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INTENSITY MEASUREMENTS IN THE ARC SPECTRUM OF THALLIUM*

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Abstract

Measurements were made by the photographic method of the ratio of the intensities of the lines $2p_2-2s$, $2p_1-2s$ in the arc spectrum with a current of 1.6 amp. using alloys of lead and thallium in varying proportions. The ratio increased with decreasing concentration of thallium reaching a limit at about 0.01 per cent, the effects of absorption being negligible at this stage. The limiting value for $\overline{a_2^2}/\overline{a_1^2}$ is 0.388, where $I=a^2\nu^4$. Commercial lead was found to have a considerable thallium content making it necessary to use chemically pure lead. Measurements of the ratios of intensities of doublets in the principal series $2s-mp_1$, $2s-mp_2$ were made for $m=4$, 5, 6 and 7 the values obtained for $\overline{a_1^2}/\overline{a_2^2}$ being respectively 4.5, 5.7, 6.4 and 7 of which the last two are very uncertain. The values were found to be independent of concentration of thallium and of the current over a restricted range of tests. The fraction of light transmitted through an antimony film reducer was found to vary with wave-length as follows: λ, 6550, 0.270; λ, 5530, 0.243; λ, 5350, 0.243; λ, 4890, 0.175; λ, 3780, 0.093. The diffraction effects recorded by Shenstone were observed and photometer diagrams are given in illustration.

A CONSIDERABLE amount of work has been done by several investigators on the measurement of intensities of doublets in the arc spectra of the alkalies and a number of interesting and important results have been obtained such as the relations between the ratio of intensities in the doublet, the effective quantum number and the atomic number, found by Sambursky.[1] It is therefore a matter of interest that similar observations should be made with another metal giving doublets but belonging to a different group and for this reason this investigation on the arc spectrum of thallium was commenced.

The method employed was the photographic one developed by Professor Ornstein and in general use in the Physical Laboratory in Utrecht.[2] A Hilger quartz spectrograph, type E-2, was used with photogaphic plates of several kinds, namely, Ilford Iso-Zenith, Ortho-Chromatic, Pan-Chromatic and Soft Gradation Pan-Chromatic according to the spectral region being examined.

Density marks were taken on all the plates; these consisted of continuous spectra from a quartz tungsten band lamp, the varying slit method being employed. For the calibration of the lamp and the calculation of the spectral distribution of the energy for the various currents used I am indebted to Mr.D Vermeulen. With most of the plates for each exposure, both of arc and continuous spectra, two intensities were obtained by means of a reducer placed

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* Communication from the Physical Laboratory, the State University of Utrecht.

[1] S. Sambursky, Zeits. f. Physik, **49**, 731 (1928).

[2] L. S. Ornstein, Proc. Phys. Soc. London **37**, 334 (1925).

in front of the slit of the spectrometer. This consisted of a quartz plate on half of one surface of which a thin film of antimony had been deposited by evaporation in vacuum. By this means it was possible to overcome the difficulty arising from the very great differences between the intensities of the lines on the plates found with some of the doublets examined though in the case of each pair, by selection of suitable times of exposure and the use of absorbing screens, many comparisons were made using the same half of the spectrum for both lines so that errors due to inequalitities in the comparatively narrow spectrometer slit were negligible. The two intensities were used mainly to extend the range of calibration of the plate and as a means of checking the trustworthiness of the work by the parallelism of the two graphs obtained when the photometer records of the density marks were plotted against the logarithms of the slit widths. In all cases the transmission of the antimony screen was determined photographically from the distance between the two curves thus obtained so that the values are free from any error which might be introduced in a direct determination with a somewhat different optical system.

Several of the lines examined, in particular that of wave-length 5350A occur in a region where the sensitiveness of the plate changes to a marked degree for a very small spectral displacement, and special care was needed in the calibration of the plates with the photometer in these cases. It was found that when the plateholder was moved up and down in the camera its path was slightly curved so that if the plate were aligned in the photometer in such a way that the images of a given line in spectra at the top and bottom of the plate passed across the middle of the thermopile slit, the images of corresponding lines in spectra in the middle of the plate were appreciably displaced from this position. The path of the plateholder was, however, reproduced with sufficient exactness when the up and down motion was repeated and errors arising from this were minimized by taking many arc spectra on the plate with not more than two continuous spectra between successive arc spectra. By aligning the plate in the photometer for each successive pair of arc spectra satisfactory records were obtained for the intervening continuous spectra, as was shown by the two graphs being continuous and parallel.

THE DOUBLET $2p_1-2s$, $2p_2-2s$.

The first pairs of lines examined was the first doublet in the Sharp series, $2p_1-2s$, $2p_2-2s$ of wave-lengths 5350. 46 and 3775.72. Some difficulty was experienced with these lines because of the feature of plate sensitiveness discussed above and because of the very great disparity between the ratio of intensities of the two lines on the plates and the ratio of the intensities of the continuous spectrum in the same regions. In the final cases with the tungsten band at a temperature of 2750°K the slit widths making the continuous spectrum equivalent to the lines were in the ratio of 40:1, that for the ultraviolet line being the greater. It was found convenient to use in the path of the light a screen consisting of a glass cell containing a dilute aqueous solution of potassium ferrocyanide, which absorbed the ultra-violet to a much greater extent than the green though of course the same occurred in the case of the continuous spectrum. The fact that the transmission of the antimony reducer was more than 2.5 times as great for the green as for the ultra-violet line was also helpful.

These two lines are strongly reversed when the intensity is at all great and to make a satisfactory determination of the ratio of intensities it was necessary to obtain conditions under which the absorption causing this reversal does not occur.

In the first trials an arc was used between poles made of an alloy of lead and thallium; these were rods, 12 mm in diameter forced into slightly smaller hollows in heavy copper rods. The relative intensities of the two lines were measured using alloys with several different concentrations of thallium it being expected that when the proportion of thallium was reduced the effect of absorption would become less because of the smaller amount of thallium vapor in the arc so that the true value of the ratio would be approached. The current was kept at the same value, 1.5 to 1.6 amp. throughout, the supply voltage being 440. With decreasing concentration it was found that the ratio of intensity of the ultra-violet to the green line increased, this being explained by the absorption being greater in the case of the line of shorter wave-length so that this line should gain relatively when the conditions favored decreased absorption. With the strongest concentrations used, probably 2 or 3 percent thallium, a wide range of values was obtained the explanation of which is the lack of homogeneity of the poles, there being comparatively large regions relatively rich or poor in thallium, so that the arc at different times corresponded with alloys of different concentrations. With smaller concentrations of thallium more regular results were obtained, due probably, in part to a more nearly homogeneous alloy, and in part to the fact that the exposures were longer, minutes instead of seconds, so that various parts of the pole surfaces were in turn the source of the vapor in the arc and a more uniform average value was obtained.

The ratio of intensities was found still to increase with extremely small concentrations and, as it was found at this stage that the commercial lead used in making the alloys contained an appreciable amount of thallium, it became uncertain whether even the dilution in this lead without the addition of any thallium would give the limiting ratio sought. Other specimens of lead examined were found to contain thallium but some "chemically pure" lead was obtained in which the thallium content, if any, was certainly very much smaller so that fresh trials were made in which this lead was used to make the alloys. The results of the experiments with the impure lead are shown in the upper part of Fig. 1, the ordinates being proportional to the ratio of intensities (ultra-violet to green) and the abscissas to the logarithms of the concentration of thallium on an arbitrary scale. The latter are certainly incorrect being based on the assumption that the lead was free from thallium.

As in the first method of producing the arc there was a considerable loss of material through the melting of the poles a new method had to be employed with the chemically pure lead, especially as it was clear that very small concentrations of thallium would be required, and therefore very long exposures. A Pfund type of arc was used with copper poles, the alloy being placed in a cup shaped hollow on the lower one. The current had the same value as in the earlier experiments, 1.6 amp. Generally it was not found possible to maintain the arc between the upper pole and the alloy for a long time; either the arc would go out or else run to the side of the lower pole. When this occurred the light was at once cut off and the copper cup scraped free of the layer of lead oxide formed on it and a fresh supply of alloy introduced when the arc could be re-started. In this way spectra were obtained in which the copper lines were relatively weak. When the arc passed from copper to copper the thallium lines were still present but of course corresponded with a much smaller concentration of thallium than that in the alloy under examination. It was much easier to maintain a larger current in this way but the small current seemed more likely to give the limiting value for the ratio of intensities.

By this method of experiment consistent results were obtained with various concentrations of thallium and it was found that a point was reached at which a reduction in the proportion of thallium gave no further increase in the ratio of intensities. Several values with very much smaller concentrations confirmed this.

TABLE I. *Ratio* $\overline{a_2^2}/\overline{a_1^2}$ *for the doublet* $=2p_2-2s,\ 2p_1-2s$ *for various concentrations of thallium.*

Percentage of thallium	Number of observations	Mean value of $\overline{a_2^2}/\overline{a_1^2}$	Mean error
0.072	5	0.093	0.009
0.040	3	0.236	0.040
0.087	10	0.372	0.045
0.0051	2	0.395	0.018
0.00143	1	0.382	
0.00024	2	0.388	0.032

The results are given in Table I and shown graphically in the lower part of Fig. 1. The alloys of lower concentration were made by melting stronger ones with lead and the actual numerical values of the concentrations may not be correct because the lead might contain an amount of thallium comparable with that intended in the weakest concentrations and because in melting the product was always less than the sum of the constituents used there being always some dross in which the metals might be in very different proportions from those in which they are placed in the crucible. In the case of the larger concentrations the errors cannot be great and that the concentration became successively less is shown by the fact that the time needed for satisfactory intensities of the lines became greater for each dilution so that there is no room for doubt that the limiting value was attained. On account of the long exposures required with the smallest concentrations—of the order of an hour—the effect of the "continuous spectrum" became relatively great and the value is not very accurate. On the other hand the others are trustworthy it being considered for example that the error in that for concentration 0.0087 percent is not more than 2 percent.

In Table I and Fig. 1 the ratio $\overline{a_2^2}/\overline{a_1^2}$ is obtained from the ratio of intensities I_2/I_1 by multiplying by the factor λ_2^4/λ_1^4, a_1 and a_2 being the amplitudes of the virtual resonators given by the equation $I=a^2\nu^4$.

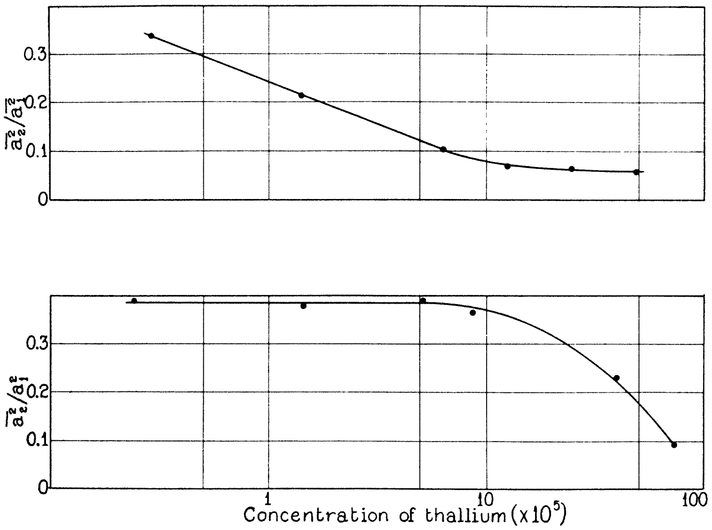

Fig. 1. Values of $\overline{a_2^2}/\overline{a_1^2}$ as a function of thallium concentration.

The values of I_2/I_1 were of course obtained from the ratio determined from the photometer records multiplied by factors for the relative intensities of the lamp radiation at the two regions and for the relative dispersion of the spectrometer.

The limiting values found are

$$I_2/I_1=1.56\ ;\quad \overline{a_2^2}/\overline{a_1^2}=0.388$$

where the suffixes 1 and 2 refer respectively to the line of longer and shorter wave-length.

The last column of Table I gives the mean of the differences between the individual observations and the mean.

THE PRINCIPLE SERIES $2s-mp_1$, $2s-mp_2$.

Measurements were next made of several doublets in this series. The first, occurring in the infra-red could not be attacked by this method but trustworthy determinations were made in the case of the second and third doublets and values were obtained for the fourth and fifth which must be taken simply as indicating the order of the true values as large errors may have been made in their measurement.

The problem is simpler than that of the lines first examined because the separation of the doublets is less and because the effects of absorption are negligible. The Pfund arc was employed, generally with pure thallium though some determinations were made with a lead alloy of 50 percent thallium, and some with a current of 3.5 amp. instead of 1.6, used in most of the work. No appreciable differences were found in the results, justifying the view that the effects of absorption are negligible. That no error was introduced by copper lines in the proximity of lines examined in the case of the first two doublets measured was shown by obtaining spectra of a copper arc with a current of the same value, 1.6 amp., with exposures longer than any used in the measurements. Such lines did not appear, though with a copper arc of 6 amp. copper lines in the neighborhood of the first pair, 6700-6500, were recorded.

The results obtained with these two doublets, recorded below in Table II, show the ratio of intensities, that of shorter wave-length to that of longer, to be distinctly greater for the pair of greater quantum number and attempts were made to obtain values for doublets of higher order. As much longer exposures were needed with these, difficulties arose from the greater continuous spectrum and from the presence of neighboring copper lines not obtained before with the relatively short exposures. Spectra were obtained using poles of carbon and other materials in the hope of obtaining better results. In several cases, mostly with the copper arc, the conditions were such that both lines of one or both doublets were obtained free from appreciable reinforcement from neighboring lines of other elements and of sufficient intensity to allow measurements to be made.

TABLE II. *Ratio* $\overline{a_1^2}/\overline{a_2^2}$ *for doublets in the principal series* $2s-mp_1$, $2s-mp_2$.

m	Wave-lengths	Number of observations	Mean value of $\overline{a_1^2}/\overline{a_2^2}$	Mean error
4	6549.77 6713.69	8	4.5	0.44
5	5527.90 5583.88	11	5.7	0.92
6	5109.47 5136 84	1	6.4	
7	4891.11 4906.3	3	7	1

The values obtained for the doublets in this series are given in Table II. The ratio of $\overline{a_1^2}/\overline{a_2^2}$ rises with the quantum number but in view of the possibility of large error in the last two values it is impossible to decide whether the values conform with the equation found by Sambursky[1] in the case of the alkalies, namely

$$I_1/I_2 = cn^a_{eff}$$

where n_{eff} is the effective quantum number.

As it was impossible for me to remain longer in Utrecht further work could not be done at this stage. It is my intention to continue this investigation on my return to Sydney.

Note 1. The fraction of light transmitted by the antimony screen was determined in the individul cases with an error not exceeding 2 percent. The values, however, were found to vary somewhat according to the part of the screen employed and as it was frequently removed and replaced between the taking of one plate and another a fairly wide range of values was obtained particularly for the shortest wave-length employed. The mean values obtained have some interest and are given in Table III.

TABLE III. *Transmission of antimony film.*

λ	fraction transmitted	λ	fraction transmitted
6549	0.270	4891	0.175
5527	0.243	3776	0.093
5350	0.243		

Note 2. In the first stage of the work there was in many of the photometer records of line 3776 an indication of a companion line on the red side as illustrated in Fig. 2 a. Further examination with altered conditions of the optical system showed that this was a diffraction effect and that similar effects were obtained with many of the intense lead lines. A lack of symmetry of the diffraction pattern in many cases and abnormal intensities of the fringes were observed similar to those recorded by Shenstone[3] whose paper came to hand while this work was in progress. In Fig. 2b is given a photometer record of line 3776 the spectrum being taken with a fine spectrometer slit. In this case the pattern is symmetrical and measurement of the displacements agree closely with those calculated from the ordinary theory.

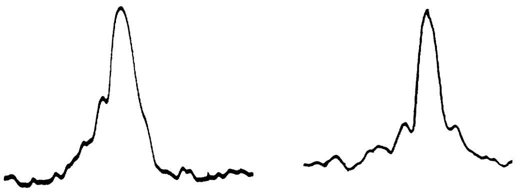

Fig. 2. Photometer records of line 3776 showing presence of secondary maxima, (a) obtained with wide spectrometer slit giving unsymmetrical pattern, (b) with narrow slit, nearly symmetrical.

In conclusion I wish to express my warm thanks to Professor Ornstein for giving me the opportunity, during my stay in Utrecht, of obtaining an intimate knowledge of the research methods used in his laboratory and in particular for his continued interest and help in this work.

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[3] A. G. Shenstone, Phys. Rev. **34**, 726 (1929).