THE EFFECT OF TEMPERATURE UPON THE ABSORPTION SPECTRUM OF A SYNTHETIC RUBY.

BY K. S. GIBSON.

INTRODUCTION.

THE absorption and fluorescence spectra of the ruby have been studied by Becquerel,[1] by du Bois and Elias,[2] and by Mendenhall and Wood.[3] There are in the spectra a number of lines[4] and narrow bands. The ordinary and extraordinary spectra differ somewhat and are quite simple compared with those of many other crystals. For these reasons, these investigators have considered the spectrum of the ruby as one of the best available for the study of the Zeeman-effect. While primarily engaged in the study of this and allied phenomena, they have also noted the change in the positions of the lines and bands which occurs upon a change in temperature.

The coefficient of absorption throughout the spectrum is also greatly influenced by temperature. In this paper are given the results of an investigation into the effect of temperature upon the coefficient of absorption of the ruby, as well as upon the positions of the various lines and bands in its absorption spectrum.

THE ABSORPTION CURVE.

For studying the changes in the absorption curve, a Lummer-Brodhun spectrophotometer was used. Light from an acetylene flame was passed through the ruby (which could be placed either in a furnace for high temperatures or in a Dewar flask for low temperatures), and was then reflected by a mirror into one of the collimators of the spectrophotometer where its intensity was compared in the usual way with the intensity of light from the same source reflected by another mirror into the other collimator of the instrument. Temperatures were measured by means of a thermo-junction and potentiometer. The apparatus was practically the same as was previously used in the study of the absorption curves of

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[1] J. Becquerel, Compt. Rend., Vol. 151, p. 859; Vol. 151, p. 1344; Vol. 152, p. 183.

[2] H. du Bois and G. J. Elias, Ann. der Phys., Vol. 27, p. 233; Vol. 35, p. 617.

[3] C. E. Mendenhall and R. W. Wood, Phil. Mag., Vol. 30, p. 316.

[4] The word line, as used in this paper, refers to exceedingly narrow bands, which, in the spectrometer, appear to the eye as lines.

certain glass specimens, and is described in detail in a recent number of The Physical Review.[1]

The ruby was irregular in shape, and it was possible to send light through it in two directions. Unfortunately, however, the optic axis of the crystal was nearly at 45° with each of these directions; and for this reason it was found impossible to measure separately and satisfactorily the ordinary and extraordinary absorption curves. As the color of the extraordinary ray is red while the ordinary ray has a violet shade, decidedly different spectra could be expected. Even with this specimen there was a considerable difference in the shape of the ordinary and extraordinary absorption curves at room temperature; but the results were so unsatisfactory that they are not given, and no attempt was made to separate the two spectra at the other temperatures.

Much better results were obtained however in the study of the unpolarized spectrum. Even here trouble was experienced on account of the fact that the faces of the specimen were not quite parallel; and it was found that the intensity of the transmitted light when the ruby was placed in the furnace or in the Dewar flask was not as great as when placed at the same temperature directly in front of the slit of the spectrophotometer. There was however practically a constant ratio between the intensity of the transmitted light at various wave-lengths when the specimen was directly in front of the slit and when in the furnace, and also a constant though different ratio between the intensity when in front of the slit and when in the Dewar flask. Therefore all the values of the per cent. transmission obtained when the specimen was in the furnace or in the Dewar flask were changed by means of the proper ratio to correspond to the values obtained at 20° C. when the ruby was directly in front of the slit.

The values of the coefficient of absorption K were computed by the formula $K = (\log 1/P)/x$, where P represents the per cent. of the incident light transmitted (after correcting approximately for the light reflected at each surface) and x is the average thickness of the ruby, 2.9 mm. The values of $\log 1/P$ were obtained graphically from a curve plotted between values of P and $\log 1/P$.

The transmission and absorption curves are shown in Figs. 1 and 2. The temperatures at which observations were made are indicated in each figure. In order to avoid confusion, some of the values obtained for the per cent. transmission between .50 μ and .58 μ are not plotted in Fig. 1; and in Fig. 2, the curves for the temperatures $-85°$, 100°, and 320° C. are omitted. The amount of spectrum included by the slit-width used (.40 mm.) is indicated in each figure at .46, .56 and .66 μ.

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[1] K. S. Gibson, Phys. Rev., N.S., Vol. VII., p. 194, 1916.

A number of interesting things may be seen from the curves. As the temperature is increased, the point of maximum transmission in the blue shifts from about .469 μ to .493 μ; and there is a shift of the absorption band in the green from about .548 μ to .566 μ (Fig. 2). It is interesting to see how much more the absorption changes with temperature on the red side of the band than on the blue side. This results in a broadening of the absorption band as the temperature is increased.

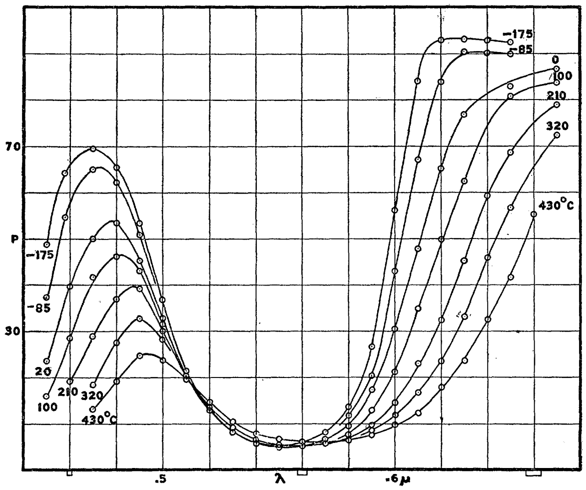

Fig. 1.

Variation of the per cent. transmission P with wave-length λ at different temperatures

It will also be noticed how the transmission band in the blue is nearly cut out at the high temperatures on account of the violet side changing so much faster than the red side. As might be expected, this increased absorption in the blue results in a marked change of color. At 430° the ruby loses all of its rich violet shade and becomes a very light pink. Throughout most of the spectrum there is a large increase in the absorption as the temperature is raised, but in the blue-green the absorption is decreased. It should be remembered that these changes shown by the curves are the result of two separate changes, one in the ordinary and one in the extraordinary spectrum. The curves from .58 μ towards the red are very similar in shape to the curves obtained with the specimens of Cd Se glass studied by the writer, and the changes in absorption are of the same order of magnitude.

THE LINES AND BANDS IN THE ABSORPTION SPECTRUM.

For investigating the changes in the wave-lengths of the narrow absorption bands and lines, a Hilger constant-deviation spectrometer was used. The ruby was placed in a furnace or in a Dewar flask, and light from a carbon arc was passed directly through the ruby and into the slit of the spectrometer. The apparatus was arranged so that readings could be taken of any line or band desired; then the furnace or Dewar flask containing the ruby was rotated out of the path of the light, and readings taken of the known lines of some other source of light; and then the ruby was brought back into position and the previous readings checked.

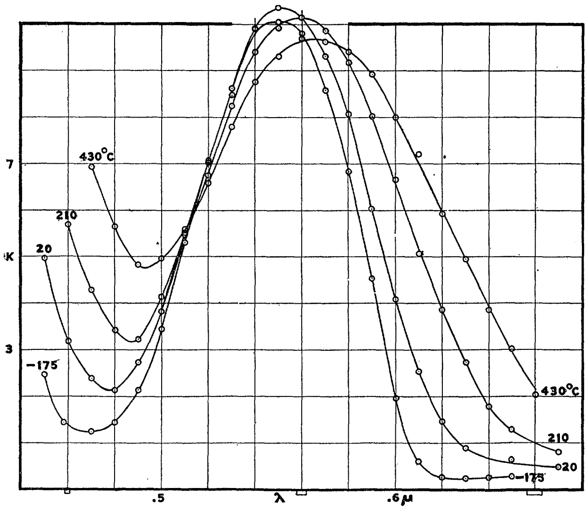

Fig. 2.

Variation of the coefficient of absorption K with wave-length λ at different temperatures.

The absorption lines and bands in the spectrum of the ruby at 20° C. are situated as follows, wave-lengths being given in Ångström units. In the red there are two heavy lines, one at 6943, R_1, and the other at at 6928, R_2; faint bands at 6688, R_3, and 6593, R_4; and in the blue, stronger bands at 4768, B_1, 4753, B_2, and 4687, B_3. In the case of the bands, the wave-length given is for the point of maximum absorption as estimated by the eye. Since the bands are very narrow, this could be done quite accurately.

The known wave-lengths used to determine the positions of R_1 and R_2 were the chromium lines 6978.9, 6924.9 and 6882.7, obtained by drilling a hole in the positive carbon of a carbon arc and filling with Cr_2O_3. The known wave-lengths used to determine R_3 and R_4, and the bands that appeared in the yellow upon cooling, were the lines from a Hg arc; and those used to locate B_1, B_2 and B_3 were the zinc lines 4810.7, 4722.3 and 4680.3, obtained by putting ZnO in a carbon arc.

From five to fifteen readings were always taken upon any one line or band, both in the absorption and in the comparison spectra. The total variation among a given set of readings in the red was never more than five Ångström units and usually not more than three, while in the blue on account of the greater dispersion the variation was very seldom more than two units. The values as given for the lines and bands in the red part of the absorption spectrum are therefore probably accurate to within two or three Ångström units and those in the blue to within one Ångström unit.

In Table I. are given the wave-lengths of the various lines and bands as found at the temperatures indicated, and also the wave-lengths as given by other investigators.

TABLE I.

Number.	Character.	Temperature.	Wave-lengths.			
			Observed.	du Bois and Elias.	Wood.	Becquerel.
R_1......	Line	−180° C.	6934	6932	6934	6932
	"	+ 20°	6943	6941	6946	
	"	210°	6956	(225°) 6960		
	"?	430°	6974			
R_2......	Line	−180°	6919	6918	6920	6918
	"	+ 20°	6928	6926	6932	
	"	210°	6938	(225°) 6945		
	"?	430°	6956			
R_3......	Band?	−180°	6681	6667, 6689		
	"	+ 20°	6688	6666–6701		
R_4......	Band?	−180°	6585	6575–6598		
	"	+ 20°	6593	6575–6605		
Y_1......	Band	−180°	5965	5960–5974		
Y_2......	Band	−180°	5905	5881–5912		
B_1......	Line	−180°	4763	4763		4763
	Band	+ 20°	4768	4769		
B_2	Line	−180°	4747	4746		4746
	Band	+ 20°	4753	4753		
B_3......	Band	−180°	4681	4680		
	"	+ 20°	4687	4684		

As stated before, the wave-length given for the bands is for the point of maximum absorption as estimated by the eye. du Bois and Elias give the wave-length of the edges of most of the bands. At − 180° it was questionable whether R_3 and R_4 were bands or doublets. At 430° it was difficult to distinguish R_1 and R_2 as they are merging into a single band at that temperature. Bands Y_1 and Y_2 break off from the broad absorption band in the green as the temperature is lowered to − 180°. Bands B_1, B_2 and B_3 are very narrow at 20°. B_1 and B_2 become sharp heavy lines at − 180°, but B_3 is not greatly affected. At 210° the increase in the general absorption in the blue, as shown in Figs. 1 and 2, made it impossible to get accurate readings on these bands.

In general, as can be seen from the table, the results obtained agree closely with those obtained by the other investigators, except that the large number of fine absorption lines between 6950 and 7100 which were found by Becquerel and by du Bois at − 190° could not be detected even through a thickness of 14.8 mm. There seems to be quite a discrepancy between the wave-lengths of R_1 and R_2 at 20° as given by du Bois and by Wood.

A detailed investigation into the positions and characteristics of the various lines and bands in both the ordinary and extraordinary spectra has been made by du Bois and Elias. They give colored maps which show very well the appearance of the absorption and fluorescence spectra in the red. The temperature was carried beyond 1000° C. R_1 and R_2 were found to merge into a single band at the higher temperatures.

In Table II. are given the values of the mean wave-length λ, *i. e.*, $(R_1 + R_2)/2$, at various temperatures T from − 190° to 845° C. as found by them.

TABLE II.

T	−190°	−79°	+18°	225°	300°	435°	540°	630°	845° C.
λ	6925	6930	6934	6952	6956	6969	6983	6995	7037

They mention the fact that these values show that the position of the lines changes faster than the temperature, but otherwise make no use of the data.

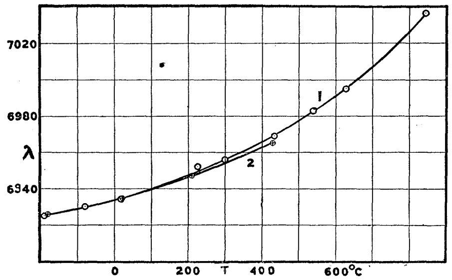

Fig. 3.

Variation of the mean wave-length λ of the absorption doublet, *i. e.*, $(R_1 + R_2)/2$, with temperature T. Curve 1: from values given by du Bois and Elias. Curve 2: as found by the writer.

In Fig. 3 these values are plotted as a curve; and in the same figure a second curve is drawn with the mean wave-length of R_1 and R_2 as found by the writer.

The equation of these curves is of the form,

$$\lambda = a + be^{kT}, \tag{1}$$

where T is the absolute temperature and a, b and k are constants. These constants may be obtained as follows. From equation (1),

$$\log (\lambda - a) = kT + \log b. \tag{2}$$

From this, by differentiation,

$$\frac{d\lambda}{dT} = k\lambda - ak. \tag{3}$$

Therefore if a curve be plotted between values of $d\lambda/dT$ and λ, it should be a straight line, whose slope is equal to k and whose x-intercept gives the value of a.

In Table III. are given values of the wave-length λ at every 100° and also of the slope $d\lambda/dT$ in Ångström units per degree as obtained graphically from the curves in Fig. 3.

TABLE III.

From Curve 1, Fig. 3.

T	$-100°$	$0°$	$100°$	$200°$	$300°$	$400°$	$500°$	$600°$	$700°$	$800°$ C.
λ .	6928.5	6933.4	6939.8	6947.2	6956.0	6965.8	6978.2	6990.8	7006.5	7025.5
$\frac{d\lambda}{dT}$.	.0433	.0555	.0675	.0803	.0908	.1053	.1255	.1457	.1713	.2080

From Curve 2, Fig. 3.

T	$-100°$	$0°$	$100°$	$200°$	$300°$	$400°$ C.
λ	6928.5	6933.4	6939.5	6946.0	6954.0	6962.5
$\frac{d\lambda}{dT}$ ...	.0433	.0535	.0625	.0715	.0820	.0928

These values of $d\lambda/dT$ are plotted against λ in Fig. 4, and evidently lie along a straight line. The value of a seems to be exactly 6900 for both curves. Therefore equation (2) becomes,

$$\log (\lambda - 6900) = kT + \log b.$$

Now if the values of log (λ − 6900) be plotted against the corresponding temperatures, they should give a straight line whose slope is equal to k and whose y-intercept (*i. e.*, the value of log (λ − 6900) when $T = -273°$ C.) gives the value of log b. In Table IV. are given the values of log (λ − 6900), as computed from the values of λ and T given by du Bois and Elias, and as found by the writer.

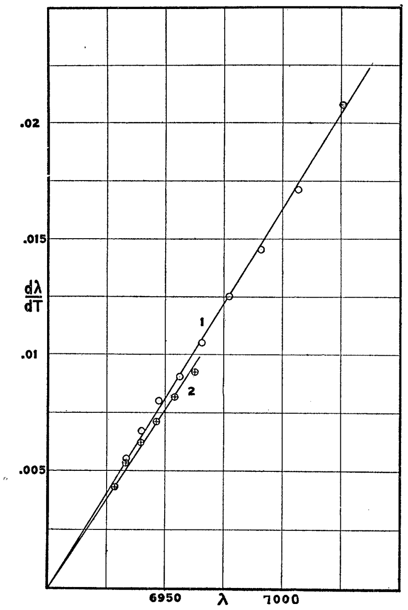

Fig. 4.

Variation of $d\lambda/dT$ with wave-length λ. Values of $d\lambda/dT$ obtained graphically from the curves in Fig. 3.

Table IV.

From Values of λ *and T Given by du Bois and Elias.*

T	—190°	—79°	+18°	225°	300°	435°	540°	630°	845°
λ....................	6925	6930	6934	6952	6956	6969	6983	6995	7037
log (λ–6900)..........	3.219	3.401	3.526	3.951	4.025	4.234	4.419	4.554	4.920

As Found by the Writer.

T	—180°	20°	210°	430°
λ................	6926.5	6935.5	6947	6965
log (λ–6900).......	3.277	3.569	3.850	4.147

In Fig. 5 these values of log (λ — 6900) are plotted against temperature and in each case lie along a straight line. From Curve 1, log b = 3.082 and b = 22. From Curve 2, b = 23. From Curve 1, Fig. 4, and Curve 1, Fig. 5, k = .0163. From Curve 2, Fig. 4, k = .0154, and from Curve 2, Fig. 5, k = .0147, or average k = .015.

Therefore equation (1) becomes, for Curve 1, Fig. 3,

$$\lambda = 6900 + 22e^{.0163T},$$

and for Curve 2, Fig. 3,

$$\lambda = 6900 + 23e^{.015T}.$$

It seems hardly probable that this perfectly definite relation between wave-length and temperature for this pair of absorption lines is accidental. Unfortunately the other lines and bands in the spectrum of the ruby are so broad and indefinite at temperatures much above 20° C. that accurate values of their wave-lengths cannot be determined. The shift of B_1 and B_2 between $-180°$ and $20°$ is fairly definite, but this variation in temperature is too small to be of any value in this connection.

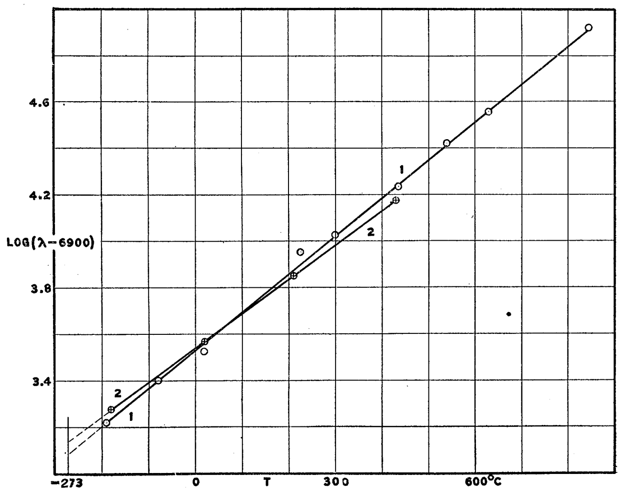

Fig. 5.

Variation of log (λ − 6900) with temperature T. Curve 1: from values of λ and T given by du Bois and Elias. Curve 2: from values found by the writer.

It would be very interesting to know whether or not the lines in different parts of a spectrum obeyed this same general relation, and if so, how the constants varied. It would also be important to know whether the absorption lines in the spectra of other substances obeyed a similar relation; *i. e.*, whether or not the wave-lengths of any or all other absorption lines could be expressed as a similar function of the temperature.

As far as the writer has been able to discover, such a relation between wave-length and temperature has not been previously observed; and with the exception of the above values, taken from the work of du Bois and Elias, no data have been found which would be of value in testing out this relation.

These fluorescence and absorption lines are due to a slight admixture of Cr_2O_3 in the Al_2O_3 of which the ruby is made. It is thus probably more than a coincidence that the chromium spectrum, which was used as a standard in determining the wave-lengths of these two absorption lines, has the three brilliant lines, previously mentioned, in the exact region of the spectrum in which these two absorption lines are situated. And the fact that these lines are due to the slight mixture of Cr_2O_3 in Al_2O_3 may furnish a clue as to the meaning of the relation found above. It is possible that the wave-length 6900, as found, is the mean wave-length of the two lines corresponding to the natural frequencies of the resonators of the active material; *i. e.*, the wave-length corresponding to the frequencies which these resonators would possess if uninfluenced by the surrounding molecules of Al_2O_3 composing the crystal. If that be true, the additional wave-length of 22 or 23 Ångström units at absolute zero might be considered as due to the decrease in frequency of the resonators, brought about by the influence of the surrounding material; and the factor e^{kT}, by which the 22 or 23 is multiplied, would indicate the effect of temperature in changing this influence. This of course is purely a guess, and no attempt has been made to go deeper into the theory of this relation until it is found whether or not a similar relation exists for absorption lines in other substances. It is hoped soon to make such an investigation.

Summary.

1. The effect of temperature upon the absorption spectrum of a synthetic ruby has been studied, and curves drawn showing how the per cent. transmission and the coefficient of absorption vary with the wave-length at different temperatures.

2. The wave-lengths of the various lines and bands in the absorption spectrum have been determined. These values check closely with those obtained by other investigators.

3. A relation has been found between the wave-length λ and the absolute temperature T for an absorption doublet in the red part of the spectrum. This relation is of the form

$$\lambda = a + be^{kT},$$

where a, b and k are constants which may be determined graphically.

The writer wishes to express his gratitude to Professors Nichols, Merritt and Gibbs for their interest and for their many helpful suggestions in connection with these investigations.

Cornell University,
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