posures and with more sensitive plates, to obtain information on this and other points. It is, perhaps, not too much to hope that the further knowledge of the spectrum of the nebulæ afforded us by photography, may lead by the help of terrestrial experiments to more definite information as to the state of things existing in those bodies.

III. "On the Disappearance of some Spectral Lines and the Variations of Metallic Spectra due to Mixed Vapours." By G. D. Liveing, M.A., F.R.S., Professor of Chemistry, and J. Dewar, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received March 11, 1882.

The theory of spectral lines most commonly received is that the otions of the luminiferous ether producing them are not directly due to any motion of translation of the molecules of the emitting substance, but to relative motions of the parts of the same molecule, or in other words, to vibrations occurring within the molecules; and that the mutual action of the molecules, while it may give rise to irregular vibrations of the ether, affects the regular vibrations producing the lines only in an indirect manner, by converting part of the motions of translation into internal vibrations. On this theory the spectral lines which any given substance can readily take up will in general be limited to a certain number of fundamental lines and a number of others harmonically related to them, though not necessarily simple harmonics of the fundamental lines. And variations of temperature, by altering the rapidity and the violence of the action of one molecule on another, will alter the intensities of the several vibrations, but not their periods, unless the violence should extend to the disintegration of the molecules, which would be equivalent to the formation of new molecules with new fundamental periods of vibration. In view of this theory, the observations on the spectrum of magnesium have a special interest, because from the close analogy of magnesium to zinc and cadmium, it is inferred that the molecules of magnesium vapour are chemical atoms of that substance, that is to say, they pass apparently undivided through all the chemical changes to which magnesium may be subjected; and it seems reasonable to suppose that any subdivision of the chemical atoms could not fail in this case to be attended with a change of chemical qualities, which, in the presence of other elements, would give rise to new compounds. No such new compounds have in fact been detected. We have already described in detail the differences between the spectra of magnesium as seen in the flame of the burning metal, the electric arc, and the spark discharge, and we have now some further observations upon them to place before the Society, which are confirmatory of the received theory.

We have observed the spectrum of a block of magnesia, rendered incandescent by an oxyhydrogen jet. In the visible part of this spectrum we found no discontinuity, no lines bright or dark (except the inevitable D lines), no sign of the blue channelled spectrum of magnesia. Drs. Huggins and Reynolds ("Proc. Roy. Soc.," vol. 18, pp. 547, 551) have recorded the appearance of the *b* group under these circumstances, but we failed to get sight of it. In the ultra-violet region photographs still show a continuous spectrum, extending far beyond the limit of the solar spectrum, in fact as far as we have hitherto observed any lines of magnesium to occur, but on this continuous spectrum one line, and only one, comes out, which is the strongest line of burning magnesium and of the arc spectrum, at wave-length 2852 (2850 Cornu). This line shows sometimes bright, sometimes reversed, against the continuous background. In this case, where the appearance of the lines depends on their relative brightness, as compared with the continuous spectrum, there is no advantage, so far as the visible rays are concerned, in the photographic method over that of observation by the eye; there may be a disadvantage, as the photograph presents only the mean result of a certain time. But where the faint lines of a discontinuous spectrum are in question the photographic method has the advantage, for when the vibrations are too feeble to produce any sensible impression on the retina, they may yet, by integration of their effects during a lengthened exposure, produce a definite effect on the photographic plate. In general we have only exposed our plates for such times as would give us the best defined images, so that very faint lines are not developed in them; but by using a prolonged exposure we find that in many cases the disappearance of lines from the arc or spark is more apparent than real, and is attributable to a variation of intensity, not to an absolute cessation of the vibrations corresponding to the evanescent lines. Thus of the quadruple group between wave-lengths 2789 and 2802 in the spark spectrum of magnesium only the stronger two lines are usually seen in photographs of the arc with short exposure, but the whole four produce their impressions on the plate if sufficient time be given. Again, the triplet in the arc spectrum at wave-length about 2942—2937·5 is not usually seen in the spectrum of the spark, but when the plate has had a lengthened exposure the strongest two lines of this triplet make their appearance in the spectrum of the spark. Even the triplet near M, so strong in the flame of burning magnesium, but not before recognised either in the arc or spark in photographs taken with short exposure,* comes out in plates of the spectrum of the Spottiswoode induction spark (if we may give this name to the method of stimulating the induction coil by the intermittent current of a

* Dr. Huggins has informed us that his old photographs of the magnesium spark taken with an induction coil in the ordinary way show this triplet distinctly.

magneto-electric machine, see "Proc. Roy. Soc.," vol. 30, p. 175) between magnesium electrodes which have had four or five minutes' exposure. These observations tend to confirm the theoretical view that alterations of temperature cannot put a stop to any of the fundamental vibrations of a molecule; at the same time we cannot be sure that the impulses communicated by an electric discharge may not be in some respects different from those resulting from mere increment of temperature.

There is, however, a further point for consideration, which is, how far the presence of a mixture of molecules of different elements affects the respective vibrations. This is a condition which obtains in most or all of our observations of the arc in crucibles, as well as in the solar atmosphere, so that it is important to see if any effects can be traced to such a condition of matter. Indeed, in order to arrive at any probable explanation of the variations observed in the spectra of sun-spots and of the chromosphere, we require to study the phenomena produced by such mixtures of vapours as exist in our crucibles, and not merely the spectra produced by the isolated elements, either in arc, spark, or flame.

It is only on some such supposition as that above suggested that we can account for the absorption lines produced by admixtures of magnesium with sodium and potassium respectively ("Proc. Roy. Soc.," vol. 27, p. 353); and it is possible that the very remarkable effect of hydrogen in producing the reversal of chromium lines (*ib.*, vol. 32, p. 405) and of other lines (*ib.*, vol. 28, p. 472) is a result of analogous action. We have more particularly observed the effect of a current of hydrogen on the iron lines at wave-lengths 4918, 4919·7, and 4923. These lines, as seen in the arc in a magnesia crucible, usually have about the same relative strengths as are shown in Ångström's map of the solar spectrum; Thalén gives their intensities as 2, 1, 3 respectively. They are all developed simultaneously when iron is dropped into the crucible, the first being sometimes reversed, the second frequently reversed for some time, the third much strengthened but not reversed. After a time these effects die out, but if now a *very gentle* current of hydrogen is led in through one of the carbons perforated for the purpose, the line at 4919·7 is again strongly reversed, that at 4918 expanded, while that at 4923 becomes very bright but remains sharply defined. These effects of the hydrogen were observed several times. In all cases the line at wave-length 4923 seemed to maintain about the same relative strength compared with the other two lines, and never showed any variation at all corresponding to the prominence it holds in Young's catalogue of chromospheric lines, where it has a frequency of forty, while that at 4918 has only half that frequency, and the strongest line of the three does not figure at all.*

* Mr. Lockyer's figure ("Proc. Roy. Soc.," vol. 32, p. 205) accompanying his

Some further observations on this group of lines are contained in the sequel.

The effects of mixtures of metallic vapours in developing bright lines are equally marked, and in general more easily observed. We have before noticed ("Proc. Roy. Soc.," vol. 30, p. 97) "that certain lines of metals present in the crucible are only seen, or come out with especial brilliance, when some other metal is introduced. This is the case with some groups of calcium lines which are not seen, or barely visible, in the arc in a lime crucible, and come out with great brilliance on the introduction of a fragment of iron, but are not developed by other metals such as tin." Effects of this kind are most frequent in the case of metals which produce a large number of lines. They are specially noticeable in the case of nickel and titanium. Both these metals produce many lines, but a comparatively large quantity of nickel may be introduced into a crucible of magnesia, through which the arc of a powerful Siemens dynamo-electric machine is passing, without the lines of nickel being strongly developed; they show steadily as sharp but not specially bright lines; but after several other metals—iron, chromium, &c.—have been put in in succession, the nickel lines frequently come out with great brilliance and considerably expanded, and remain so for a long time. The titanium lines are generally very persistent when that metal (as cyanide or oxide) has been introduced into the crucible, but are subject to continual variations of intensity; sometimes they are twinkling, at other times steady; but they can frequently be brought out with great brilliance by dropping in iron or other metals. In such cases the metals put into the arc can hardly be supposed to increase the resistance or the temperature, but they may assist the volatilisation of each other, and may also act by reduction, and so by increasing the incandescent mass strengthen the weaker lines. Chlorides, however, which seem to have the effect of helping the volatilisation and diminishing the resistance so that the arc can be drawn out to a greater length, usually sweep out the fainter lines.

In many cases when a fragment of a metal is dropped into the crucible brilliant lines, hitherto unrecorded, come out for a short time and quickly die out. It is hardly possible in such cases to say without prolonged observations whether these lines belong to the newly introduced metal or to some of those previously put in and developed by the presence of the new metal. How much remains to be done in the study of these lines, and how much light this may throw on the phenomena of the solar lines, will be seen from the following account of our observations of some very small portions of the spectrum of the

paper on the spectra of sun-spots showing "what happens with regard to three adjacent iron lines under different solar and terrestrial conditions," is at variance with our observations, in so far as the line at 4923 is represented as absent from the arc.

arc in a magnesia crucible. The portions selected are of special interest, because in these regions a remarkable outburst of broad Fraunhofer lines, not usually visible, is recorded by the Astronomer Royal as having occurred in a sun-spot ("Monthly Not. Ast. Soc.," 1881).

Fig. 1 shows the principal (not all the) lines which were in the same field of view when the spectrum of the 4th order produced by a Rutherford grating (17,296 lines to the inch) was observed, the light being that of the arc of a Siemens machine in a magnesia crucible. A small piece of copper was first put in and then some nickel, and by the lines of these metals the portion of the spectrum under examination was identified. The iron lines were as usual also present. The symbols affixed to the several lines show those which came out when the metals indicated were introduced. Thus, when chromium was dropped in, a very brilliant line came out near the middle of the field, a little below the iron line wave-length 5090·4; titanium cyanide brought out a line at about wave-length 5086, cobalt one at 5094, uranic oxide one at 5087, and cerium (which may have contained lanthanum and didymium) a number of lines. These lines were very bright for a second or two, and soon became much less brilliant, but were revived when more of the metal was put in. Lead brought out a very evanescent diffuse band represented in the figure by dotted lines. The distances of the several lines from the extreme nickel lines were measured hastily by a micrometer, and are here reproduced to scale. One line at wave-length 5096, though constantly present, did not seem to be affected by any of the metals introduced. An iron line is indicated on Ångström's map at this place, but the introduction of iron, which expanded the neighbouring line at wave-length 5097·3, had no effect on it. It is remarkable that this region in Ångström's normal solar spectrum is particularly bare of lines, though Vogel gives several faint lines between those marked by Ångström. It is, however, a region in which many lines have been observed in sun-spots (Greenwich Spectroscopic and Photographic Results, 1880), and the most prominent of these lines seem to correspond to lines developed by cerium, chromium, and cobalt, though more exact measures than we were able to take at the times that those observations were made are needed in order to establish an exact coincidence.

Fig. 2 represents the lines brought out in a similar way in another short portion of the spectrum, which is also remarkably bare of lines in the solar spectrum.

Fig. 3 shows lines brought out in another place by the several metals indicated. Other lines were visible in this region but were not specially developed by the metals introduced.

The line at wave-length 4923, which occurs so often in the chromo-

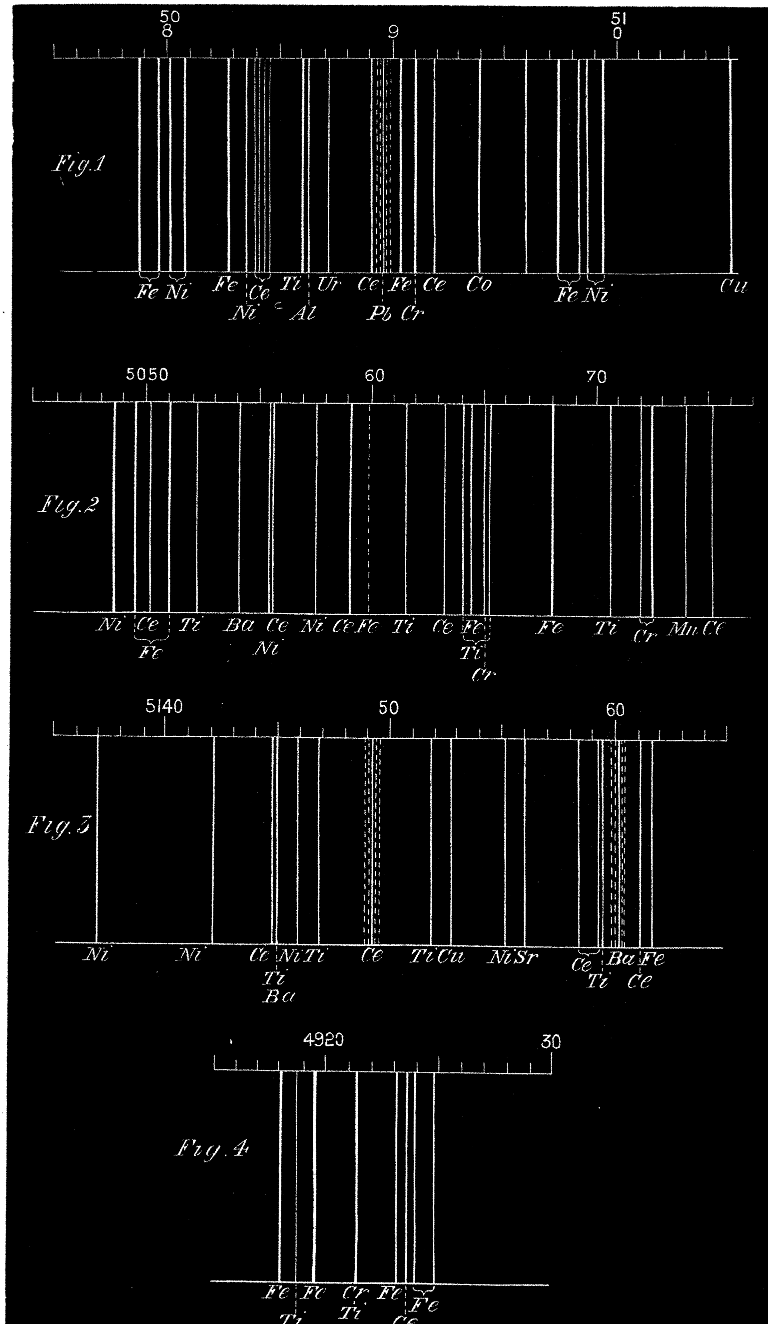
Fig. 1
50 8
9
51 0
Fe Ni Fe Ce Ni Ti Al Ur Ce Pb Fe Cr Ce Co Fe Ni Cu
Fig. 2
5050
60
70
Ni Ce Fe Ti Ba Ce Ni Ni Ce Fe Ti Ce Fe Ti Cr Fe Ti Cr Mn Ce
Fig. 3
5140
50
60
Ni Ni Ce Ti Ba Ni Ti Ce Ti Cu Ni Sr Ce Ti Ba Fe Ce
Fig. 4
4920
30
Fe Ti Fe Cr Ti Fe Ce Fe

sphere, according to Young and Tacchini, and is assumed to be due to iron, is so near to lines which come out in our crucibles on the introduction of other metals, that we cannot help feeling some doubt as to its absolute identification with the iron line; the more so as in Young's catalogue bright lines are sometimes assigned to two metals, of which the real lines differ by nearly a unit of Ångström's scale. This is the case, for example, with the line at wave-length 5017·6, which is ascribed to iron and nickel. And where lines are broadened, as in sun-spots, the identification with either of two very close lines becomes very difficult.

Fig. 4 shows the lines which come out in the neighbourhood of wave-length 4923. A pair of lines are developed by iron close to this line, and a very bright but evanescent line comes out at about 4923·5, on the introduction of cerium. This is an exceedingly brilliant line for the time, and might easily be mistaken for the iron line unless examined under high dispersion, and it seems to show that metallic cerium is readily volatile under these conditions. The iron line at 4923 seems to disappear on the addition of titanium, which, on the other hand, brings out the lines marked titanium in the figure. Nickel brings out the cerium line strongly. The line which comes out at 4921·3 on the addition of chromium and titanium is most likely the line seen by Young in the chromosphere thirty times, which up to the present time has not been recognised as due to any element but sulphur.

Both the nickel line at 5016·5 and the adjacent iron line at 5017·5 are seen in the arc in our crucibles, but the nickel line is much the stronger and more persistent. Cerium when put into the crucible brightens the titanium lines, as well as the line at 5017·5. An alloy of manganese, iron, and titanium had the effect of making the nickel line broad and diffuse, without strengthening the 5017·5 line.

These are but samples of the large amount of work which remains to be done before we can pronounce that any of the solar lines are not due to terrestrial elements, or can draw any safe inferences from observed variations in their relative strengths or apparent coincidences; and no real scientific advance can be made by attempting generalizations with the knowledge which we at present possess.

Fig. 1

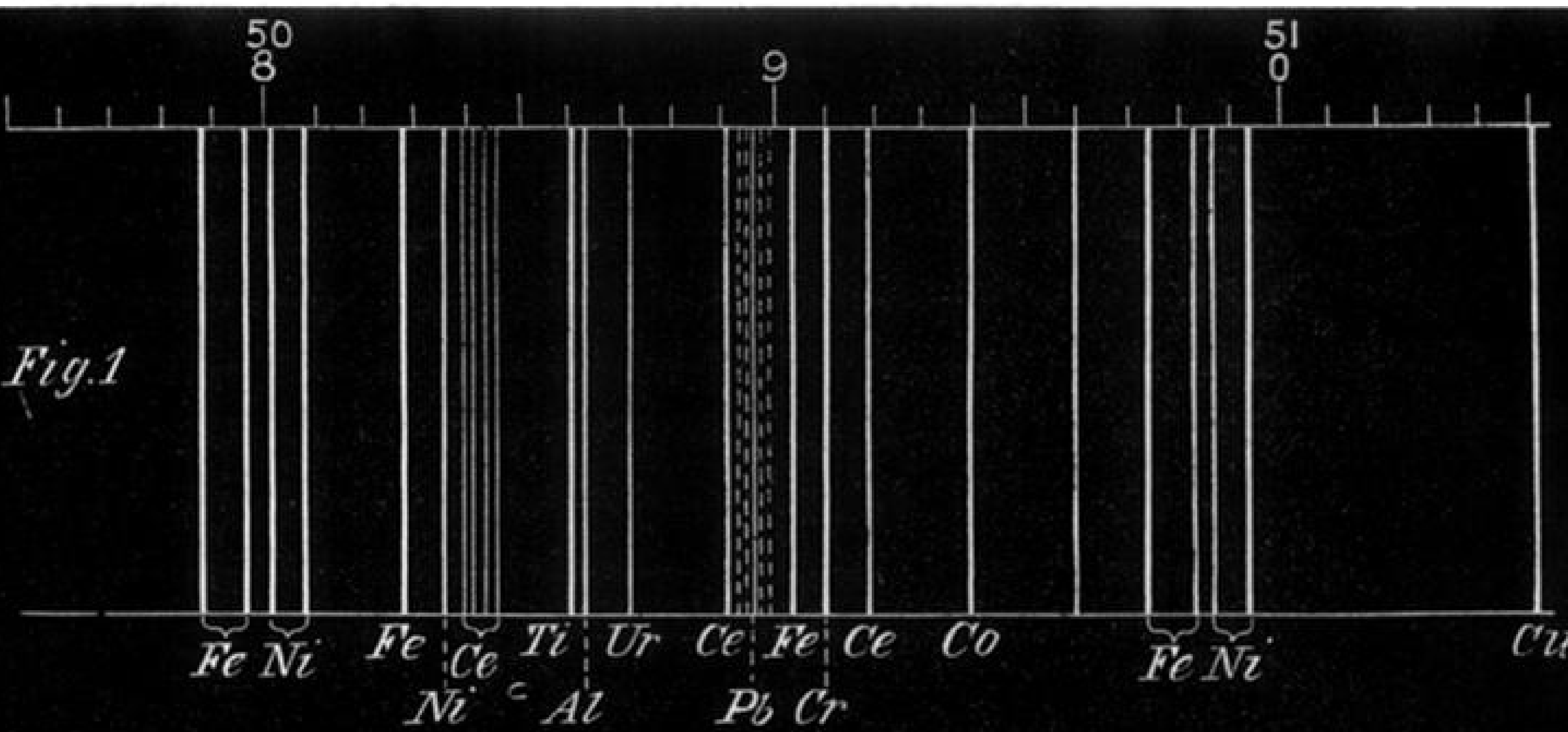

Fig. 2

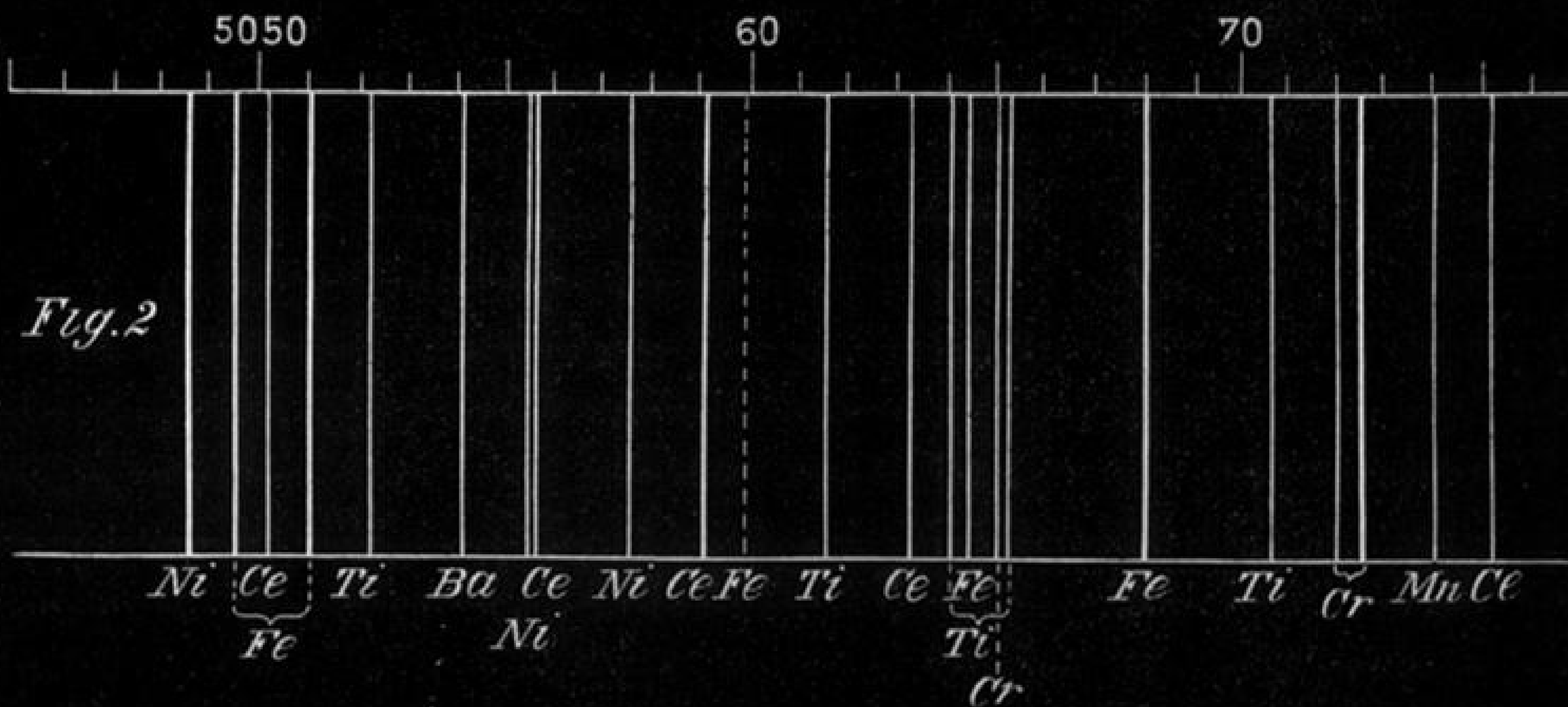

Fig. 3

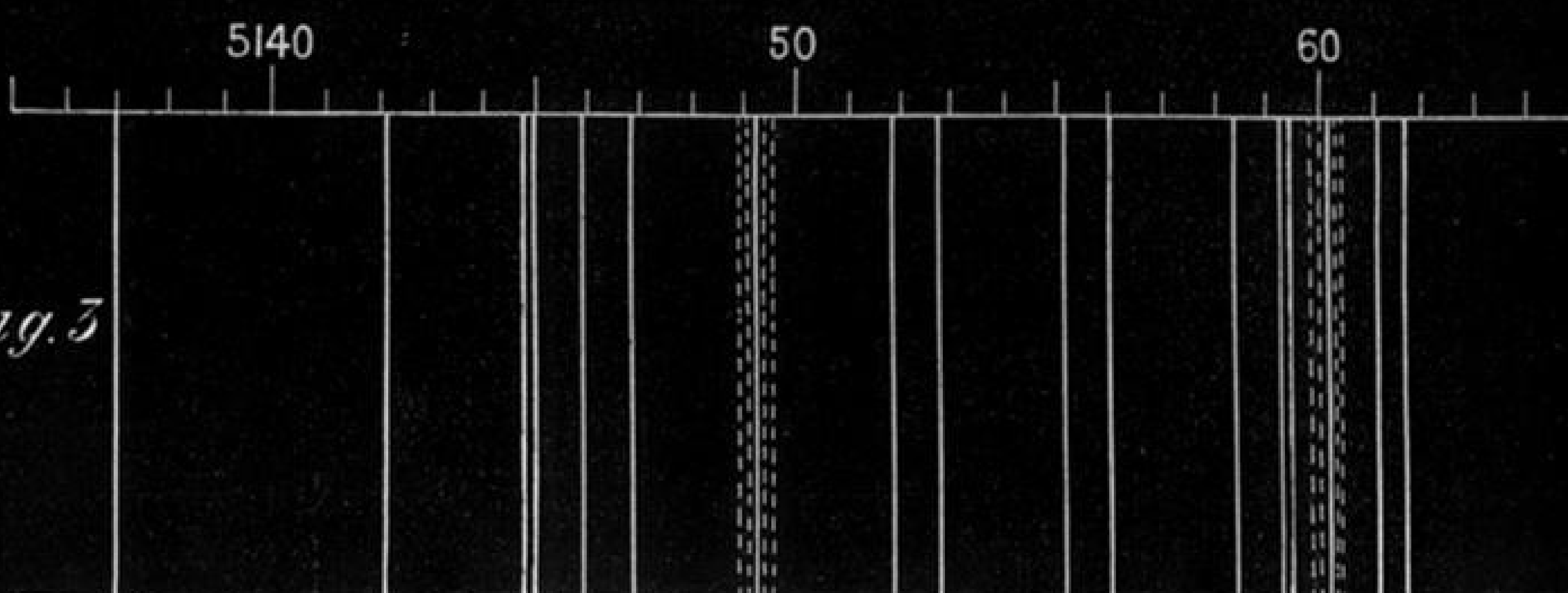

Fig. 4