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ON THE RESONANCE LINES OF THALLIUM AND THEIR PROBABLE ABSENCE IN THE SUN

BY

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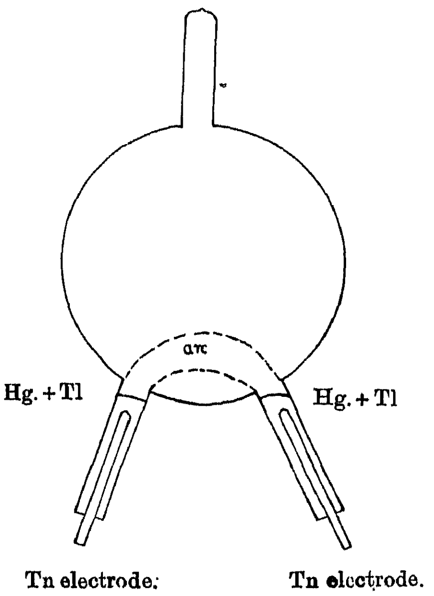
Abstract.—Using a specially constructed vacuum arc containing a two per cent amalgam of mercury and thallium, the wavelengths of the two resonance lines of Thallium λλ 5351 and 3776 (6^2P-7^2S) have been determined by the interferometer method and their intensity variation with current has been studied. The fine structure of these lines has been investigated by using a quartz Lummer-Gehrcke plate (8 mm × 200 mm), a glass Lummer-Gehrcke plate (4·8 mm × 135 mm) and etalons of fused silica plates 2 and 2·5 mm in thickness. The probability of the existence of thallium in the sun has been discussed.

The identification of Fraunhofer lines with those of elements known on the earth is of special interest and importance in view of the fact that, apart from other things, it tells us what constituents are common to the sun and the earth. One of the important methods of identification is based on coincidences with the solar lines. It requires accurate determination of wavelengths. Thallium[1] is represented in the solar spectrum by the two lines 5350.505 and 3775.712 of intensities (− 3) and (− 2) respectively which are the most persistent lines of the element. The existing laboratory measures are correct only to two decimal places. Owing to the fact that the pressures in the reversing layer and chromosphere are very minute the wavelengths in the vacuum arc should furnish an accurate basis of comparison of laboratory wavelengths with solar wavelengths. No attempts have thus far been made to determine the wavelengths of these lines in vacuum. In order to determine whether traces of thallium are to be found in the sun by a more accurate investigation, experiments were started by the author to determine the wavelengths of the important arc lines of thallium in vacuum and to study the behaviour of these lines under different conditions of excitation. In order to eliminate self-reversal and to produce sharp lines, a special type vacuum arc lamp (Fig. 1) was constructed. It was made of pyrex glass into which tungsten electrodes were sealed. The side tubes carrying the electrodes contained a 2 per cent amalgam of mercury and thallium.

Fig. 1.
Hg − Tl vacuum arc.



The cathode was throughout kept cooled by surrounding it with running water. Owing to the very low partial pressure of thallium the lines were found to be extremely sharp. At the same time the lines of mercury served as standards of comparison for wavelength measurements. The wavelengths of the lines were determined by using fused silica etalon plates of different thicknesses. The ring system was projected on the slit of the spectrograph by means of an achromatic focussing lens. Besides this, photographs were obtained also of the arc in air using the second order of a parabolic grating of 11 feet focus. A 12 mm Pfund type of arc with iron poles, carrying a current of four amperes was used. A small quantity of the metal or its salt was placed in a cupshaped hollow in the lower electrode. In this way iron lines which served as standards were photographed simultaneously. It is interesting to note in this connection that with smaller concentration of Tl more consistent and regular results were obtained. The investigations of Dr. T. Royds on the apparent tripling of certain lines in the Arc Spectra (Proceedings of the Royal Society, A, Vol. 107, pp. 360–367) which showed that the behaviour of the Tl 5350 line can be explained as different stages in the self-reversal, will explain the reason for this behaviour.

Wavelength Determination.

For rays of light of wavelength λ incident on an etalon of thickness t, a bright ring will be produced in the focal plane of the lens if $n+\alpha=2t\cos i$. If α is the fractional part of the order of interference at the centre of the ring system, d_p and d_q be the measured diameters of any two rings p and q of the system it can be easily shown that

$$\alpha = \frac{(p-1)\,dq^2-(q-1)\,dp^2}{dp^2-dq^2}$$

The values of α can therefore be calculated from a knowledge of the diameters of any two rings. Knowing α the value of λ can be determined from the relation $2t = n_0\lambda = (n+\alpha)\lambda$.

To determine the thickness t with precision, the etalon was first measured with a gauge. The value was then improved from measurements of known standard mercury lines. The following results were obtained for the thickness of the two etalons used in this investigation:—

	By measurement.	By calculation.
Etalon No. 1	2.55 mm.	2.55397 mm.
Etalon No. 2	1.99 mm.	2.0110 mm.

Experiments show that the penetration into the silver film depends on the wavelength and the distance between the two films varies for wavelength to wavelength. This is interpreted as being due to the change of phase at reflection from silver which varies slightly with wavelength. The usual method of finding the small correction required on this account is by obtaining measurements for the same film but for different thicknesses. In these experiments, it was not possible to adopt this method as the etalons were plane parallel plates of silica. Using the wavelength values of Hg, given above, the values of (phase-change) for different wavelengths were obtained from the following equation :—

$$\epsilon_2 = P_1\frac{\lambda_1}{\lambda_2}\left(1+\frac{d_1^2}{8R^2}-\frac{d_2^2}{8R^2}\right)-P_2$$

When the values for phase-change were obtained for each of the silverings used in these experiments, it is surprising to find that the deviations in the values of phase-change are decidedly large. Attempts will be made shortly to deposit films of silver by cathode discharge and by evaporation in vacuum and determine the range of variation of phase-change. The following mean values were actually obtained for phase-change :—

$$\epsilon = -\ .020 \text{ for } \lambda = 3775.7$$
$$\text{and } \epsilon = -\ .006 \text{ for } \lambda = 5350.5$$

For the determination of wavelengths of the two resonance lines of Tl the following Hg lines were used as standards :—

λ I.A.	λ I.A.	λ I.A.
5790.659 A.	4916.051 A.	3662.880 A.
5769.597 A.	4358.342 A.	3654.832 A.
5460.741 A.		

From the deviations of the individual measurements of the diameters of the rings the probable error of an individual measure is found to be .0035A. In the following table are given the mean values of the wavelengths of the two resonance lines in vacuum arc, by the interferometer method;—

Line designation.	Vac. arc.	In sun.	Sun-Arc.
$6^2P_{\frac{3}{2}}-7^2S_{\frac{1}{2}}$	5350.527	5350.505	-.022
$6^2P_{\frac{1}{2}}-7^2S_{\frac{1}{2}}$	3775.7241	3775.712	-.012

The mean values of λ obtained in arc reversals by the parabolic grating are

5350.4980 A*
and 3775.7297 A.

As the effect of pressure on these wavelengths is not known with definiteness, these values could not be reduced to vacuum.

In Tl as in the allied elements Hg and Bi, complex structure is manifest to a high degree. A study of the fine structure of the two resonance lines by the author has shown that the lines have four or more components spread over a range of nearly 0.15A. On account of this highly complex structure, naturally the accuracy of the results will by no means be the highest of which the method is susceptible. This renders comparison with solar lines difficult.

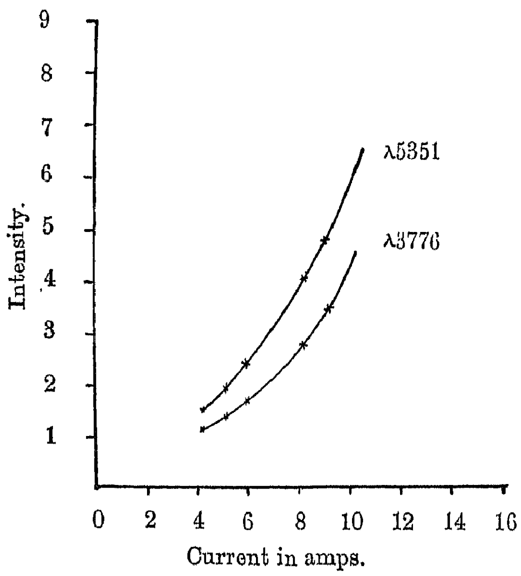
Experiments were tried to determine how the intensity of these resonance lines, produced by the above method, varied with current. Exposures were taken with currents varying from 3 to 10 amperes through the arc. The spectrograms were then measured on a Cambridge Microphotometer for densities.

If d is the density of the line,

$$d = \log_{10} \frac{I_1}{I_2} = \log_{10} \frac{w_1}{w_2}$$

where I_1, I_2 are the intensities of light through the blackened and unblackened portion respectively and w_1 and w_2 are the electrometer deflections. In Fig. 2, the intensities of the lines are plotted against the current and it will be seen that above 6 amperes there is a rapid increase in intensity with current. The increase is more marked in the case of λ5351A.

Fig. 2.



To determine the intensity of the lines in the source in each case density-intensity curves were first plotted for the two lines in the following way. Light from Hg-Tl vacuum arc, carrying a steady current of four amperes is made to fall on a ground-glass screen by a condensing lens. Light from the central uniformly illuminated area on this screen is then allowed to fall on the slit of the spectrograph and spectrograms were obtained with slit widths of 0.4, 0.8, 1.2 and 1.6 mm and the same exposure times. The intensity of light coming through different slit widths and the same exposure as spectrograms is proportional to the slit-width. The plate was microphotometered for density values. Intensity-density curves were constructed from these data at the wavelengths of the two resonance lines.

Hyperfine Structure of the Resonance Lines.

Several investigators have found from time to time that the arc lines of Tl exhibited a fine structure and that the fine structure separations are much smaller than the splitting due to the couplings between the extra-nuclear electrons. Fine structure observed in spectral lines might be due to (*a*) the "Isotope Effect" arising from the difference in the structure of the nucleii and (*b*) a spinning nucleus. In the latter case it is the interaction between the magnetic nucleus and the resultant mechanical moment of the extra nuclear electrons "J" that contributes to the hyperfine splitting of the levels. By analogy with the spinning electron, a spinning nucleus is associated with a mechanical moment ($= \frac{ih}{2\pi}$) where i is the corresponding spin moment quantum number of the nucleus. It has been shown in recent years that there is a close similarity between the ordinary multiplets and the hyperfine multiplets. The theory predicts that the fine structure separations

* It is quite possible that this low value is due to the high density employed blending the main components.

follow the interval rule accurately From the hypothesis of nuclear spin several investigators obtained intensity formulae which are found to hold good exactly in the case of several h f s There are, however, large discrepancies between the predicted and observed intervals even in relatively simple cases

The fine structure of the arc lines of Tl has previously been studied by Ruark and Chenault[2], by Back[3], by Wali Muhammad[4], and more recently by McLennan and Crawford[5], by Schular and Keyston[6] and by Jackson[7] There seem to be considerable differences between the results of the different investigators The deviations in some cases are so large that it is difficult to interpret them as such

Fine structure patterns are not generally completely resolved owing to the effect of electric fields and pressures in broadening spectral lines Owing to the extremely low partial pressure of Tl vapour in the above mentioned source, it was felt that it would be particularly useful for the study of fine structure A systematic study of the fine structure of the arc lines of Tl, particularly the two resonance lines, was therefore undertaken by the author, using for the purpose a quartz Lummer-Gehrcke plate (8 mm × 200 mm), a glass Lummer-Gehrcke plate (4 8 mm × 135 mm) and fused silica plate etalons of 2 and 2 5 mm thickness

Discussion of Results

As there seemed to be a considerable amount of divergence in the results of the earlier investigators, it is proposed to deal in the following lines, only the more recent results

In a note to "Nature" (October 17, 1931) it was pointed out by the author that λ 5351A was a quartet and that its structure could be interpreted by assigning an isotope displacement of about 0 05 cm^{-1} and that the line λ 3776 exhibited a very complex structure consisting of five components though no isotope effect was found in this case Schuler and Keyston independently found a similar isotope displacement in the case of λ 5351 while McLennan and Crawford discovered no trace of isotope shift

Schuler and Keyston and Jackson found the line λ 3776 to be a triplet and the structure was interpreted by the former by supposing the absence of an isotope shift Further observations were made by the author on the structure of this line under different conditions of excitation These subsequent photographs clearly showed the line to be a group of six components The following table gives the structure of these lines as observed by the author —

Line	Fine structure components		In A	In cm^{-1}
λ 5351	a		0 000	0 000
		A	−0 015	0 053
$6^2P_{\frac{3}{2}} - 7^2S_{\frac{1}{2}}$	b		−0 110	0 385
		B	−0 128	0 448
λ 3776	a		0 000	0 000
		A	−0 007	0 050
$6^2P_{\frac{1}{2}} - 7^2S_{\frac{1}{2}}$	b		−0 054	0 380
		B	−0 064	0 450
			−0 117	0 820
	c		−0 154	1 080
		C	−0 165	1 150

From a consideration of the distribution of the satellites indicated in the above table it is found that the complex structure of λ 3776 could be quantitatively interpreted if we suppose that the "${}^2P_{\frac{1}{2}}$" term like the "${}^2P_{\frac{3}{2}}$" term shows an isotope displacement of about 0 060 cm^{-1} Microphotometric traces of the Lummer pattern for λ 3776 for two different current values are shown in Fig. 3. The level schemes are shown in Fig. 4. There is however a component at − 0·117A which does not find a place in the above scheme.

Fig. 3 (*a*).

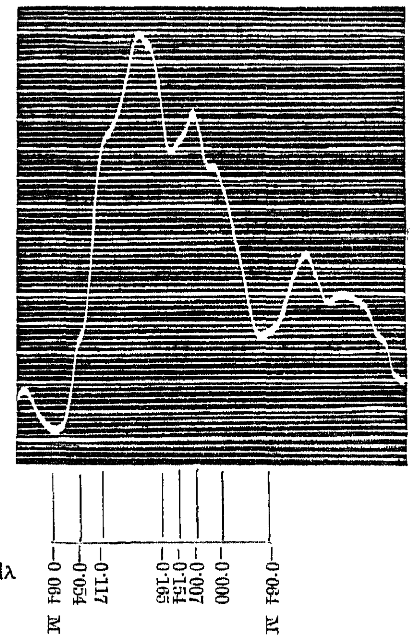


Fig. 3 (*b*).

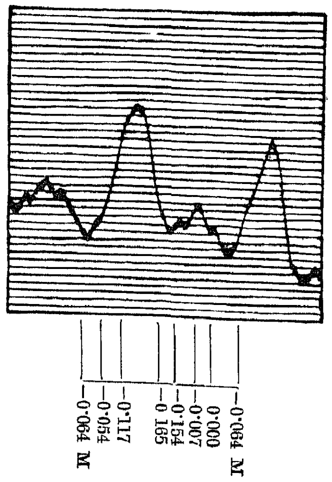
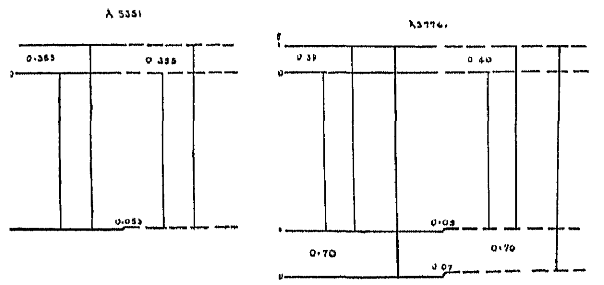
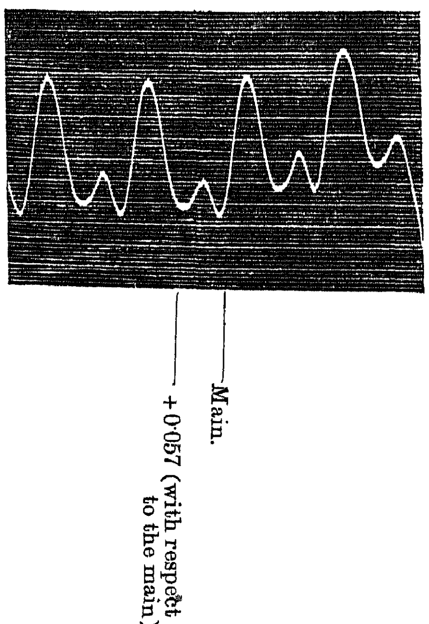


Fig. 4.



This has also been observed by Wali Muhammad. The structure now given removes the anamoly noted by Schuler and Keyston in the isotope displacement of $^2P_{\frac{1}{2}}$ term. It is interesting to note in this connection that Jackson [8] also made more careful observations and revised his former results and recently proposed a level scheme which is substantially the same as mine. Only, the satellite at − 0·117A is not found in his measurements.

Fig. 5.



As has recently been pointed out in a note in "Current Science," [9] it is very remarkable that slight variations in the excitation result in marked changes in the relative intensities of the components as will be seen from the microphotometric traces. Pressure conditions seem to be very important in the excitation and therefore in the intensity relationships of the fine structure patterns. It is nevertheless difficult to see how these slight variations in excitation can influence the interaction between the nucleus and the electron shell. Fig. 5 represents the microphotometric trace of the same line, when photographed with a fused silica plate etalon of thickness 2 mm and shows the satellite at 0·057A (with respect to the main) which is obviously almost as intense as the main line itself.

In the case of spectral lines like these which exhibit a complex structure, particularly when there are two or more components whose intensities are nearly equal, it would appear more reasonable to take the centre of gravity of these components constituting the radiation as the position for the wavelength measurements.

Absorption of Resonance Lines.

Some time back the author studied the absorption of $\lambda\lambda$5351 and 3776 of Tl by a column of nonluminous vapour. It was found that as the temperature of the vapour was raised, general absorption of the central doublet commenced at about 600°C and it was completely extinguished at about 800°C while at this temperature the satellite was but a very little absorbed. With further increase of temperature, absorption of the satellite took place till it was complete at about 1000°C.

Further, in view of the fact that both these lines coincide with very faint solar lines and the line λ 5351 does not appear to be strengthened in the spot spectrum while generally all the arc lines are considerably enhanced, it would appear that the evidence for the identification of thallium in the sun is very meagre. The available evidence for Tl as a probable constituent of the sun does not therefore appear strong enough to justify its inclusion. It is more probable that these coincidences are due to chance. And we must conclude that there is no evidence at present for the existence of Tl in the sun.

In conclusion, it is a pleasure to express my thanks to Dr. T. Royds, the Director, for his unfailing interest.

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