

M =	43429	44819	03251	82765	11289	18916	60508	22943	97005	80366
	65661	14453	78316	58646	49208	87077	47292	24949	33843	17483
	18706	10674	47663	03733	64167	92871	58963	90656	92210	64662
	81226	58521	27086	56867	03295	93370	86965	88266	88331	16360
	77384	90514	28443	48666	76864	65860	85135	56148	21234	87653
	43543	43573	17253	83562	21868	25				

which is true, certainly to 272 and probably to 273 places of decimals.

IV. "On the Crimson Line of Phosphorescent Alumina." By WILLIAM CROOKES, F.R.S., V.P.C.S. Received December 30, 1886.

In a paper which I had the honour of communicating to the Royal Society* in March, 1879, I described the phosphorescence of alumina and its various forms when under the influence of the electrical discharge *in vacuo*, in the following words:—"Next to the diamond, alumina in the form of ruby is perhaps the most strikingly phosphorescent stone I have examined. It glows with a rich, full red; and a remarkable feature is that it is of little consequence what degree of colour the earth or stone possesses naturally, the colour of the phosphorescence is nearly the same in all cases; chemically precipitated amorphous alumina, rubies of a pale reddish-yellow, and gems of the prized 'pigeon's blood' colour, glowing alike in the vacuum, thus corroborating E. Becquerel's† results on the action of light on alumina and its compounds in the phosphoroscope. . . . The appearance of the alumina glow in the spectroscope is remarkable. There is a faint continuous spectrum ending in the red somewhere near the line B; then a black space, and next an intensely brilliant and sharp red line, to which nearly the whole of the intensity of the coloured glow is due. . . . This line coincides with the one described by E. Becquerel as being the most brilliant of the lines in the spectrum of the light of alumina, in its various forms, when glowing in the phosphoroscope."

In 1881‡ I again returned to the subject, describing a large number of fresh experiments; and I may add that the red glow of alumina has been, off and on, a subject of examination with me since the year first named down to the present time.

In the papers above quoted I gave as accurate measurements of the alumina line as my instrumental means would then permit. I have recently had occasion to go over these measurements again in a

* 'Phil. Trans.,' Part 2, 1879, pp. 660, 661.

† 'Annales de Chimie et de Physique,' vol. 57, 1859, p. 50.

‡ 'Roy. Soc. Proc.,' vol. 32, pp. 206—208.

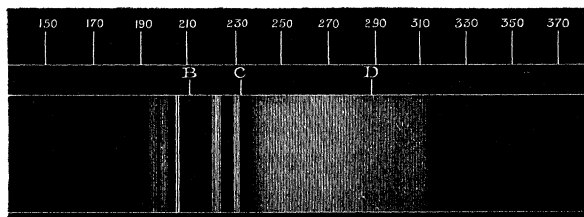
large spectroscope of very accurate construction, and the results, I think, are sufficiently important to be worth bringing before the notice of the Royal Society.

The spectrum consists firstly of an exceedingly faint and hazy pair of bands; these are too faint to measure, but they appear to be in about the same position as the bands 1986—2009, and 2031—2075 in the spinel spectrum given further on. Next is seen the characteristic crimson line of the alumina spectrum; this, when examined with a fine slit and high power eyepiece, is seen to be double, the distance apart of the components being about half the distance separating the D lines. Then come a pair of fainter and rather nebulous orange lines; beyond them is a dark space followed by a continuous spectrum extending to the green. The following are the measurements of the spectrum:—

Scale of spectroscope.	λ .	$\frac{1}{\lambda^2}$.	Remarks.
10·550°	6942	2075	The first component of the double crimson line.
10·548	6937	2078	The second component of the double crimson line. These lines are nearly as sharp as the components of D.
10·450	6707	2223	Approximate centre of a narrow band, shading off at each side.
10·400	6598	2297	Approximate centre of a narrow band, shading off at each side. This band is somewhat sharper and brighter than the one at 2223.
10·360	6514	2357	Approximate commencement of the continuous spectrum which extends into the green, shading off too indefinitely to admit of measurement.

The accompanying cut (fig. 1) gives the spectrum drawn to the $\frac{1}{\lambda^2}$ scale.

FIG. 1.



The Alumina Spectrum.

It is known that spinel (magnesium aluminate) phosphoresces with a red light, and shows a crimson line in its spectrum.* On examination in the high power spectroscope the spectrum of the light emitted by spinel under the radiant matter test is seen to differ from that emitted by ruby and alumina under the same test, and to closely approximate to the description given by E. Becquerel in 1859.

The spectrum first shows, in the extreme red, a faint double band, then a narrow crimson line, which, however, is not double like the alumina line, neither is it quite so bright and sharp. Four hazy red bands follow, the fourth being wider and more indistinct than the others. Here the spectrum of most spinels fades away. Sometimes, however, a spinel is seen to glow with a greenish tint; in these the spectrum is the same as the others up to this point, and there is also seen a bright concentration of light in the green.

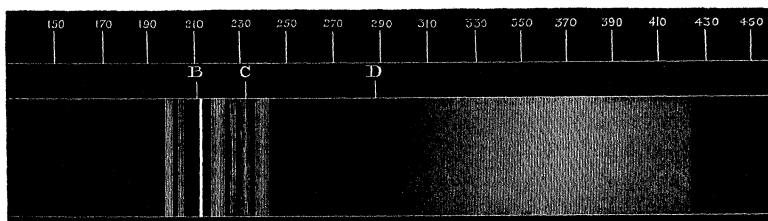
The measurements of the spinel spectrum are given in the following table:—

Scale of spectroscope.	λ .	$\frac{1}{\lambda^2}$.	Remarks.
10·610°	7096	1986	Approximate commencement of first component of ill-defined double band.
10·595	7055	2009	Approximate end of ditto.
10·580	7017	2031	Commencement of ill-defined second component.
10·550	6942	2075	End of ditto.
10·515	6857	2127	Centre of sharp crimson line.
10·490	6798	2164	Approximate commencement of broad hazy band.
10·450	6707	2223	End of ditto.
10·440	6683	2239	Commencement of second component of group.
10·405	6608	2290	End of ditto.
10·400	6598	2297	Commencement of third component.
10·380	6555	2327	End of ditto. This band is somewhat sharper and brighter than the other components of this group.
10·370	6534	2342	Commencement of fourth component of ditto.
10·330	6454	2401	End of ditto.
9·730	5541	3257	Approximate commencement of luminous concentration in the green seen in some spinels.
9·440	5234	3650	Position of maximum luminosity of this concentration of light. From this point the spectrum appears to be continuous, shading off gradually towards the blue and violet.

The drawing (fig. 2) shows the spectrum, drawn to the $\frac{1}{\lambda^2}$ scale.

* E. Becquerel, 'Annales de Chimie et de Physique,' vol. 57, p. 58; W. Crookes, 'Roy. Soc. Proc.,' vol. 32, p. 208.

FIG. 2.



Spectrum of Spinel (Magnesium Aluminate).

In the 'Comptes Rendus' for December 6th last* appears a brief note by M. de Boisbaudran, in which he announces, "*to take date, that alumina, calcined and submitted to the electrical discharge in a vacuum, has not given him a trace of red fluorescence. This fluorescence, as well as its special spectrum, shows itself brilliantly when the alumina contains $\frac{1}{100}$ th and even $\frac{1}{1100}$ th of Cr_2O_3 . With the $\frac{1}{10000}$ th part of Cr_2O_3 we still obtain very visible rose colour. . . . From these observations the presence of chromium appears to be indispensable to the production of the red fluorescence of alumina.*"

This statement being opposed to all my experience, I immediately instituted experiments with a view, if possible, to clear up the mystery. I started with aluminium sulphate, which I knew to be tolerably pure, and in which ordinary tests failed to detect chromium. On ignition and testing in the usual manner in a radiant matter tube, the alumina line was brightly visible in the spectrum of the emitted light. Different portions of this aluminium sulphate were now purified by various processes for the separation of chromium. All gave as a result the absence of this impurity. The most trustworthy process being that devised by Wöhler,† I used it to purify the bulk. The salt was dissolved in water, and excess of caustic potash added till the precipitate first formed redissolved. Chlorine was now passed through till no more precipitate fell down and the liquid retained a strong odour of chlorine. The whole of the chromium would now be in solution, whilst the alumina would be in the precipitate. The alumina was filtered off, well washed, and a portion tested in the radiant matter tube. It gave as good an alumina spectrum as did the original sulphate, the crimson line being very prominent.

The alumina thus purified was a second time dissolved in caustic potash and submitted to the chlorine purification. Again in the radiant matter tube the alumina gave its characteristic crimson line spectrum.

* 'Comptes Rendus,' vol. 102, p. 1107.

† 'Select Methods in Chemical Analysis,' 2nd edition, p. 124.

The filtrate from the alumina, which should contain all the chromium present in the form of potassium chromate, was supersaturated with hydrochloric acid and boiled till free from volatile chlorine compounds. Alcohol was then added, and it was again boiled to reduce to the state of sesquichloride of chromium any chromic acid which might be present. Ammonia in excess was now added, and the whole was boiled; a very small precipitate of a brownish colour fell down; it was filtered and washed. This precipitate, which was not more than the $\frac{1}{50000}$ th part of the alumina from which it was derived, contained no chromium whatever; it was too small in quantity to admit of a complete analysis being made, but all the tests which I could apply showed it to be a mixture of ferric oxide and alumina.

One part of this precipitate was mixed with 100 parts of the pure alumina from which it had just been separated, and the mixture was tested in the radiant matter tube. The phosphorescence was the same as in the two previous experiments, the crimson line being neither better nor worse.

I now prepared aluminium chromate, and tested its action in the radiant matter tube. It was almost black after ignition, and refused to phosphoresce. A mixture was then made of aluminium chromate and alumina in the proportion of one part chromium to 100 parts of aluminium. After ignition the colour of the mixture was almost white. Tested, it gave very poor phosphorescence; the alumina line was faintly visible.

Aluminium acetate was mixed with 5 per cent. of ammonium bichromate, ignited with sulphuric acid, and tested in the radiant matter tube. There was no phosphorescence. The same mixture was heated to a high temperature before the blowpipe, when it gave a very feeble phosphorescence, but I could detect no line in the spectrum.

Pure alumina was mixed with 5 per cent. of ammonium bichromate, and moistened with sulphuric acid. After ignition it phosphoresced with a reddish colour, and the spectrum showed a concentration of light in the orange, but no alumina light was visible. The tube was opened, and the contents heated to a very high blowpipe temperature. In the radiant matter tube it gave the same results as before.

A mixture of 0.5 per cent. ammonium bichromate, 10 per cent. of lime, and 89.5 per cent. of pure alumina was ignited with sulphuric acid, and tested in the usual way. The calcium brought out a trace of yttrium and samarium bands, but no crimson line was to be seen.

Alumina precipitated from its ammoniacal solution by boiling was found to glow with a green light in the vacuum tube and to give no crimson line in its spectrum. The tube was now opened, and some of its contents removed and heated in a hot blast blowpipe to the

melting point of platinum for about five minutes. Re-tested in a vacuum tube this alumina was seen to glow at the points and edges of the lumps where the heat had been fiercest, with a red light, giving a faint line spectrum. The bulk of the mass, however, gave out the original green glow.

To get the crimson line most brilliantly, it is necessary to ignite the earth to the highest temperature of the blowpipe flame. With a slightly less heat the phosphorescence is not strong, and the line is faint. When the temperature has not been raised high enough the colour of the emitted light in most aluminas is green, and no line is visible; whilst the same earth raised to a higher temperature glows with a red light, and the red line comes into view. The most brilliant crimson line, when seen at all, has always been obtained when the alumina has been kept near the melting point of platinum for some time.

Physical differences, or perhaps even difference in molecular composition, also exert a great influence on the phosphorescence of alumina. In this connexion, I ask permission to quote a sentence from my paper of May, 1881, already mentioned:—"Two earthen crucibles were tightly packed, the one with sulphate of alumina, the other with acetate of alumina. They were then exposed, side by side, to the most intense heat of a wind-furnace—a heat little short of the melting point of platinum. The resulting aluminas were then tested in the molecular stream. The alumina from the sulphate gave the crimson glow and the spectrum line. The alumina from the acetate gave no red glow or line, but a pale green phosphorescence."

Experience gained in the yttria research has taught me that the possibility of the molecule of aluminium being composed of two or more submolecules, only one of which is capable of giving the crimson line phosphorescence, must not be overlooked. To test this hypothesis alumina, as pure as I could prepare it, was submitted to three separate processes of fractionation, the operations in each case being repeated from twenty to thirty times. Alumina giving the crimson line always concentrated towards one end of the fractionations, whilst at the other end the alumina sometimes phosphoresced of a green tint, and at others scarcely phosphoresced at all, the crimson line being either very feeble or entirely absent in the spectrum. The earths were always ignited for the same time and, as nearly as possible, to the same temperature.

In no case could chromium be detected at either extremity of the fractionations.

These experiments are perhaps too few to permit any important inference being drawn from them. There seem, however, to be four possible explanations of the phenomena observed:—

1. The crimson line is due to alumina, but it is capable of being suppressed by an accompanying earth which concentrates towards one end of the fractionations.
2. The crimson line is not due to alumina, but is due to the presence of an accompanying earth concentrating towards the other end of the fractionations.
3. The crimson line belongs to alumina, but its full development requires certain precautions to be observed in the time and intensity of ignition, degree of exhaustion, or its absolute freedom from alkaline and other bodies carried down by precipitated alumina, and difficult to remove by washing; experience not having yet shown which of these precautions are essential to the full development of the crimson line and which are unessential.
4. The earth alumina is a compound molecule, one of its constituent molecules giving the crimson line. According to this hypothesis alumina would be analogous to yttria.

It is not unlikely that a chemist wishing to obtain alumina of exceptional purity might submit it to a series of operations, akin to fractionation, which would have the effect of giving earths phosphorescing either with a strong crimson line, or with little or no crimson line; and either of these samples of alumina might be looked upon by him as pure. It is possible that some such explanation as this may be at the bottom of the contradictory statements respecting the crimson line of alumina.

Presents, January 13, 1887.

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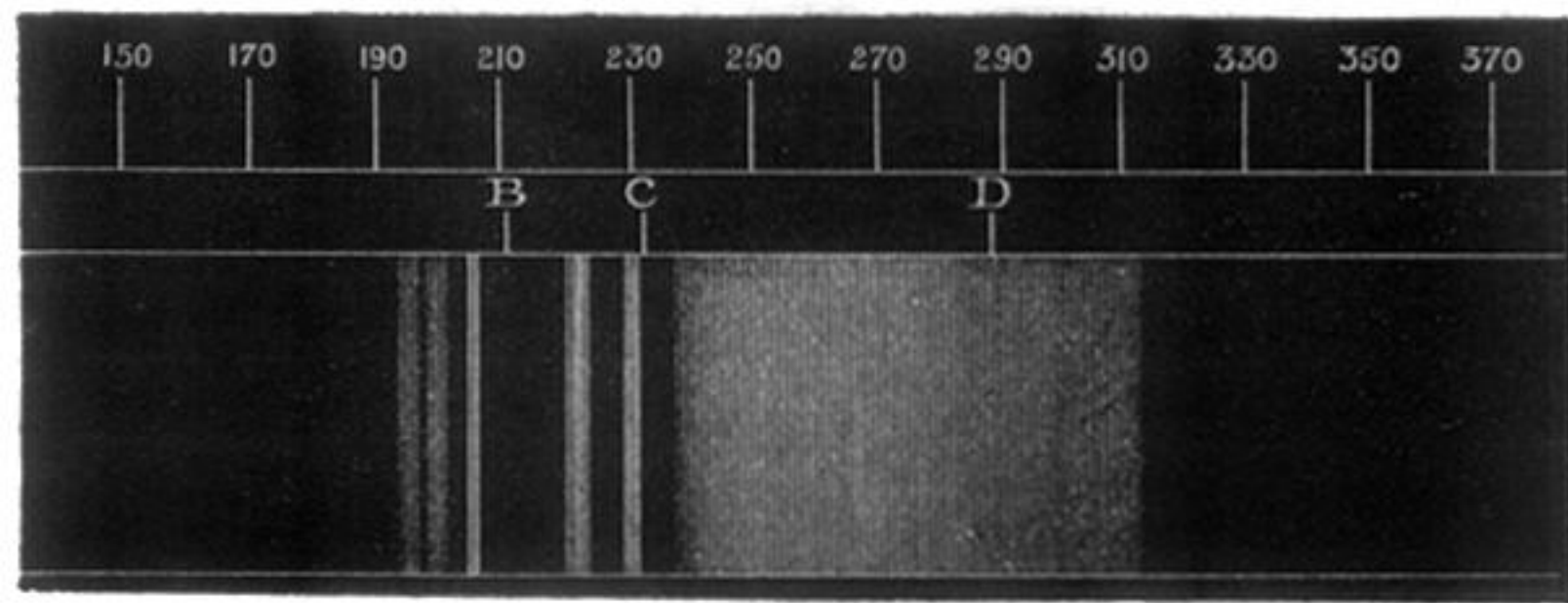
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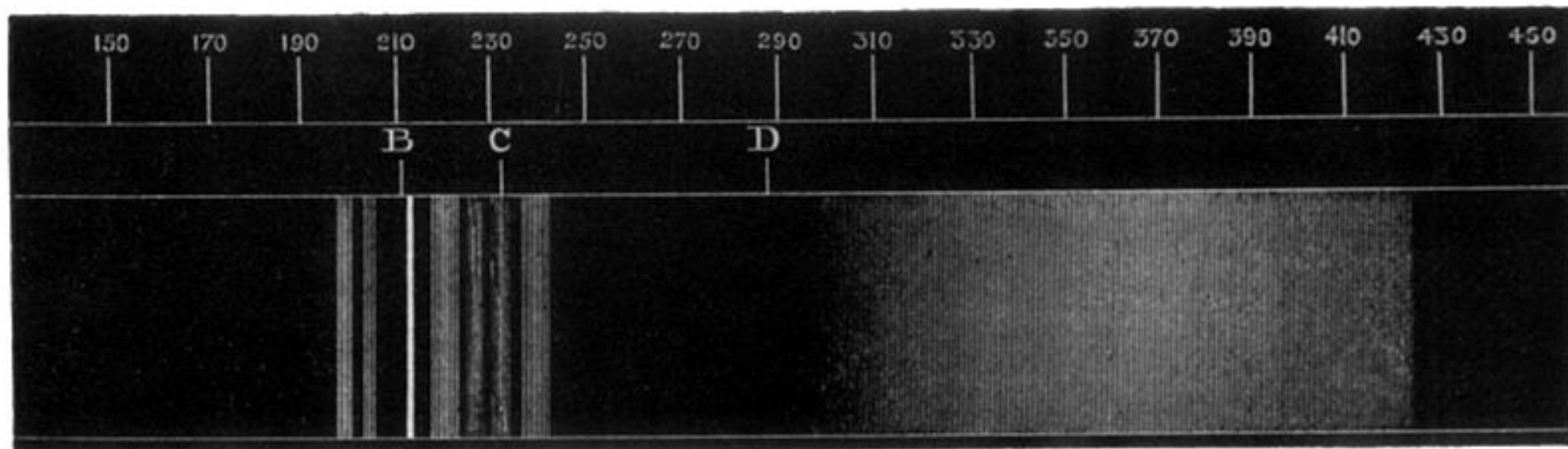
The Society.

FIG. 1.



The Alumina Spectrum.

FIG. 2.



Spectrum of Spinel (Magnesium Aluminate).