

This sum is known, and is equal to $\pi^2/\sin^2 \pi r d$, so that at every point, the sum of the ordinates amounts to τ .

¹ Lewis and Mayer, these PROCEEDINGS, 14, 569 and 575 (1928).

² W. Heisenberg, *Zeits. Physik*, 43, 172 (1927).

³ E. Schrödinger, *Phys. Zeits.*, 27, 95 (1926).

⁴ For a discussion of this phenomenon, see W. C. Mandersloot, *Jahrb. Radioakt. und Elektronik*, 13, 1 (1916). Since, however, our assumptions are different from his, our equations are of a different character.

⁵ Knauer and Stern, *Zeits. Physik.*, 39, 764 (1926).

THE TRANSFORMATION SPECTRUM OF THE RUBY*

BY E. L. NICHOLS AND H. L. HOWES

PHYSICAL LABORATORY, CORNELL UNIVERSITY

Read before the Academy November 19, 1928

The luminescence of the ruby under cathodo- and also under photo-excitation has been investigated, among others, by G. C. Schmidt,¹ J. Becquerel,² Miethe,³ DuBois and Elias,⁴ Mendenhall and Wood,⁵ K. S. Gibson.⁶ As the result of their studies the following characteristics have been established:

1. The activator is chromium, presumably in the form of a chromium oxide, in solid solution in aluminium oxide.

2. The sensitiveness of Al_2O_3 to activation by chromium is extreme—so much so that it is difficult to procure or produce Al_2O_3 which does not glow with the characteristic ruddy glow of the ruby when subjected to cathodo-bombardment.

3. Strictly pure Al_2O_3 does not exhibit luminescence of this type.

4. The most striking feature of the luminescence spectrum is the well-known doublet of narrow bands at 0.6918μ and 0.6932μ .

5. Coinciding as to wave-length with these are narrow absorption bands and it is possible by suitable adjustments to get reversals suggestive of the reversals of the bright lines of flame spectra.

6. In addition to these bands there are in the spectrum various other narrow bands and that these correspond to absorption regions is strikingly shown by maps of the red portion of the spectrum by DuBois and Elias.

7. The bands of both luminescence and absorption are narrowed to line-like proportions by cooling the crystal under observation to the temperature of liquid air, a fact that was utilized by DuBois and Elias in their search for the Zeeman effect.

The similarity of the phenomena summarized above to those brought out in our own studies of the luminescence of the uranyl salts and of solid

solutions activated by traces of the rare earth elements led us to inquire whether the bands in the spectrum of the ruby occur in sets with constant frequency intervals and further to study the cando-luminescence of this interesting substance. The term cando-luminescence is used here, as in a recent monograph,⁷ to denote selective radiation of incandescent bodies not directly ascribable to their temperature. We have found such radiation to be strictly analogous in so many respects to the fluorescence of the same bodies at temperatures below the red heat as to warrant the designation of it as luminescence.

Transformation Bands of the Incandescent Ruby.—To study the visible radiation, a small and somewhat irregular slab of synthetic ruby with unpolished but fairly smooth faces was mounted upon the tip of a vertical splinter of alundum and was heated by the direct application of a hydrogen flame with a reinforcement of oxygen sufficient to give the crystal a temperature somewhat above 1000°C. Under these conditions the spectrum was continuous with regions of unusual intensity in the green and blue. No narrow emission bands were discernible. When the flame was lowered or entirely extinguished and the crystal allowed to cool, various bands appeared, narrow but not line-like. These persisted through a considerable range of temperature, vanishing only as the continuous background disappeared at a lower stage of incandescence. By repeated heatings and coolings it was possible to locate twenty-one such bands between 0.760 μ and 0.426 μ . Some of these could be picked up during rise of temperature also but with greater difficulty.

Temperatures of Appearance and Disappearance.—By the use of a simple device employed and carefully tested out in previous studies of incandescence we were able to determine the upper and lower limits of the range of temperature within which these bands were observed. The method consisted in moistening a minute area, i.e., four or five square millimeters, of the surface of the crystal, with a solution of some uranyl salt, such as the chloride. This upon heating was changed to a thin black coating of oxide which gave with close approximation black-body radiation.

When viewed in the field of an optical pyrometer of the Leeds and Northrup type, the greater brightness of the uncoated crystal as compared with the contiguous "black" patch of uranium oxide was strikingly apparent. This was in agreement with previous studies of the incandescence of the ruby in which three regions of the spectrum (0.42 μ , 0.52 μ and 0.65 μ , respectively) were found to be in excess of ten times as bright at 1000°C. as a black body of the same temperature.⁸

To follow changes of temperature with the pyrometer and to pick up a band promptly as it emerges or disappears, respectively, against the continuous background of the spectrum, requires two observers. Even under

the best conditions the operation is by no means of high precision. A rapid change of temperature favors the prompt recognition of the band but renders the temperature measurement more uncertain. Our determinations gave as the approximate temperature of the appearance of the bands in the red, on cooling 775°C. , and for their disappearance about 610° . By rising temperature (a more uncertain observation) 610° for appearance and 750° for disappearance.

We term this banded structure superimposed upon the continuous spectrum the *transformation spectrum* because the definite temperature range within which it is visible coincides with a striking change in the optical properties of the substance. When a ruby is heated it turns black as viewed by reflected light, and the transmitted light loses the ruddy color characteristic of this material when cold. This change is indicative of and is the result of the profound modifications in the general absorption of the crystal described several years ago in a detailed study by K. S. Gibson.⁹

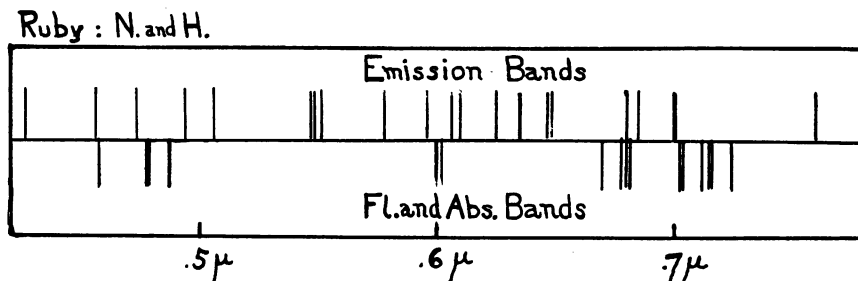


FIGURE 1

The blackening of the ruby upon heating, with loss of color of the transmitted light, was fairly abrupt, and we were able to note that it coincided in temperature with the appearance of the transition bands. A setting with the pyrometer of this change of color in fact gave again the temperature as 610° .

The relation of the twenty-one transition bands to the bands of fluorescence and absorption mapped by DuBois and Elias is somewhat obscured by the very large shift of the bands recorded by these writers toward the longer wave-lengths. That at least one such band persists over a range of more than one thousand degrees (i.e., from -190°C. to $+845^{\circ}\text{C.}$) was noted by them and they determined its position at nine temperatures throughout that range, finding a gradual and constant movement from 0.6925 to 0.7033 or 112\AA. Their settings were made upon the middle position of the strong doublet R_1R_2 which at higher temperatures tends to merge into a single band. We assumed for the purposes of comparison that all bands of the absorption-fluorescence system undergo a similar shift and adjusted the readings of the twenty-three bands given by them

to positions corresponding to the temperature at which our transformation bands were observed.

As may be seen from Table 1 and also from figure 1 there is no obvious relation between the two, beyond the fact that the emission bands tend

TABLE 1

TRANSFORMATION N. AND H.	ABSORPTION AND FLUORESCENCE DUBOIS AND ELIAS	TRANSFORMATION N. AND H.	ABSORPTION AND FLUORESCENCE DUBOIS AND ELIAS
0.760 μ	0.724 μ		0.599-0.602 0.600-0.601
	0.716	0.592	
	0.725		
	0.712	0.578	
	0.704	0.552	
	0.703	0.549	
0.700		0.547	
	0.689	0.506	
	0.686	0.494	
0.685			0.4873
	0.680		0.4865-0.4871
0.679	0.679		0.4849-0.4857
	0.678		0.4856
	0.669-0.670		0.4785-0.4794 0.4777-0.4779
0.649			
0.647		0.473	
0.640			
0.635			0.4575
0.625			0.4570
0.609-0.610		0.456	
0.607		0.426	

to fill in the gaps between the groups of fluorescence-absorption. This is clearly a result of the greatly increased absorption at the higher temperatures which tends to merge individual bands into regions of continuous absorption and to bring out such bands where none were strong enough to be observed at room temperature.

It does not follow that because among the bands of fluorescence and absorption, corrected for the temperature shift as above described, and the emission bands of the incandescent ruby only one coincidence was observed, the two do not belong to the same system. On the contrary when wave-numbers ($1/\mu \times 10^3$) are taken in place of wave-lengths both fall equally well into the same sets of equal frequency interval, as shown in Table 2. The common frequency difference is 36.7, a value very close to the lower interval given by Tanaka¹⁰ in his study of chromium as an activator when in solid solution in CaO, i.e., 36.4.

A convenient method of showing graphically the relation between sets is to plot wave-numbers ($1/\mu \times 10^3$) as abscissae and to divide the or-

dinate axes into equal steps each representing the frequency interval. Since the distance between members of a given set is always an exact multiple of the interval the members will occupy the same position within the steps in which they occur and will lie along a vertical line, and the lines representing the various sets will be parallel.

To bring out upon a greatly exaggerated scale the departures from exactitude of the individual readings a form of diagram suggested by Mr. D. T. Wilber and worked out in detail for the data in the present paper by Miss M. A. Ewer may be used. In this form of diagram the entire base line represents the magnitude of a single step and ordinates are plotted as

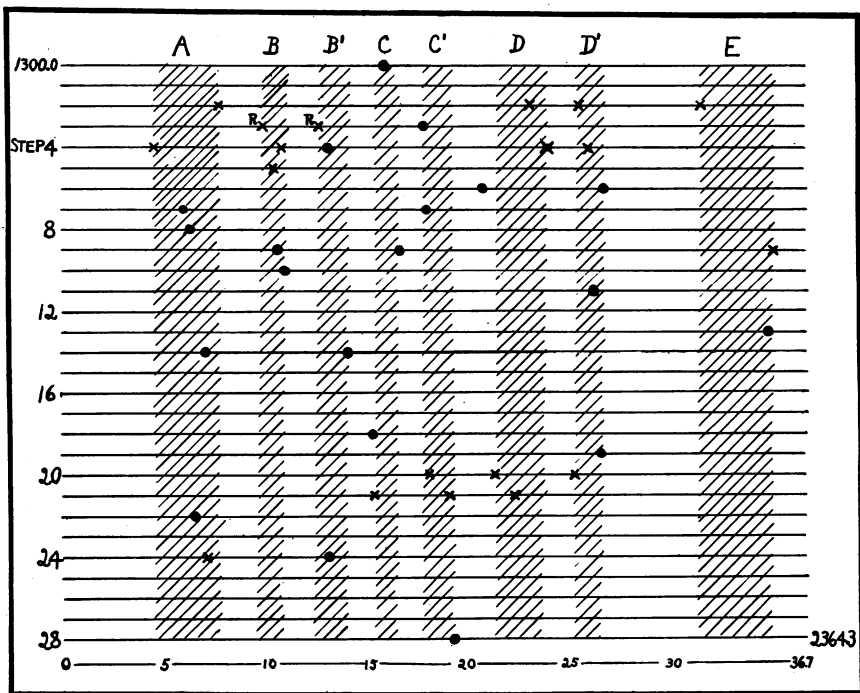


FIGURE 2

wave-numbers arranged in steps. If now readings are expressed in terms of their proper position in the steps in which they occur, by subtracting from each the wave-number corresponding to the beginning of the step,¹¹ their departures from a vertical line, as in figure 2, will show the size and sign of the errors. In the diagram the vertical shaded areas show for each set the limits within which lie all but one somewhat aberrant reading (representing an emission band belonging presumably to Set D).

The absorption spectrum, in addition to the well-known doublet R_1R_2 , with a frequency difference of three units, has other similar pairs of bands;

and if we assume three close-lying pairs of sets with the frequency interval 36.7 ($B-B'$, $C-C'$ and $D-D'$), so located as to contain the members of these doublets, also a single set A, all the known bands of fluorescence, absorption, or emission fall into one or another of these sets excepting two absorption bands and one emission band. The three readings thus excluded are so situated that they could not possibly be considered as belonging to any of the above sets. They are separated, however, from each other by distances which are very closely exact multiples of the frequency interval (36.7), and are therefore put in a set by themselves (E), of which they may be regarded as the only members to be found under the conditions which happened to prevail. It is obvious that throughout broad regions such bands might be invisible because of too great transparency of the crystal at low temperatures, and be obscured at temperatures of incandescence by the strong continuous radiation.

It is notable that although the transformation bands detected by us and some of the absorption and fluorescence bands recorded by DuBois and Elias were of considerable width, there is no instance where the set to which a band belongs is in doubt. The average departure of the readings from the exact corresponding place in the set is, in fact, only 0.7 and there are only three cases out of forty-four where the departure exceeds 1.6 frequency units.

Summary.—1. The spectrum of an incandescent ruby heated in a hydrogen flame was found to have superimposed upon the general radiation a number of rather narrow emission bands.

2. The temperature-range within which the bands are visible, i.e., circa 600°C. to 775°C., corresponds to profound changes in the absorption of light by the ruby.

3. These so-called transformation bands occur in sets having a constant frequency interval of 36.7, of which sets all the known absorption and fluorescence bands of the ruby are likewise members.

4. The phenomena described in this paper are clearly analogous to those previously observed in the incandescence of solids containing various rare earths as activators.

* An investigation carried out under a grant from the Hecksher Fund of Cornell University.

¹ G. C. Schmidt, *Ann. Physik*, **xiii**, 625, 1904.

² J. Becquerel, *Phys. Zeits*, **viii**, 932, 1907.

³ Miethe, *Verh. d. physik. Ges.*, **xi**, 715, 1907.

⁴ DuBois and Elias, *Ann. Physik*, **xxvii**, 233, 1908; **xxxv**, 617, 1911.

⁵ Mendenhall and Wood, *Phil. Mag.*, [6], **xxx**, 316, 1915.

⁶ Gibson, K. S., *Phys. Rev.*, [2], **viii**, 38, 1916.

⁷ Nichols, Howes, and Wilber, "Cathodo-luminescence and the Luminescence of Incandescent Bodies," Carnegie Inst. of Washington, 1928. Publ. No. 384.

⁸ Nichols, Howes and Wilber, op. cit., p. 341.

⁹ Gibson, K. S., *Phys. Rev.*, [2], viii, 38, 1916.

¹⁰ Tanaka, J. *Opt. Soc. Am.*, viii, 287, 1924.

¹¹ The beginning of the first step is chosen arbitrarily and determines the beginnings of all the following steps.

THE EFFECTS OF AN HOMOLOGOUS SERIES OF AMINES
ON THE MOBILITIES OF IONS IN HYDROGEN GAS

BY LEONARD B. LOEB AND KARL DYK

Communicated December 19, 1928

Introduction.—One of the writers¹ has undertaken a study of the mobilities of ions in gaseous mixtures with the hope of arriving at some clue as to the nature of the gaseous ion. That this study has not been in vain is shown in a recent summary of the results published by one of the writers.¹ It indicates that while in some gaseous mixtures the mobilities follow Blanc's² law which indicates no change in the fundamental nature of the ion (its physical radius, not the electrical shortening of its mean free path) in mixing the gases, other mixtures show marked changes. One type of change indicates what may be a sort of change in ionic dimensions, (a statistical clustering); the other the formation of a definite ion due to the rearrangement of the molecule or molecules surrounding the ion caused by an especially great affinity of the ion for one of the type of molecules of the mixture. In such mixtures the first trace of the more active constituent added to a binary mixture abnormally decreases the mobility of the ions, or, using a more convenient form of representation, abnormally increases the resistance to the motion of the ion so that a marked departure of the linear law of resistances in mixtures characterizing Blanc's behavior manifests itself.

One of the most striking results obtained was with NH_3 ⁶ in air and hydrogen where the mobility of the positive ion is increased to nearly the value of the negative ion for quantities of NH_3 of the order of 0.1% or less. This indicates the formation of a less bulky ion (possibly NH_4^+), due to the replacement by NH_3 of some large molecule of impurity to which the positive ion normally attaches itself in air or H_2 . In discussing this phenomenon with Professor C. A. Kraus the latter suggested that a study of some of the amines might prove of interest in this connection since in those cases the size of the molecule could be varied without markedly changing the electro-chemical properties of the gas. Measurements were therefore undertaken in mixtures of hydrogen and methyl-amine (CH_3NH_2) and hydrogen and *N* propyl-amine $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{NH}_2$. The chief difficulty in such studies of organic derivatives lies in the difficulty of obtaining