases at low pressures, where the displacement is small, the error in the measured displacement may be a large one, amounting to even 20 per cent.; for higher pressures, of course, the probable percentage error of the measured displacement is much reduced.

Calcium Fluoride.

This compound gives three bands fading towards the violet end of the spectrum with heads at $\lambda\lambda$ 6036.96, 6050.81, 6064.49. In the first experiments the powdered fluoride was introduced into an opening bored into ordinary carbon poles, but it was found that the arc did not burn as well under high pressures as with the carbons which are sold commercially for flame arcs and which contain large quantities of calcium fluoride. The latter were therefore used in the final experiments.

Each of the three bands was found to shift towards the red; the components of the same band shifting the same amount.

Table I gives the mean values of the displacements, in Ångström units, at

* R. S. Hutton and J. E. Petavel, 'Phil. Trans.,' A, vol. 207, p. 421 (1908).

each pressure taken from the two sets of photographs in the first and in the second order.

Table I.

| Band with head at λ . | Pressure in atmospheres (excess above one atmosphere). | | | | | |
|----------------------------------|--|-------|-------|-------|-------|-------|
| | 5. | 10. | 15. | 20. | 30. | 40. |
| 6036·96 | 0·073 | 0·120 | 0·149 | 0·165 | 0·275 | 0·371 |
| 6050·81 | 0·051 | 0·092 | 0·112 | 0·138 | 0·201 | 0·261 |
| 6064·49 | 0·068 | 0·113 | 0·150 | 0·183 | 0·275 | 0·372 |

Table II gives the mean displacement per atmosphere and also the Zeeman separation in the magnetic field as found by Dufour. In the last column the direction of rotation is called normal when, as with ordinary metallic lines, it agrees with that deduced from the assumption that the electron giving rise to the observed oscillation is negative. An abnormal rotation may, but does not necessarily mean, that the electron is positive as has been pointed out by Dufour in his latest publications.

Table II.

| Band with head at λ . | Mean displacement per atmosphere in Å.U. | Magnetic separation in Å.U. H = 10,000 (Dufour). | Direction of circular polarisation (Dufour). |
|----------------------------------|--|--|--|
| 6036·96 | 0·0105 | 0·31 | abnormal |
| 6050·81 | 0·0078 | 0·22 | " |
| 6064·49 | 0·0103 | 0·30 | normal |

The relative intensity of the bands is not affected by pressure; the band with head at λ 6050·81 being always much less intense than the other two both at atmospheric and under high pressure.

The components of the bands were always found to be reversed, at atmospheric and at high pressure.

The band having the greatest tendency to reverse is, however, λ 6036. For in one photograph at atmospheric pressure taken in a preliminary experiment with a graphite pole containing small quantities of calcium fluoride, λ 6064 is an emission band; λ 6050 is faintly reversed; while λ 6036 is strongly reversed.

All components in which the bands are resolved widen out under pressure; but those of the band λ 6064 to a greater extent than those of the bands λ 6050 and λ 6036.

Strontium Fluoride.

Strontium fluoride gives five bands, fading away towards the violet, and with heads at $\lambda\lambda$ 6418·82, 6511·84, 6527·39, 6632·43, 6655·40.

The positive pole was a graphite tube about 1·5 cm. outside diameter and 1 cm. inside diameter.

Powdered graphite was mixed in a mortar with an equal amount of strontium fluoride and with a very small quantity of sugar solution in water, and a paste as homogeneous as possible was thus prepared. The graphite tube was then filled with the paste and baked in an oven at about 400° C. The sugar carbonised and a fairly hard and homogeneous mass was left inside the pole; such poles were found to burn under pressure far better than if the bored pole had been filled with the fluoride alone, or with mixed fluoride and graphite alone. Using the latter methods the fluoride is partly blown away by the arc and partly melted, falling to the bottom of the hole, with the result that the bands are weakened, and a much longer exposure is required.

Graphite was used instead of carbon, because it contains less impurities, burns slower, and is a better conductor.

Owing to the long wave-lengths of these bands, coloured screens would have been necessary to prevent overlapping if the work had been carried on in the second order spectrum, and also longer exposures would have been required. Photographs were therefore taken in the first order only.

Table III gives the displacements in Ångström units; Table IV gives the mean shift per atmosphere and the magnetic separation.

Table III.

| Band with head at λ . | Pressure in atmospheres (excess above one atmosphere). | | | |
|----------------------------------|--|-------|-------|-------|
| | 10. | 15. | 20. | 25. |
| 6511·84 | 0·122 | 0·141 | 0·178 | 0·261 |
| 6527·39 | 0·094 | 0·109 | 0·146 | 0·192 |
| 6632·43 | 0·083 | — | 0·150 | 0·184 |
| 6655·40 | — | — | 0·137 | 0·171 |

These bands were emission bands at atmospheric pressure; but under higher pressures, λ 6511 and λ 6632, were found to be reversed.

As the pressure increases the intensity of the two bands at λ 6632 and λ 6655 decreases more rapidly than the intensity of λ 6511 and λ 6527.

Table IV.

| Band with head at λ . | Mean displacement per atmosphere in Å.U. | Magnetic separation in Å.U. $H = 10,000$ (Dufour). | Direction of circular polarisation (Dufour). |
|-------------------------------|--|--|--|
| 6511·84 | 0·0112 | 0·40 | abnormal |
| 6527·39 | 0·0079 | 0·40 | " |
| 6632·43 | 0·0077 | 0·43 | normal |
| 6655·40 | 0·0068 | ? | probably abnormal |

Barium Fluoride.

The poles were prepared in the same way as those for strontium fluoride.

The bands with heads at $\lambda\lambda$ 4050·85, 4992·25, and 5000·71 were studied; these bands fade away towards the red. The displacements in Ångström units are given in Table V; the mean displacement per atmosphere and magnetic separation in Table VI.

Table V.

| Band with head at λ . | Pressure in atmospheres (excess above one atmosphere). | | |
|-------------------------------|--|-------|-------|
| | 5. | 12·5. | 15·5. |
| 4950·85 | 0·060 | 0·089 | 0·121 |
| 4992·23 | 0·093 | 0·145 | — |
| 5000·71 | 0·062 | 0·095 | — |

Table VI.

| Band with head at λ . | Mean displacement per atmosphere in Å.U. | Magnetic separation in Å.U. $H = 10,000$ (Dufour). | Direction of circular polarisation (Dufour). |
|-------------------------------|--|--|--|
| 4950·85 | 0·009 | 0·24 | abnormal |
| 4992·23 | 0·015 | 0·12 | " |
| 5000·71 | 0·010 | 0·24 | normal |

The intensity of these bands decreases rapidly with pressure. At 15 atmospheres the bands λ 4992 and λ 5000 have vanished, and at 20 the band λ 4950 has also disappeared. At atmospheric pressure they were always found to be emission bands. At 5 atmospheres λ 4992 is still an emission band, λ 5000 is faintly reversed, and λ 4950 is completely reversed. Under pressure, the band at λ 5000 broadens out more than the other two.

It will be noticed that the highest pressure employed was only 15.5 atmospheres in the case of barium, and 40 in the case of calcium. Experiments at still higher pressures were not practicable for the following reasons:—The banded spectra of these fluorides are almost entirely due to light emitted by the outside layers or “flames” of the arc. Under pressure, the arc shortens very much; at 50 atmospheres, it is only a few millimetres long; it is very bright, but the flashing “flames” of a long arc which are obtained at atmospheric pressure seem to become more and more rare as the pressure increases. A long exposure would be required to obtain a good photograph under such conditions. This drawback was most marked when the barium fluoride was used; at 20 atmospheres, no sign of the bands appeared on the plate for the ordinary exposure. A still longer exposure would have fogged the plate owing to the continuous spectrum given by the incandescent poles whose images, in consequence of the shortness of the arc, could not always be kept away from the slit.

Although it is clear that these particular bands which show the Zeeman effect are also displaced by pressure, there seems to be no obvious relation between the magnitudes of the two effects. For example, in the case of the calcium fluoride bands the displacements due to pressure are proportional to the magnetic separation; while in the case of the barium fluoride the larger the Zeeman effect the smaller the pressure-shift. In the case of the strontium fluoride there does not seem to be any relation at all between the magnitudes of the two effects.

The amount of pressure-shift apparently does not depend upon whether the circular polarisation agrees in direction with that deduced from the motion of positive or negative electrons. The displacements found for these bands under pressure are of the same order of magnitude as those found by other observers on line spectra. The linear relation between displacement and pressure found for line spectra seems to hold roughly also for these bands.

Many thanks are due to Prof. Rutherford for placing the necessary apparatus at my disposal and for the great interest he has taken in this work.

To Dr. W. G. Duffield I must also express my thanks for the experience I gained under him during the last few years in high pressure work.
