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LIII. *The Electrical Resonance of Metal Particles for Light-Waves. Third Communication. By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University.*

SINCE the appearance of the two preceding papers (Phil. Mag. vols. iii. & iv., 1902; Proc. Physical Soc. *antea*, pp. 166, 276) on the above subject I have made further investigations, which appear to confirm the provisional hypothesis of electrical resonance, which was adopted to explain the very brilliant colours of films made up of metal granules of the order of magnitude of light-waves.

I have succeeded in obtaining the coloured films in prismatic form, and have established the fact that they exhibit anomalous dispersion for waves longer and shorter than the ones which are refused transmission. This was observed for electrical waves passing through a prism built up of tinfoil resonators by Garbasso and Aschkinass. I have obtained the coloured films on the walls of a tube in which I had fused a quantity of magnalium alloy *in vacuo*. The film was permanent in air, but the colours vanished as soon as the film was moistened with a little very dilute acid, owing to the conversion of the metal granules into a salt. I have also obtained coloured films by the cathode discharge from an electrode of selenium, though the colours in this case were not nearly as brilliant as those obtained by the distillation of the alkali metals. The microscope showed these films to be granular, and experiments with the quartz spectrograph demonstrated that they were very transparent to ultra-violet light, for which homogeneous films of selenium of the same thickness are absolutely opaque.

The silver films, red, purple, and blue, which I described in my second paper, seemed most suitable for continuing the experiments, owing to the comparative ease with which they are prepared and their permanency in air. On attempting to repeat the experiment, I was somewhat annoyed to find that the silver solution dried on the plates with no trace of colour, a thin deposit of a black powder being the only result. This powder, if rubbed with the finger,

gave a blood-red streak on the plate, which resembled in every respect the coloured deposits obtained last year. I tried cleaning the glass more carefully, using fresh chemicals and distilled water ; but all to no purpose. It finally occurred to me, however, that I had formed the original deposits on some old lantern-slide plates, from which the gelatine had been removed with hot water. Possible a film of gelatine of infinitesimal thickness might have been the necessary factor. To test this I wetted a sheet of glass and rubbed it over with a small thread of Nelson's photographic gelatine. The plate being cold, only the slightest trace of gelatine could have dissolved in the film of water. The plate was then drained off and dried on a hot metal plate. On flowing this plate with the silver solution and drying it rapidly as before, I obtained a most wonderful film, as red as the densest ruby-glass over most of its extent, but with several patches of deep blue-violet, as rich in colour as dense cobalt-glass. The presence of the gelatine seems in some way to keep the small particles from collecting into aggregates (the black powder). It will be remembered that in my first paper I alluded to an experiment in which the cooling of a bulb, and the condensation of the hydrocarbon vapour on the coloured film, sometimes destroyed the colour permanently, the minute sodium particles collecting into larger aggregates, which diffracted the light, and showed the pearly lustre, but exhibited no trace of colour by transmitted light.

As the formation of these films makes a most brilliant lantern experiment, I will give more explicit directions for their preparation. The solution is one described by Carey Lea. Three solutions are prepared ; a 30-per-cent. one of ferrous sulphate, a 40-per-cent. one of sodium citrate, and a 10-per-cent. one of silver nitrate. Fourteen c.cms. of the citrate solution are mixed with 10 c.cms. of the ferrous sulphate solution, to which is then added 10 c.cms. of the silver nitrate solution. A dense black precipitate at once forms, and the whole is at once poured into a filter. As soon as the liquid has entirely run through, the precipitate is washed with 10 cms. (*not more*) of distilled water. This is to remove the salts which make the precipitate insoluble. After the water has entirely passed through the filter, about 25 c.cms.

of distilled water are poured into the filter, and the blood-red solution which runs through collected. As it does not keep very well, it is best to prepare it on the day on which it is to be used.

A sheet of glass is washed clean, rinsed with fresh water, and the wet surface rubbed over with some shreads of gelatine. It is then drained for a few seconds and dried on a hot plate. A little of the silver solution is flowed over it, the surplus being drained off. If too much gelatine has been used, precipitation is apt to take place, the deposit taking the form of floating shreads of a reddish membrane. If no considerable precipitation occurs, the plate, which should have been quite warm when flowed, is placed once more on the hot plate until dry. The films formed in this way are usually deep red in colour, though sometimes patches of deep violet form, with sharply defined edges. As one may make a dozen trials without obtaining the violet patches, I endeavoured to find some way of producing them at will; and finally hit upon the right expedient. When the plate is about half dry, with a steaming film and a few small pools of the hot solution, it is removed from the hot plate, held at an angle, and treated with a few drops of alcohol, which are allowed to run down across the still damp portion of the plate. These portions speedily dry into a most gorgeous mosaic of red, purple, and violet patches, the experiment being especially striking in the lantern, as it occupies but a few seconds, and the colour-display spreads over the plate like the blaze of a sunset. So far as I have been able to find, these brilliantly coloured films were never obtained by Carey Lea, though the solution used is one that he employed in his experiments on allotropic silver.

Any desired depth of colour can be obtained with these films by merely allowing more or less of the solution to remain on the plate. I have films of such a deep red that they are almost opaque, a gas-flame being barely visible through them. The light which does get through is regularly transmitted, that is, the films are not turbid media. The spectroscope shows that the absorption-band is wider and less sharply defined than is the case with some of the purple potassium films, which have a rather narrow and very black band in the yellowish green. This can be explained by

assuming that there is not a great regularity in the size of the particles, and consequently less sharp selective resonance. Inasmuch as some of the sodium films had a bright apple-green colour, in other words absorbed both the red and blue, it seemed worth while to see whether the silver films exhibited the same phenomenon. Red and violet films were formed on a quartz plate, and the absorption-spectra photographed with a quartz spectrograph. It was found that they were transparent to the whole ultra-violet region, even the last two faint cadmium lines which almost all media cut off, appearing on the plate. If a second band is present it must be located in the infra-red region.

Before continuing the experiments with these highly coloured silver films, it seemed best to establish beyond any doubt that they were analogous in every respect to the films obtained with the alkali metals. One respect in which they differ is the absence of much effect when they are moistened with ligroin. It will be remembered that the films formed by distillation in exhausted bulbs showed most remarkable colour-changes when the hydrocarbon vapour was caused to condense on the wall by the local application of cold. This difference is not of serious moment; for it is quite possible that the silver particles are already immersed in some medium (possibly gelatine) which prevents the ligroin from entering. As I have mentioned in my previous paper, a very slight change of colour is produced by the ligroin; but only close examination makes it evident. The red films of silver can be changed to purple and blue by the local application of heat. This was also true of the alkali metal films. I mentioned in my first communication that where the sodium deposits were very scant the particles scattered a bright green light, the appearance being somewhat as if the inside of the bulb had been washed over with a solution of fluoresceine. This light was of the wave-lengths of the light absorbed where the film was thicker. Only films too thin to show any colour by transmitted light exhibited this phenomenon. For convenience I spoke of this light as the "fluorescent light," without intending to convey the idea that it has any real connexion with fluorescence.

It remained only to be seen whether silver deposits could be obtained which showed this peculiarity. A plate was flowed with the silver solution, and then partly rinsed off with distilled water and dried.

By transmitted light there were traces of colour in patches, though most of the plate appeared colourless. On holding it in a beam of strong sunlight in a dark room there appeared many patches which exhibited a bottle-green diffused light, not quite as bright and pure as that shown by sodium, but in every way analogous to it.

Inasmuch as all of the peculiarities shown by the films of the alkali metals have been observed to a greater or less degree with the silver films, it seems safe to conclude that the cause of the colour is the same in the two cases.

An attempt was now made to determine whether the films show anomalous dispersion as we should expect them to do if the colour is due to resonance.

A sheet of thin plate-glass was prepared with gelatine and flowed with the silver solution. A number of glass tubes were then laid side by side on the plate, the fluid being drawn up by capillarity into prisms. The plate was then warmed until the prismatic strips of fluid had dried, when the glass tubes were removed. On examining the plate it was found that some very perfect prisms had formed, which resembled closely the cyanine prisms which I have described in a previous paper. The portion of the plate which seemed to carry the most perfect prism was cut from the glass sheet and mounted on the table of the spectrometer, a small portion of the glass having been previously cleaned to enable a reading to be taken of the undeviated image of the slit. The prism was screened with black paper to cut off the light which did not pass through the most perfect portion, and the slit of the instrument illuminated with light from a monochromatic illuminator. By alternately exposing the clear glass and the prism, readings of the deviated and undeviated images could be taken. It was found that when blue-violet light was employed the prism did not deviate the image by any measurable amount, while with red light the deviation amounted to several times the width of the image of the slit.

The latter was considerably broadened by diffraction, as is always the case with strongly absorbing prisms.

The prism was of a deep red colour, but transmitted violet freely, the absorption-band being in the green. It was found that the deviation was less for the extreme red of the spectrum than for the orange-red, which is just what we should expect. The absence of any deviation in the case of the violet light means of course that the refractive index does not differ much from unity for these waves. To determine the index for the red it is necessary to know the angle of the prism. This was determined by observing the images of the slit reflected from the strip of clear glass and the surface of the prism, the required angle being one-half of the observed angle. This angle was found to be $1' 15''$, while the deviation for red light was $2' 42''$. The refractive index calculated from these observations turns out to be 3.15, or about that of selenium for yellow light.

This is practically proof positive that the cause of colour is resonance, though the question is still open as to whether it is resonance of small metal particles in a manner analogous to the action of the tinfoil resonators on electro-magnetic waves, or a resonance within the molecule, as in the case of the aniline dyes. Though I have not yet devised any crucial experiment which enables me to distinguish between the two, I have observed differences in the behaviour of these metal films from that of films formed of dye-stuffs, which makes it seem extremely probable that the action is different in the two cases.

To these arguments may be added the one that it seems unlikely that so many different metals should exhibit such similar molecular absorption, and that the granular condition should be essential to the production of colour, for I have succeeded in detecting the granules in every case by means of the microscope.

Let us now consider some of the differences between the action on light of these coloured films and films formed of aniline dyes. A film of granular silver can be formed which resembles very closely a film of cyanine, both having absorption-bands in the middle of the visible spectrum. If a very

thin film of silver is prepared which exhibits a light purple colour by transmitted light, the colour is much less marked, *i. e.* the absorption is less, when the plate is held at an angle of say 30 degrees with the incident light than it is at normal incidence. Moreover, the colour changes from purple to red, the absorption-band appearing to move down the spectrum a trifle. Possibly a simple broadening of the band would produce this same colour change owing to the greater sensitiveness of the eye for red. A cyanine film does not exhibit this peculiarity, the colour of the transmitted light remaining nearly constant for varying angles of incidence.

The change in depth and hue of the colour when the incidence is made oblique is probably due to the fact that the absorption is different when the incident light has a component of the electric vector perpendicular to the surface, which, of course, is not the case when the incidence is normal. If the light is polarized to start with, this is found to be the case, the colour of the transmitted light being bluish-purple when the electric vector is perpendicular to the plane of incidence, and red when it is parallel to this plane in which case there is a component normal to the surface. These changes are not obtained with the film of cyanine. In the course of a recent discussion of the problem which I have had with Professor J. J. Thomson, he expressed the opinion that the capacity of a sheet of resonators would be greater, and the period of vibration consequently longer, when the electric vector was parallel to the sheet. This is in agreement with the observations which I have made with the silver films, the absorption-band moving towards the red when the plane of polarization is so oriented that the electric vector has no component normal to the surface.

With sodium and potassium films I have obtained just the opposite effect, the absorption-band moving in the other direction. These results appeared at first to be very confusing, until I finally discovered what I believe to be the explanation.

I have studied the behaviour of the films at oblique incidence with polarized light with considerable care, and have obtained results which appear to be concordant among themselves.

If the plane of incidence is horizontal and the electric vector is parallel to this plane, *i. e.* with a component perpendicular to the surface, we find for example a heavy absorption-band in the green. As the plane of polarization is rotated through a right angle the band in some cases shifts its position in the spectrum (sometimes in one direction and sometimes in the other) and sometimes simply fades away entirely without undergoing any shift. On examining the spectrum with greater care, however, I found that in general other bands are present. If the band in the green moves towards the red, a band comes into the spectrum from the red end to meet it, and another band which was originally in the violet moves out of the spectrum in the direction of the ultra-violet. It is difficult to say at present whether the appearance and disappearance of these two fainter bands is due to their motion along the spectrum, or to the fact that one fades away and the other springs into existence, as in the case above cited. This difficulty is due to the fact that a part of the band lies outside of the visible spectrum, and a fading away can easily be mistaken for a drift. I am of the opinion that in some cases we are dealing with one phenomenon, and in other cases with the other.

I have examined several films in which a band in the yellow and one in the blue distinctly approached each other when the plane of polarization was rotated through a right angle. This explains why it is that a single band near the centre of the spectrum is sometimes seen to move in one direction and sometimes in the other.

In the one case it was doubtless the right-hand band of a pair which approached (the other lying in the invisible portion of the spectrum), in the other case it was the left-hand band of an approaching pair. Some typical cases of the changes which occur when the plane of polarization is rotated are shown in the diagram. The plane of incidence is horizontal in every case, *i. e.* the sheet of resonators stands vertical, and at an angle of about 45 degrees with the incident light. The direction of the electric vector is indicated by the double arrow. In general the band drifts without much change in intensity, though in some cases it fades away almost to the

vanishing point when the plane of polarization is at 45 degrees to the plane of incidence. A case of this kind is shown in

the last three spectra of the figure. The band in this case was crooked, as the slit of the spectroscopic was placed at a point where the colour of the film changed quite abruptly from blue to purple.

The appearance of several bands in the spectrum suggests that we are dealing with something of the nature of multiple resonance, and it is to be hoped that some of the mathematical physicists will work out the behaviour of a sheet of small spherical resonators at normal and oblique incidence for vibrations polarized in different planes.