"BAND SPECTRA ASSOCIATED WITH THE MOLECULES OF ZIRCONIUM"

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BAND SPECTRA

ASSOCIATED WITH THE

MOLECULES OF ZIRCONIUM

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GENERAL INTRODUCTION.

The fourth group in the periodic table is distinguished in that the elements lying in it are extensively observed in stellar and solar spectra. In fact compounds of three of the elements of this group C_2, TiO and ZrO characterize three different spectral classes. Most of the elements within the group possess extensive band systems for their oxides, fluorides, hydrides etc. More systems are known for CO than for any other oxide.

While an appreciable amount of data has been furnished for molecules like CO, CH, CN, SiO, SiH, SiN, GeO, SnO etc. from laboratory work, very little is known for the corresponding molecules of TiO, TiN, TiH, TiF, ZrO, ZrF or ZrH. Complaints have been made from time to time about the extreme inadequacy of the experimental data for the compounds of Titanium and Zirconium. Both of these are important from the point of astrophysics. If spectra of various molecules of Titanium and Zirconium are obtained in the laboratory, possibly many of them may be identified in stellar spectra as well. Two very prominent band spectra observed in the stars are those due to TiO and ZrO. Even here the laboratory data are inadequate. Some of the bands already assigned remain doubtful, while a great number of conspicuous bands have not been classified. Doubts have, recently, been raised about the nature of the energy levels involved in the systems already classified. There also appears to be some doubt about the accuracy of the evaluated

molecular constants.

This inadequacy in the analysis may partly be due to the complicated nature of the band spectra of the compounds of Titanium and Zirconium, but the spectra of CO, SiO, GeO, SnO etc. have been worked out far more completely than those of TiO or ZrO, although they hardly command any astrophysical importance. The demand for more experimental work for TiO and ZrO is thus understandable.

Moreover, there is complete absence of knowledge about the spectra of molecules other than TiO, ZrO and TiCl. Molecules like TiH, ZrH and TiF, ZrF may very possibly exist in stellar atmospheres. It is difficult to prove their existance or absence until we have produced their spectra in the laboratory. Also, this failure to produce the spectra of these molecules cannot all be attributed to experimental difficulty, but we have to admit that little effort has been directed in this direction, so far.

Finally, there are the spectra of HfO and ThO. Both of these may be supposed to be very similar to TiO and ZrO. Though both of these molecular spectra are known to exist, it is certain that almost no effort has been made to classify them.

The author undertook the study of the spectra of the compounds of Zirconium. Three molecules ZrO, ZrF and ZrH were subjected to extensive study. While previous data were available for ZrO, nothing was known about the spectra of ZrF and ZrH. The author succeeded in improving our information about the molecule of ZrO, and reported several new systems for it. Spectrum of ZrF has

been obtained, but no analysis has been possible; while all efforts failed to produce the corresponding spectrum for ZrH, in spite of the use of a wide variety of sources.

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ZIRCONIUM OXIDE.

INTRODUCTION:

(Experimental data for ZrO & TiO already known from previous work).

Early work in this field was undertaken by The Astrophysicists. Prof. Fowler[1] in 1904 measured the band heads of Titanium Oxide, and identified them in M type stars. In 1922, Merrill[2] photographed the spectrum of ZrO from a Carbon arc in air, on whose lower pole had been placed some Zirconium compound. He also identified these bands in stellar absorption, and recognised a new class of stars, later designated as S, wherein bands of ZrO appeared in absorption. In 1926, A. S. King[3] observed the band spectra of TiO and ZrO in his furnace experiments. A small quantity of metallic powder was placed in a graphite tube, which was electrically heated, and through which a stream of Oxygen was constantly passed. While TiO bands appeared at 1900°c, and attained a max. intensity around 2550°c, ZrO showed up only at about 2400°c, while the full spectrum of ZrO could only be observed at 2550°c.

Bands of TiO and ZrO have also been observed in spark spectra. Quite recently Johnson[4] has also photographed and measured the bands of ZrO. However he only confirmed the work of his predecessor, Miss Lowater[5], who is the chief contributor in the field and whose work we will report in rather more detail.

The TiO spectrum was the first to be analysed. Christy[6] in 1927 photographed the spectrum on a 10-ft. grating using a carbon arc, on the lower pole of which had been placed a quantity of TiO.

An effort to produce the TiO spectrum from a discharge tube filled with streaming vapour of $TiCl_4$ and Oxygen (method for SiO used by Jevons) was not very fruitful. Christy studied the bands of TiO lying in the blue region and presented a vibrational analysis of these bands. He also analysed the rotational structure of the (o,o), (1,o) and (o,1) bands. The numbering of branch lines could not be carried right down to the origin, as the bands remained unresolved to both at the origin and at the head. Using the combination principle he determined, B_o'', D_o'', B_1'', α_o'', B_o', B_1', D_o' and α_o' from rather large J valves.

As Christy's work had left many bands in the orange, the red and the infra-red still unclassified, Miss Lowater[7] in 1927 analysed two more systems for the TiO molecule in these regions. Where as the more extensive of these three systems (designated as γ) appeared to extend from red to infra-red, and was a triplet system like the one observed by Christy (now designated as α), system β consisted of a single (o,o) sequence with single R and single Q heads. (Since that time many fruitless efforts have been made to relate the bands in this system β to triplet levels). Miss Lowater came to the conclusion that system α was due to a $^3\Pi \rightarrow {}^3\Pi$ transition and system γ was due to a $^3\Sigma \rightarrow {}^3\Pi$ transition, the final $^3\Pi$ level being common to both. She further concluded that system β involved a $^1\Pi \rightarrow {}^1\Sigma$ transition. By postulating an analogy between the spectra of TiO and Ca she came to the conclusion that the $^1\Sigma$ level was likely to be the ground state of TiO.

In 1937, Wurm and Meister[8] reported more bands of TiO in the region $\lambda\lambda$ 8260-11250, and identified them in stellar spectra. In the same year Dobranravin[9] published the analysis of the above bands; and discovered one more triplet system involving a $^3\Sigma \rightarrow {}^3\Pi$ transition in the far infra-red. By his work Dobranravin established the analogous nature of the spectra of TiO and ZrO; and showed that they both possessed three conspicuous triplet systems, the first two of them involving a $^3\Sigma \rightarrow {}^3\Pi$ transition and the third a $^3\Pi \rightarrow {}^3\Pi$.

System β of TiO remained doubtful, and was until recently considered to be related to unidentified triplet levels. The formulae Miss Lowater furnished for it was as follows.

$$\nu_R = 17909.04 - 99.54\,(v+\tfrac{1}{2}) - 0.302\,(v+\tfrac{1}{2})^2$$

and $$\nu_Q = 17890.06 - 99.58\,(v+\tfrac{1}{2}) - 0.257\,(v+\tfrac{1}{2})^2$$

For the energy levels in systems α, γ and the one analysed by Dobranravin the following constants were determined.

Levels	ν_o	ω_e	$\chi_e\omega_e$	B_e	α_e	D_e
$X^3\Pi$	o	1009.07	4.75	0.53515	0.00276	-6.040×10^{-7}
$A^3\Sigma$	11284.2	908.8	2.3	----	----	----
$B^3\Sigma$	15037.7	866.24	3.82	----	----	----
$C^3\Pi$	19349.29	837.86	4.55	0.49022	0.00372	-6.71×10^{-7}

The multiplet separations in the $X\,^3\Pi$ state were 68.2 and 74.8 cm^{-1} while in the $C\,^3\Pi$ state they were 64 and 66 cm^{-1}.

THE SPECTRUM OF ZrO.

Band spectra of Zirconium Oxide have been reported as early as

1905, when Hgenbach[10] and Konen[11] observed them in the spark in air between Zirconium electrodes. Later on Eder[12], Valenta[13] and Bachem[14] also published wavelength data of these bands. The last of these authors attributed to the same molecule (Zirconium Oxide) five other bands degrading to the shorter wavelength in the region λ 3090 to λ 2178 . Finally in 1922, Merrill[2] photographed the bands of Zirconium Oxide in the visible from an arc, and identified these bands in the spectra of some of the stars. His conclusions regarding the temperatures of these S type stars were later on confirmed by Kings experiments with his electric furnace.

In 1931, Miss Lowater[5] photographed the band spectrum of Zirconium Oxide on larger dispersion. She extended the observations and the measurements both in the infra-red and the ultra-violet. The source used by her was a Pfund arc, with iron or copper poles, on the lower pole of which was placed a quantity of chemically pure Zirconium Oxide. A current of about 5 amps was necessary to maintain the bands from the iron arc, while 9 amps were required with that of copper. It appears that the best excitation condition of the Zirconium Oxide bands were not attained, and impurities of the atomic spectrum of Zirconium and the pole material were fairly strong. To quote Miss Lowater:

"Many iron lines appeared within the band spectrum, and were used as standards; they enabled one to avoid errors that might otherwise arise from a slight shift between the band and comparison spectrum ..... The wavelengths of the heads of the bands which were hidden by iron lines in the band spectrum were determined from

spectograms taken with copper arc. The numerous atomic Zr lines included in the spectrum were identified by reference to the tables of the wavelengths of Zr lines published by King and by Kiess[15]."

From her analysis of these bands, Miss Lowater proved that the emitter was the ZrO molecule. She established the identity of three systems. The one lying in the red and extending to the infra-red was a $^3\Sigma \rightarrow {}^3\Pi$ system. It was also the strongest of the three. The chief feature of this ~~spectrum~~ system γ was the presence of three separate sequences to each main sequence, consisting of sharp and strong R heads, and comparatively weaker diffused QX heads to the longer wavelength. Miss Lowater was not certain whether these X heads were in the Q or in the P branch. At the other end of the visible spectrum, in the blue, was a system, quite as conspicuous, though a little weaker, and distinguished by the absence of X heads. The three separate sequences had very small separations, and each band had a sharp single head in the R branch. This system, α, was postulated to be due to a $^3\Pi \rightarrow {}^3\Pi$ transition sharing the final level with system γ. Finally in the yellow region of the spectrum was another system, β, partially superposed on system γ. Although system β resembled system γ very much in possessing as large triplet separations and strong X heads attached to sharper R heads, the transition responsible for this system was somewhat doubtful. However Miss Lowater came to the conclusion that it was also due to

a $^3\Sigma \rightarrow {}^3\Pi$ transition, the final triplet level being the same as that in systems α and γ . Designating the energy levels of ZrO as identified by Miss Lowater, by the usual X, A, B, C etc. notation, the three systems α, β and γ involved the following levels:-

Red system	γ	$A\ ^3\Sigma \rightarrow X\ ^3\Pi$
Yellow system	β	$B\ ^3\Sigma \rightarrow X\ ^3\Pi$
Blue system	α	$C\ ^3\Pi \rightarrow X\ ^3\Pi$

The vibrational constants of these levels, as evaluated by Miss Lowater will be presented later on. At this stage it should be mentioned that in-spite of the classification of the ZrO spectrum into three triplet systems, a large number of bands were left unidentified. Many of these unclassified bands are fairly conspicuous, and are also observed in stellar absorption. The classification is most complete in the red and the blue regions. Most of the unclassified bands were in the ultra-violet and the yellow regions.

Here we should mention that Miss Lowater was not satisfied about the discontinuities, and gaps in the Deslandres table for the system α . Not that this made the analysis doubtful, but that explanation of the incompleteness of the table was not forthcoming. On the next page we reproduce the Deslandres table for the system α as constructed by Miss Lowater. The discontinuities are fairly evident.

Less conspicuous bands in the ultra-violet could not be classified into a system, for the bands differed in general appearance from systems α, β and γ, and the expected triplets could not be recognised.

TERM ANALYSIS TABLE FOR SYSTEM OF Pr^3
(after Nies Lowater)

v/v''	0	$0\ \Delta''\frac{1}{2}$	1	$1\ \Delta''\frac{3}{2}$	2	$\Delta''\frac{5}{2}$	3	$\Delta''\frac{7}{2}$	4
0 a	21639.8	(931.3)	20708.5		-------		18868.9	(910.6)	17958.3
0 b	21556.0	(931.2)	20624.8		-------		18784.6	(908.6)	17876.0
0 c	21543.1	(930.9)	20612.2		-------		-------		17863.4
	(814.7)		(815.5)						
$\Delta'\frac{1}{2}$	(812.6)								
	(814.3)								
1 a	22454.5	(930.5)	21524.0		-------		-------		
1 b	22368.6		-------		20513.3		-------		
1 c	22357.4		-------		20502.4	(914.8)	19587.6		
$\Delta'\frac{3}{2}$	(808.9)						(804.6)		
2 a	-------		-------		-------		-------		
2 b	23177.5	(930.8)	2246.7		-------		20403.5		
2 c	-------		2234.6		-------		20392.2		
$\Delta'\frac{5}{2}$			(799.5)				(802.4)		
3 a			-------		-------		-------		
3 b			-------		22121.3		-------		
3 c			23034.1	(922.6)	22111.5	(916.7)	21194.6		
$\Delta'\frac{7}{2}$					(797.8)				
					(794.9)				
4 a					-------				
4 b					22919.1				
					22906.4				

THE ROTATIONAL STRUCTURE OF ZrO.

Spectograms of the (1,0), (0,0) and (0,1) bands of system α were obtained by Miss Lowater[16] in The Third order of the ten ft. grating. In-spite of having resolved the lines down to 0.03 A the band heads remained unresolved. However she was able to carry out the numbering of branches right down to the origin, although the presence or absence of low J lines could not be established with certainty, and consequently the Ω values for different sub-levels of 3Π states could not be determined in this way. However in a $^3\Pi \rightarrow {}^3\Pi$ transition the intensity in Q branches is proportional to Ω^2. The intensity of Q branches in $^3\Pi_2 \rightarrow {}^3\Pi_2$, $^3\Pi_1 \rightarrow \Pi_1$ and $^3\Pi_0 \rightarrow {}^3\Pi_0$ transitions will be in 4, 1, 0 ratio. Since Q branch could only be established with certainty in $^3\Pi_a \rightarrow {}^3\Pi_a$ bands, it was concluded that a, b and c sub-levels corresponded with $\Omega = 2$, 1 and 0 respectively. The tentative diagram of ZrO as previously constructed by Miss Lowater, had to be slightly altered. Miss Lowater determined the rotational constants in the C $^3\Pi$ and X $^3\Pi$ states of ZrO with great accuracy.

Recently Tanaka and Horie[17], photographed the (0,0 and (1,1) bands of γ system in the first order of 20 ft. grating. Their present work inspires little confidence; as it contradicts from place to place certain deductions by Miss Lowater. The X heads, which have been observed by Miss Lowater and whose existance in system γ has been evidenced by Johnson, Merrill, and finally the present author, were not observed at all by Tanaka and Horie, who tried to explain the fact, by assuming that they originated from a level other than $A\,^3\Sigma$ (the initial level of system γ). They

also tried to confirm this by showing that the levels in $A\,^3\Sigma$ state were perturbed, the perturbation being maximum for J=0 level and decreasing for higher levels asymptotically. Furthermore, they were able to discover the Λ type doubling in the $X\,^3\Pi$, ground state of ZrO. They found that $\frac{1}{2}\{\varphi_c(J+1) - \varphi_d(J+1)\} + \frac{1}{2}\{\varphi_c(J) - \varphi_d(J)\}$ was about 1.5 cm^{-1} for $^3\Pi_0$ level and zero for $^3\Pi_1$, and $^3\Pi_2$ each.

Isotopic lines due to $Zr^{92}O^{16}$ and $Zr^{94}O^{16}$ were discovered both by Miss Lowater and by Taneka and Horie. Other bands of ZrO, in the infra-red have been reported by Meggers and Keiss[13], while Herbig[19] has tried to prove that λ3682 band of ZrO is due to a $^1\Sigma - ^1\Sigma$ system.

NITRIDE.

Main State	Sub-States	ω_e cm^{-1}	$x_e\omega_e$ cm^{-1}	B_e cm^{-1}	α_e cm^{-1}	$D_e \times 10^7$ cm^{-1}	r_e A°
X $^3\Pi$	$^3\Pi_0$			0.6244	0.0107	-11.088	1.406
	$^3\Pi_1$	937.20	3.346	0.6189	0.0045	-10.778	1.413
	$^3\Pi_2$			0.6150	0.0059	-10.590	1.417
A $^3\Sigma$		856.97	3.373	0.5658	0.0077	---	1.477
B $^3\Sigma$		846.28	3.409	---	---	---	---
C $^3\Pi$	$^3\Pi_0$			0.5211	0.0054	-8.406	1.539
	$^3\Pi_1$	820.58	3.306	0.5333	0.0123	-9.009	1.521
	$^3\Pi_2$			---	---	---	---

NEW BAND SYSTEMS OF ZrO.

INTRODUCTION TO EXPERIMENTAL PROCEDURES.

The sources previously employed for the production of the band spectrum of ZrO have usually been various types of arcs. However, in 1924, A. S. King[3] used a furnace to heat the metallic Zirconium, in a stream of Oxygen, and thereby obtained the ZrO bands. The author has not tried this method, as such a furnace was not available. The only source for the production of ZrO spectra, that has been employed for large-dispersion photography is the Zirconium arc in air.

Miss Lowater used a Pfund arc or a similar one with copper poles, pure ZrO being put on the lower electrode. The current required to maintain the bands was 5 amps and 9 amps respectively with iron and copper electrodes.

The best excitation conditions for ZrO bands were not obtained, since the atomic spectra of both Zr and the electrode material are very strong, and sometimes hide weak bands. The atomic spectrum of Zr is a very complicated one with many weak lines, sometimes closely grouped together. If weak lines fall on the bands; it becomes very difficult to assess the true position of the heads, as the weak lines appear very similar to the band heads on a strong background.

Fortunately, in the visible region, the atomic spectrum of Zirconium is not very strong, and the band systems are very strong. This makes it possible to sort out the strong band heads, compute for the weaker ones belonging to the same system and search them out.

But even then the line spectrum masks many weak bands, as will

be found for system α . In the near ultra-violet region where ZrO band systems become very weak, and the corresponding atomic lines too numerous, it is not easy to locate the heads. Sometimes weak lines grouped together give the appearance of a band, at others the weak lines falling on the head conceal it. The best example of this is furnished by the ZrO band at λ3571.9, which has now been assigned to (1,0) band of the new singlet system A. This band is slightly more intense than the (2,0) band of the same system at 3539.9 A. The latter Miss Lowater has observed and measured, but overlooked the former completely. The head of the band at λ3571.9 falls in a region where many strong Zirconium lines are closely grouped, the band being virtually hidden by the strong Zr line at λ 3572.5. Other weak bands were ignored altogether. It will be seen later on that many weak bands measured by Miss Lowater in the ultra-violet, have been identified with weak lines by the author. The author has tried to ascertain the origins of these lines without success. Unfortunately in Harrison's "Wavelength Tables" these spurious bands have been included under the caption of ZrO. Evidently their wavelengths have been taken from the published papers by Miss Lowater.

The author succeeded in improving the technique and obtained spectograms in which the intensity of the atomic lines was far below the bands. In fact bands became the dominant feature in the ultra-violet region, and in the visible only a few weak lines are visible on the band structure. This made it possible to assess accurately the position of the heads, as well as to observe weaker

bands, and to study the characteristics of the bands and heads (to determine the multiplicity). In the table below, the wavelengths of the bands in the ultra-violet, reported by Miss Lowater, are compared with those thus observed.

λ	I	Author's remark	λ	I	Author's remark
3472.43	5	Observed (3)	3515.79	2	Absent
3491.84	5	Absent	3539.81	3	Observed (6)
3491.97	6	Observed (3)	3593.07	2	Absent
3506.22	5	Observed (3)	3598.92	2	Absent
3508.24	5	Absent	3682.43	6	Observed (10)
3511.93	2	Absent	3726.31	3	Absent

It will be seen that out of twelve bands measured by Miss Lowater only five have been observed. The rest appear to be spurious for one reason or the other. In the table below are reproduced the wavelengths of these bands, and the reasons for their being mistaken for band heads.

Table of γ Wavelengths of Seven Bands and Reason of their spuriousity.

Band heads as measured by Miss Lowater.	Reason for being mistaken for band heads
3491.84 (5)	A line
3503.24 (5)	A faint line - perhaps the edge of 3509.32 Zr line ?
3511.99 (2)	A very faint broad line.
3515.79 (2)	A faint line.
3593.07 (2)	A faint line on strong band
3598.92 (2)	A faint line.
3726.31 (3)	A faint line.

Miss Lowater herself was doubtful about the bands in the ultra-violet of which she speaks as follows:-

".....; in the ultra-violet region there is a system differing in general appearance from α, β and γ, for the bands are much weaker and the triplets not easily recognisable. Comparison of these less conspicuous bands with those of Titanium oxide and of Hfnium Oxide measured by Meggers and King[20] shows that they are not due to these oxides, which might be present as impurities."

Having discussed the difficulties in the production of

reliable spectra of the ZrO bands, we proceed to describe the methods employed in the present work. This is confined to the use of low and High Voltage arcs under various conditions.

LOW VOLTAGE ARCS.

In using the low voltage arcs, the only electrode material found suitable was copper. The possibility of the use of Carbon electrodes was ruled out, since the carbon arc gives the bands of C_2 in the visible, and of CN as well in the near ultra-violet if the arc is run in air. This covers about the whole of the region in which occur the ZrO bands. The iron arc on the other hand gives very strong atomic spectrum. The best conditions were obtained by manipulation of the copper arc. Improved types of arcs used are described below.

(a) ZrO arc in Air.

The lower copper electrode was shaped into a cylindrical cup about 5-7 m.m. deep, with a diameter of 3·5 m.m. inside. The walls of this cup were very thin of the order of few hundredths of milimeters. The base of the cup was also very thin, and was supported on a copper rod of about 1 m.m. diameter at its centre. This rod was about 5-7 m.m. in length, and acted as a neck between the cylindrical cup and the rest of the electrode. The idea was to decrease the conduction of heat along the length of the electrode and maintain high temperature in the cup with lower currents. The upper electrode was also of Copper but with rather larger diameter (about 1-1.3 cm) to conduct the heat very rapidly.

Having filled the cup on the lower electrode with ZrO,

making it the anode, and the upper as cathode the arc was struck. The 220 volts D.C. Supply was used. As soon as the two electrodes touched each other, a current of ~ 6 amps was set up, with a small arc gap. The temperature rise was very quick and in a matter of seconds the copper walls of the cup vaporised entirely (Vaporisation temp. 2300°) leaving a hot bead of ZrO on the rod (Vaporisation temp. about 4000°). The arc was finally maintained between the upper copper electrode, very thick in cross-section, and conducting heat rapidly, and the ZrO bead on the copper rod of the lower electrode. The ZrO bead being white or red hot became sufficiently conducting to maintain the arc. The arc gap was increased to 1.5-3 cm. as desired and the current fell to 4-2.8 amps accordingly as the resistance of the arc increased with the increase in the gap. Even with this low current of 2.8 amps the arc was very steady, running almost wholly in the ZrO vapour, the upper electrode vaporising but very little due to rapid conduction. However a small quantity of Copper or Copper oxide vapour was contributed from the rod supporting the hot ZrO bead. The electrode material spectrum was not completely overcome, but even so the lines were very weak, the corresponding Zr spectrum being several times stronger.

The chief characteristic of this type of arc was the low current, which meant smaller electron density, but very high temperature of the anode bead due to conservation of heat, resulting in its vapourisation slowly and gradually. The excitation was relatively more due to molecular bombardment than

in ordinary arcs, and the higher temperature contributed to higher excitation. Very beautiful photographs were obtained with this source. It was however found that the line spectrum was not entirely suppressed, but the relative band intensity of the ZrO spectrum had increased several times. Furthermore, a few more bands were photographed in the infra-red, whose excitation had not been observed in any other source. They appeared fairly strongly, and were readily photographed. They were neither observed by Lowater nor by King and Meggers, both of whom studied the Zr spectrum in this region, with ordinary arcs in air charged with ZrO or metallic Zr, although the region 7600 - 9000 A of these new bands is almost wholly free from lines or other ZrO bands.

The Zr lines that appear in this source are presumably due to ZrO, dissociated because of high temperature. This arc does not have any conspicuous flame, and is like a cylindrical beam of incandescent vapour rising from the hot bead and condensing on the cathode above. The line spectrum increases in intensity relative to the band spectrum as one proceeds up from the hot bead to the cathode.

(b) ZrF_4 nH_2O (KF impurity) arc in air.

A. K. Sen Gupta[21] has described the use of GeF_4 to photograph the GeO spectrum, instead of GeO, the former giving more stable arcs. It however appears that he did not try to study or adjust the condition of the arc, neither did he try to find out the best condition of excitation. In the author's view the chief

advantage in using the fluoride of materials like Zr and Ge etc. - instead of their oxides - lies in the fact that the former have relatively very low temperature of vaporisation. The present author proceeded quite independently to study the excitation conditions in fluoride arcs, and varied the conditions as desired.

The electrodes were again of copper, the upper cathode being very much like the one mentioned above (for ZrO arc), but the lower electrode was somewhat different in detail, the walls of the cup were much thicker of about 1 m.m., and the diameter of the cup a little larger. The neck was thinner, and the cup was a little deeper to increase the capacity. ZrF_4 (with impurities of KF and water of hydration) was placed in the cup. Both 220 D.C. and 110 D.C. were used for running the arc with such electrodes, but much the same results were obtained. It will be noted that once the arc is started the temperature in the anode cup begins to rise. At first the vapourising materials are K, and water vapour of dehydration. One has to wait therefore until most of these impurities have been driven off, otherwise OH gives its own strong spectrum in the ultra-violet, and K interferes with vapourisation of ZrF_4. After this delay the temperature in the anode cup again begins to rise until ZrF_4 melts in the cup. As the temperature is further increased by increasing the current, more and more vapour of ZrF_4 rises above the cup. There is, however, a critical temperature, which if reached results in a "sudden vapourisation and oxidisation" of ZrF_4 just above the surface of molten ZrF_4.

Both the vapourisation and oxidation are so rapid that in a matter of 60-90 secs., nothing is left of the ZrF_4 in the anode cup. Even then the copper walls of the cup vaporise but very little, as the temperature of liquid ZrF_4 must be below the vapourisation temperature of Cu. This critical temperature at which rapid vapourization sets in must be the oxidisation temperature of ZrF_4, the oxidisation resulting in production of heat, and greater vapourization of ZrF_4, further oxidisation, and further increase in the rate of vapourisation, the cycle gradually working up until equilibrium conditions are reached. It will thus be seen that ZrF_4 arc in air could be run in two conditions, firstly slow vapourisZaction from the anode cup and slow oxidisation in the arc, secondly very rapid vapourisation and strong oxidisation in a stormy arc. In both of these the electrode material vapourises very little, the cooling in the cathode being due to conduction along its length, and in the anode due to vapourization of ZrF_4 helping to keep the temperature down. The two conditions will be discussed separately.

(b) I: THE STEADY ZrF_4 ARC

As has already been mentioned, this kind of arc can only be maintained below the critical or the oxidising temperature of ZrF_4. The steady conditions are rather critical, and air streams, or fluctuations in the current have to be avoided. It is always better to start with low current, when the arc is struck. The arc is maintained between the thick upper cathode and the edges of the

walls of the anode cup. A fairly good coating of ZrF_4 over the cathode should be obtained by letting the vapours condense over it for some time. This is essential to overcome the copper vapour in the arc. If good coating is not obtained easily, it is better to increase the current, and consequently the temperature of the anode cup, whereby a rapid vaporization and condensation on electrode surfaces is easily obtained. A new charge of (ZrF_4 + KF) is then introduced in the cup; and the experiment started. The arc gap can now be drawn to 1.5-2.0 . with 110 D.C. and 4-5 amps. Under these conditions the temperature in the anode cup remains fairly low. As the vapour of ZrF_4 moves up, its temperature rises gradually, and a slow oxidisation of the vapour sets in. This is confirmed by observation; whereas bands of ZrF are quite strong just above the anode cup, they are absolutely absent just below the cathode, although the corresponding ZrO bands become very strong.

This kind of arc in general appearance is like ordinary Iron arcs, with an intense central region and an envelope, developing into a flame on the upper side. Discussing the parts of the arc separately we will consider the central regions of the arc above the anode cup, half way between the cathode and the anode, just below the cathode, and finally the flame of the arc.

Central Arc above the Anode Cup: The spectrum of this region is very intense, showing strongly the bands of ZrF in blue and green, strong bands of ZrO, and very strong atomic spectrum of Zr. In fact the line spectrum is too strong for this source to

be of use, especially in the λλ3000 - 4000 region where Zr line spectrum is very numerous and closely packed. However this is the only part of the arc where ZrF bands appear with appreciable intensity and fortunately the line spectrum is not very troublesome in region of the spectrum where they appear. It is useful in photographying ZrF bands.

Central Arc Half-way between Anode & Cathode: The line spectrum of Zr becomes very weak though not eliminated. ZrF bands also fade out and ZrO bands increase in intensity. But in the ultra-violet region of the spectrum Zr line spectrum is still too strong to show ZrO bands clearly.

Central Arc below Cathode: The line spectrum of Zr becomes extremely weak, only a few lines becoming photographable but copper vapour from cathode hot spot contribute some copper lines, which are also very weak. The bands of ZrO are relatively very strong, compared with the atomic spectrum, and the ultra-violet systems of ZrO seem to have gained in intensity relative to the visible systems. As the region 3000- 4200A is now about completely free from lines, and the bands are very conspicuous, this region of the arc is the best source for the excitation of ZrO bands in the ultra-violet. This region of the ZrO spectrum has been photographed and three new systems of ZrO discovered in the ultra-violet.

The Flame: In the flame the excitation temperature is low and consequently the ultra-violet ZrO bands completely fade out.

The visible triplet systems of ZrO are still strong, but the line spectrum gains very much in relative intensity. Furthermore bands of OH and O_2 (Schumman Runge) systems become visible, the former being very strong. The appearance of O_2 bands in the flame, but its absence from the central arc, is difficult to explain. These bands seem to accompany the Fluorides and the moisture, coming up only in the flame of the arc. However from our point of interest this region is of no value, as the bands of ZrO become relatively weak, and the spectral region superposed by foreign spectra.

(b) II: THE UNSTEADY, ZrF_4 ARC.

Slight increase in current is sufficient to increase the temperature of molten ZrF_4 to the oxidising temperature. As soon as this temperature is reached rapid oxidisation (perhaps in the anode cup itself) and vapourisation sets in. Instead of an ordinary arc, a vertical beam of incandescent vapour seems to extend from the anode to the cathode, the vapours moving up very fast and condensing on the electrodes. There is no visible flame or envelope region of the arc. The spectral feature is about the same all along the length of the incandescent beam. Bands of ZrO become extremely strong and corresponding atomic spectrum almost completely suppressed. The bands of ZrF are not present even above the anode cup, confirming the hypothesis of rapid oxidisation. But in the ultra-violet a very strong continium extending from λ 3000 to λ4300 suppresses the bands in the ultra-violet, even though the line spectrum is very faint. As to what is the source of this continium is hard to say. It may likely be a fluoride

forming after the oxidisation of ZrF_4. However this continium prevents the use of this arc for photography in the ultra-violet, but it is about the best source to photograph the bands of ZrO in the visible region. The bands in the visible region are very strong, with very few and weak atomic lines. This has made it possible to extend system α of ZrO, and raise doubts about some of the bands observed and measured by Miss Lowater, but which do not appear on our spectrograms suggesting that perhaps they are lines.

(c) Zr ARC IN MOIST HYDROGEN.

This is the best source of the excitation of ZrO bands both in the visible and the ultra-violet. A copper anode provided with a cup as described for Arc (b), but with the anode cup much smaller in size, is used. Powdered Zr is put in the anode cup, and a thick copper electrode forms the upper cathode. The whole chamber is vacuum-tight, is evacuated and filled with hydrogen. A few drops of water are left inside the chamber, or some provision made to keep the H_2 moist. The chamber is kept immersed in water for cooling and the arc is struck using 110 D.C. with 5 - 8 amps. The anode and cathode are kept very near to each other, the arc gap being of the order of one or two millimeters. It is not possible to make the arc gap very wide in H_2Ø. If the arc itself is photographed, it shows strong copper, Zirconium, and broad H_α, H_β and H_γ lines. However when the anode cup gets red hot, yellow coloured flames shoot out horizontally from the anode cup and last for a matter of seconds, then die out; and after some time new ones appear. These shooting flames are focussed on the

slit of the spectograph, and the spectrum photographed. The ZrO spectrum thus photographed is the purest that has been obtained. The line spectrum of Zirconium is almost completely suppressed, and the bands of ZrO are very strong. Further the intensity maxima in the bands move nearer to the heads, making the tails of the bands less intense, and weaker bands falling in the tails become more conspicuous. This shows a smaller effective rotational temperature.

The high price of metallic Zirconium is one disadvantage in the wide use of this method. The spectra obtained from ZrF_4 arcs are not very inferior, and they serve the purpose almost as well. The appearance of strong ZrO bands in the flame of the arc in moist H_2 suggests that moisture attacks metallic Zirconium suddenly, oxidising it in the flame.

HIGH VOLTAGE ARCS.

Effort has been made to photograph the ZrO spectrum from the High Voltage arc between two Zirconium electrodes; and find out if this source was any improvement on the sources previously used, viz. the low voltage arcs. It was hoped that the drastic change in the condition of excitation would alter the relative intensity of the systems, and thereby provide a clue to the analysis of unassigned bands.

The experimental set-up was not complicated. Two Zr cylindrical electrodes, a cm. long, and 3 m.m. in diameter were held in the jaws of the Crocodile clips, which were connected to the secondary of a 7 K.W. A.C. Transformer capable of giving 2.8 amps at 2500 volts or 1.4 amps at 5000 volts. Suitable variation of

resistance in series with the primary of the transformer controlled the current in the secondary, and the arc. For larger arc gaps 5000 volts were generally used drawing about 1 amp. current. However, once the arc was established and the Zr electrode tips became hot enough the arc gap could easily be increased to 1 cm. or even greater. The spectrum midway between the electrodes was chiefly dominated by the arc and spark lines of Zirconium; the bands of ZrO in the visible were conspicuous and fairly strong, but those in the ultra-violet were strongly superposed by numerous Zirconium lines. A further disadvantage was the appearance of the bands of OH, NO, and N_2 etc. (intensity decreasing in order as written).

To decrease the intensity of the arc and spark lines of Zirconium, the arc region was enveloped in a thin Bunsen flame. This allowed the spark gap to be pulled even wider to 2-3 cm.; and the line spectrum did fall in intensity. The bands of ZrO in the visible, viz. the α, β and γ systems became much more conspicuous, but even though the ultra-violet region was freer of atomic spectrum, strong CN, N_2 and OH bands developed in this region, making it entirely impossible to study the ZrO spectrum in this region. The OH and CN bands became very intense.

Finally a jet of Oxygen replaced the Bunsen flame, and played on the spark gap from below, lifting it up into an arch. The tip of the arch was most free of impurities, and the spectrum as a whole showed improvement. The ZrO bands were much more conspicuous in the visible and in the ultra-violet. Many bands

in the ultra-violet were recognised to be the same as those obtained in the low voltage arcs. This difference however, was noted that the triplet system of ZrO at 3500A was several times stronger compared to the singlet system in the same region. Strong impurities of N_2,O_2, weaker ones of NO, and OH raised considerable difficulties. The region 2600 - 3680A is full of fine rotational structure with many weak bands on it, which cannot be studied very well due to strong background.

The High Voltage Arc was in no way an improvement on ordinary arcs. Spectrograms taken on large dispersion of system α , show other faint bands, doubtful in their origin in the same region. The general result is one of complicating rather than simplifying the ZrO spectrum.

SPECTROGRAMS.

Spectrograms of ZrO, in the visible region were obtained on the Large Lithrow Spectrograph with a Dense Glass prism. Photographs were obtained in two regions, $\lambda\lambda$4200 - 5600 and $\lambda\lambda$4500-7000. The dispersion varied from 2.86 A/m.m. at λ4200 to 22 A/m.m. at λ7000. The source of the spectrum was the steady ZrF_4 arc, being exposed just below the cathode, and the Zr arc in moist H_2. The chief interest in this region was to attempt to observe missing bands in Miss Lowater's system α , and fill the gaps in the Deslandres Table. Spectrograms were also obtained in the first order of the ten ft. grating with 15000 lines/inch, and four inches of ruled surface, in the region $\lambda\lambda$ 4300 - 5900 with ZrF_4 arc in unsteady and the unsteady condition (b) II. The region of the arc exposed was

just above the anode cup.

The infra-red region from λ7600 - λ9000 was photographed in the first order of the 10 ft. grating. The dispersion in this region was about 5.5 A/m.m. The source of the spectrum was the ZrO arc in air (source (a)). Spectrograms were also obtained with High Voltage arcs, ZrF_4 arcs etc. but failed to show any bands. Filters were used to cut off the overlapping blue violet regions of the second order.

The ultra-violet regions of the ZrO spectrum were photographed on the Hilger E$_1$ spectrograph, giving a dispersion of 4.68 A/m.m. at λ2900 and 20.1 A/m.m. at λ4800. Many spectrograms were obtained in the region 2900 - 4900A with low voltage ZrF_4 arcs in steady, as well as in unsteady conditions, from various regions of the arc. With high voltage arcs spectrograms were obtained in the region $\lambda\lambda$2570 - 3680. Spectrograms were also obtained of the ZrO spectrum in the ultra-violet from λ2900 to λ3650 in the second order of ten ft. grating, with ZrF_4 steady arc. (b) I as the source, the central part of the arc above the anode cup being exposed.

In an unsuccessful effort to resolve the λ3682 band of ZrO, spectrograms were obtained in the second order of the 20 ft. grating with 11000 lines/inch, and six inches of ruled surface. Zenith plates were used to decrease the effective time of exposure.

Spectrograms were also obtained in the second order of a 20 ft. grating with 30000 lines/inch and six inches of ruled surface, in the region $\lambda\lambda$3540 - 3800. The source was the high

ZrO arc in air. The dispersion was about 0.59 A/m.m.

Ordinary, Special Rapid Ordinary, and Zenith Ilford plates were used in the Ultra-violet. Special Rapid Panchromatic, Astra III, and H.P.3 were used in the visible, while I.R.E.R. Kodak were used in the λλ7600 - 9000 region.

The following table summarises the regions measured, the spectrograms, the source and the dispersion used.

Spectral Regions measured	Spectrographs used to prepare spectrograms	Sources of the Spectrum	Dispersions
λλ9000 - 7600	Ist Order 10 ft. Grating.	ZrO arc (a) in air	5.49 A/m.m. - 5.50 A/m.m.
λλ4250 - 5300	Ist Order 10 ft. Grating. Large Lithrow Glass Sp.	ZrF_4 arc (b)I and (b)II Zr arc in moist H_2	5.55A/m.m. - 5.50A/m.m.
λλ2900 - 4800	Hilger E Quartz	ZrF_4 arc (b)II	4.68A/m.m - 20A/m.m.

On the next page a table of the wavelengths of the bands measured, with corresponding analysis, is given.

OBSERVATIONAL DATA

BAND HEADS AND ASSIGNMENTS

Wavelength λ air	I	ν_{vac}	Vibrational analysis	Remarks or the wavelengths as measured by others
2940.9	(1)	33993.7	$\varphi(0,0)R_1$	
2950.0	(1)	33888.4	$\varphi(0,0)R_2$	
2967.8	(1)	33685.1	$\varphi(0,0)R_3$	
3023.8	(0)	33061.4	$\varphi(0,1)R_1$	
3033.5	(0)	32955.7	$\varphi(0,1)R_2$	
3052.4	(0)	32752.2	$\varphi(0,1)R_3$	
3390.65	(1)	29489.7	(A)4,1	
3407.89	(0)	29335.3	(A)5,2	
3425.92	(0)	29180.9	(A)6,3	
3468.90	(1)	28819.4	(A)2,0	
3472.39	(3)	28790.5	$\delta(0,0)R_1$	3472.43*(5)
3473.62	(1)	28780.3	$\delta(0,0)Q_1$	
3486.71	(2)	28672.2	(A)3,1	
3491.80	(3)	28630.4	$\delta(0,0)R_2$	3491.84*(5)
3493.06	(1)	28620.1	$\delta(0,0)Q_2$	
3504.22	(1)	28528.9	(A)4,2	
3506.30	(3)	28512.0	$\delta(0,0)R_3$	3506.22*(5)
3507.56	(1)	27501.7	$\delta(0,0)Q_3$	
3571.96	(8)	27987.9	(A)1,0	
3589.87	(6)	27848.3	(A)2,1	3589.81*(3)
3607.61	(1)	27711.4	(A)3,2	

Wavelength λ air	I	ν_{vac}	Vibrational analysis	Remarks or the wavelengths as measured by other authors
3682.07	(10)	27151.0	(A)0,0	3682.43*(6)
3700.11	(2)	27018.6	(A)1,1	
3754.72	(1)	26625.6	(A)4,4	
3772.9?	(0)	26497.4	(A)5,5	
3791.6?	(0)	26366.7	(A)6,6	
3818.32	(4)	26182.2	(A)0,1	
3836.38	(1)	26059.0	(A)1,2	
3854.18	(0)	25938.5	(A)2,3	
3881.45	(3)	25109.4	(A)1,3	
4000.72	(0)	24989.4	(A)2,4	
4195.80	(0)	23826.77	system α R_c 4,1	4195.81* (1)
4217.0	(0)	23706.9	α R_b 5,2	-
4218.98	(0)	23695.7	$\alpha R_c(5,2)$	
4267?	(0)	23429.1	$\alpha R_c(7,4)$?	
4292.88	(1)	23287.9		
4298.38	(0)	23258.1	$\alpha R_a(2,0)$	
4313.30	(1)	23177.6	$\alpha R_b(2,0)$	4313.32* (3)
4315.57	(1)	23165.4	$\alpha R_c(2,0)$	
4323.67	(0)	23122.0		
4337.46	(1)	23048.5	$\alpha R_b(3,1)$	4337.55* (2)
4339.66	(1)	23036.9	$\alpha R_c(3,1)$	4340.18* (2)
4358.25	(1)	22938.6		
4361.96	(0)	22919.1	$\alpha R_c(4,2)$	4361.95* (3)

Wavelength λ air	I	ν_{vac}	Vibrational analysis	Remarks or the wavelengths as measured by other authors	
4364.26	(1)	22907.0	$\alpha R_c(4,2)$	4364.38+	(4)
4368.05	(1)	22887.1		4363.16+	(3)
4368.90	(0)	22882.7			
4379.30	(0)	22828.3			
4386.80	(0)	22789.3	$\alpha R_b(5,3)$		
4389.10	(0)	22777.3	$\alpha R_c(5,3)$		
4452.17	(0)	22454.7	$\alpha R_a(1,0)$	4452.21+	(1)
4460.34	(2)	22413.6		4460.39+	(2)
4469.36	(3)	22368.4	$\alpha R_b(1,0)$	4469.38+	(8)
4471.45	(3)	22357.9	$\alpha R_c(1,0)$	4471.53+	(40)
4493.76	(3)	22246.9	$\alpha R_b(2,1)$	4493.79+	(7)
4496.20	(3)	22234.8	$\alpha R_c(2,1)$	4496.24+	(8)
4499.45	(0)	22218.8			
4519.07	(0)	22122.2	$\alpha R_b(3,2)$	4519.26+	(6)
4521.12	(0)	22112.3	$\alpha R_c(3,2)$	4521.26+	(6)
4542.28	(3)	22009.2		4542.55+	(7)
4619.72	(8)	21640.3	$\alpha R_a(0,0)$	4619.82+	(15)
4637.70	(10)	21556.4	$\alpha R_b(0,0)$	4637.79	(18)
4640.43	(10)	21543.7	$\alpha R_c(0,0)$	4640.56+	(20)
4644.70	(0)	21524.0	$\alpha R_a(1,1)$	4644.68+	(10)
4662.7,0	(0)	21439.8	$\alpha R_b(1,1)$	4663.17*	(5)
4665.68	(1)	2427.1	$\alpha R_c(1,1)$	4665.27*	(4)
4692.61	(0)	21306.9	$\alpha R_c(2,2)$		

λ air	I	ν_{vac}	Vibrational classification	Remarks and measured wavelengths by other authors
4736.91	6	21105.0		4736.90+ (12)
4752.53	2	21035.6		
4826.55	1	20713.0	$Zr^{94}O^{16}$ isotopic head of $\alpha R_a(0,1)$	4827.38+ (3)
4827.45	3	20709.1	$\alpha R_a(0,1)$	4827.52+
4864.39	1	20628.2	$Zr^{94}O^{16}$ isotopic head of $\alpha R_b(0,1)$	
4847	4	20625.2	$\alpha R_b(0,1)$	4847.19+ (5)
4849.96	4	20613.0	$\alpha R_c(0,1)$	4849.72+ (3)
4873.74	2	20512.7	$\alpha R_b(1,2)$	4873.03+ (1)
4875.96	2	20503.1	$\alpha R_c(1,2)$	4876.12+ (3)
4899.60	1	20404.2	$\alpha R_b(2,3)$	4899.76+ (3)
4902.36	1	20392.7	$\alpha R_c(2,3)$	4902.47+ (3)
4926.00	0	20294.8	$\alpha R_b(3,4)$	
4929.03	0	20282.4	$\alpha R_c(3,4)$	
4994.63	0	20015.9		
4996.28	2	20009.3		
5022.95	1	19902.9		
5052.79	1	19785.6	$\alpha R_a(0,2)$	5052.91* (3)
5073.94	1	19703.1	$\alpha R_b(0,2)$	5073.96* (4)
5077.60	1	19688.9	$\alpha R_c(0,2)$	

INFRA-RED BANDS OF ZrO

λ_{air}	I	ν_{vac}	v', v''	Remark
8178.76	2	12223.44		Spurious
8185.39	1	12213.53		Spurious
8192.36	10	12203.16		
8460.25	1	11816.74		degraded to Violet
8519.07	2	11735.16		degraded to Violet
8525.15	2	11726.78		degraded to Violet
8558.48	1	11681.11		a line?
8574.02	1	11659.94		
8597.38	2	11628.12		
8684.58	2	11511.37		degraded to Violet
8695.23	(3)	11497.14	I(2,1)a	
8709.3	(3)	11478.8	I(2,1)b	
8721.3	(3)	11463.0	I(2,1)c	
8734.0	(2)	11446.4	I(2,1)d	
8744.10	(2)	11433.10	I(2,1)e	
8769.19	(2)	11400.44	I(3,2)a	
8784.5	(1)	11380.6	I(3,2)b	
8815.0	(1)	11343.8		spurious heads ?
8813.0	(1)	11341.2		spurious heads ?
8820.41	(2)	11334.24	I(3,2)c	
8822.32	(2)	11331.80		
8825.09	(1)	11328.24		

λ air	I	$\nu_{vac.}$	Vibrational classifications	Remarks
8852.43	(2)	11293.24		
8857.50	(2)	11286.76	I(4,3)b	
8867.45	(1)	11274.38		
8868.99	(1)	11272.17	I(4,3)c	
8881.23	(2)	11256.62	I(4,3)d	
8882.67	(2)	11254.80		
8892.37	(2)	11242.52	I(4,3)e	
8917.12	(1)	11211.32		
8945.31	(1)	11176.00		Degraded to violet
8950.34	(2)	11172.21		Degraded to violet
8965.51	(1)	11150.31		Degraded to violet

+ Miss Lonster

* Johnson

To the list of the bands, measured by the author, it would be desirable to add the wavelengths of the bands of ZrO, observed by Meggers and King[18] in the infra-red, as most of the bands of the infra-red seem to be related to those observed by Meggers and King.

(ZrO bands by Meggers & King)	I	ν_{vac}	Vibrational Classification by the author.
9299.56	(5)	10750.25	I (0,0)a
9315.87	(5)	10731.43	I (0,0)b
9329.93	(5)	10715.26	I (0,0)c
9343.19	(4)	10700.05	I (0,0)d
9356.12	(3)	10685.36	I (0,0)e
9358.33	(1)	10682.74	
9360.34	(3)	10680.45	
9370.74	(3)	10668.59	I (1,1)a
9387.26	(2)	10649.82	I (1,1)b
9397.21	(2)	10638.54	
9401.04	(2)	10634.15	I (1,1)c
9402.84	(2)	10632.17	
9408.92	(1)	10625.30	
9412.03	(2)	10621.79	I (1,1)d
9431.75	(2)	10599.58	I (1,1)e
9438.24	(1)	10592.29	
9443.93	(1)	10585.91	I (2,2)a
9453.55	(1)	10575.14	
9476.65	(1)	10549.36	I (2,2)c
9483.55	(2)	10541.69	

ANALYSIS OF THE NEW BANDS OF ZrO.

We will start the description of our classification of the new bands of ZrO from the ultra-violet side. The bands observed in this region are very conspicuous, and their classification seems to be correct beyond doubt. Furthermore no unassigned bands have been left in this region which may raise doubts as to the true analysis. Considering first the group of bands lying on the farthest ultra-violet side of ZrO spectrum at λ3050, it will be noticed that we have classified them as system ϕ

SYSTEM ϕ OF ZrO AT λ2940.

This system comprises of a group of six heads lying in complete isolation from the rest of the ZrO bands. The nearest conspicuous band of ZrO is more than 3000 cm^{-1} to the red. The vibrational energy differences corresponding to ZrO molecule are about one third of this. It therefore can easily be established that these bands, can in no way form a part of the system of the bands lying to their red wavelength side. The bands also differ very much in their general appearance.

The system on the whole is very weak. Only three heads at λ2940.9, λ2950.0 and λ2967.8 have any appreciable intensity. The other heads are about one half as weak. The three strong heads appear to be the (0,0) band with three R branches (consequently three heads) and the weaker ones appear to be (0,1) band. The energy differences between them are as follows:-

Heads.	Wave numbers of (0,0) band-heads	$\Delta''\frac{1}{2}$	Wave numbers of (0,1) band-heads
R_a	33993.7	(932.3)	33061.4
R_b	33888.4	(932.7)	32955.7
R_c	33685.2	(932.9)	32752.2

Average 932.6

The average value $\Delta''\frac{1}{2}$ comes to about 932.6 cm^{-1}, which is the same as in systems α, β and γ of ZrO. The system ϕ of ZrO shares a common final level with α, β and γ, viz. the $X\,^3\Pi$ ground state of ZrO.

Since three R heads, and no Q heads appear for each band, it can at once be concluded that a $^3\Pi$ state is the only possible initial level for the ϕ system of ZrO. The only levels from which transitions can take place to a $^3\Pi$ state are $^3\Sigma$, $^3\Pi$ and $^3\Delta$ states. The first and the last, if involved in a transition with another $^3\Pi$ state, give rise to three Q branches about twice as strong as the three R or three P branches, therefore the transition for system ϕ is $E\,^3\Pi \rightarrow X\,^3\Pi$. We have denoted the initial triplet level as $E\,^3\Pi$. The wave number differences in the heads are:

$$R_a - R_b = 105.3 \ cm^{-1}$$

$$R_b - R_c = 203.3 \ cm^{-1}$$

If R_a heads originate from the lowest, and R_c from the highest of E $^3\Pi$ state, the splitting in the upper E $^3\Pi$ level is as follows

$$E\,^3\Pi_2 - E\,^3\Pi_1 = 110.1 \text{ cm}^{-1} \qquad (313.4 - 203.3)$$

$$E\,^3\Pi_1 - E\,^3\Pi_0 = 186.8 \text{ cm}^{-1} \qquad (292.1 - 105.3)$$

Otherwise:

$$E\,^3\Pi_2 - E\,^3\Pi_1 = 418.7 \text{ cm}^{-1} \qquad (313.4 \quad 105.3)$$

$$\&\quad E\,^3\Pi_1 - E\,^3\Pi_0 = 495.4 \text{ cm}^{-1} \qquad (292.1 \quad 203.3)$$

It is difficult to decide between the two sets of multiplet separations of E $^3\Pi$ state, but the former one appears to be the more feasible one. The R_a head appears to be stronger of either R_b and R_c and this demands that the initial level responsible for R_a head should be the lowest in E $^3\Pi$ The argument that the multiplet separations in E $^3\Pi$ state cannot be about one half to one third as small as in X $^3\Pi$ and C $^3\Pi$ is not very appealing. Let us consider the ground state of ZrI. The multiplet separations in this state are 670.43 and 570.41 cm^{-1} respectively. A similar ^3F level at 37459.60 cm^{-1} above the ground level, has multiplet separations of only 241.48 and 400.01 cm^{-1} There are other ^3F states of ZrI which have multiplet separations of about 100 cm^{-1} The present considerations seem to increase weight in favour of adopting 110.1 and 186.8 cm^{-1} as the multiplet separations in the E $^3\Pi$ level of ZrO.

The three E $^3\Pi$ levels are therefore respectively at 33993.7, 34180.5 and 34290.6 cm^{-1} above the X $^3\Pi_0$ ground level of ZrO.

" δ SYSTEM OF ZrO"

This also is another triplet system of ZrO and on the whole appears to be a little more intense than the ϕ system at λ2940. This system is however not isolated from the rest of the systems, but its (0,0) band falls over the (2,0) sequence of the singlet A system, which we will describe later on. The (0,0) band is the only one of the whole system which appears to have any appreciable intensity, others not having been observed in spite of a careful search. This does not make the assignment of the group of bands at λ3490 to the (0,0) band of System δ, doubtful. It is true that this group of bands falls on other bands, which do not have the same assignment. But the analysis of the singlet System A of ZrO is beyond any doubt, and the constants for the system A have been established with great accuracy. The singlet system "A" possesses a Narrow Condon Parabola of Intensity, and all the bands expected at λ3490 (the region of System δ) are accounted for. After examining the following table, no doubt is left that " δ System" can in no way be a part of System A.

3468.90	(1)	System A (2,0)	
3472.39	(3)		- System δ (0,0) R_a
3473.62	(1)		- System δ (0,0) Q_a
3486.71	(2)	A (3,1)	
3491.80	(3)		- System δ (0,0) R_b
3493.06	(1)		- System δ (0,0) Q_b

3504.22	(1)	A (4,2)
3506.30	(3)	- System δ (0,0)R_c
3507.56	(1)	- System δ (0,0)Q_c

In all, six heads differing in general appearance from the heads of System A remain unassigned. While all the bands of System A occur as singlets, the six unassigned heads occur in pairs, with sharper and more intense heads in front of fainter and more diffuse heads. The sharper and stronger heads are evidently the R heads, and the weaker ones with diffused heads, the Q or X heads. The latter are characteristic of the β and γ system of ZrO. Though in both cases identification of X heads with Q heads is in doubt, it is certain that the faint heads in system δ correspond with X heads in System β and γ They may very well be the Q heads.

The δ system, therefore, seems to consist of three R heads and three Q heads. These cannot be the three double heads of the sequence of a singlet system, e.g. $^1\Sigma - {}^1\Pi$ This will demand very large values for $\chi_e''\omega_e''$ in the lower level, as the wave-number differences between the three R heads are 160.1 and 113.4 cm^{-1} Since such values of $\chi_e''\omega_e''$ are not expected this possibility cannot be asserted with any confidence.

To prove the point let us suppose that the six bands are the (0,0) sequence of a singlet system:

λ_{air}	I	ν_{vac}		
3472.39	(3)	28790.5	(0,0)R	
3473.62	(1)	28780.3		(0,0)Q
3491.80	(3)	28630.4	(1,1)R	
3493.06	(1)	28620.1		(1,1)Q
3506.30	(3)	28512.0	(2,2)R	
3507.56	(1)	28501.7		(2,2)Q

And let us suppose that the δ system has the same final level as the singlet "A". The ω_e'' and $x_e''\omega_e''$ values in the final level of System "A" are 978.07 and 5.04 cm^{-1} respectively. This will demand $x_e'\omega_e'$ equal to -5.80 cm^{-1} in the initial level, and it is quite impossible. If on the other hand, the initial level of system δ is supposed to be the same as System A, then the singlet system A should not be more intense than System δ . Furthermore, expected values for ω_e'' and $x_e''\omega_e''$ come out to be 1045.5 and 24.0 cm^{-1} respectively. Such large values of ω_e'' and $x_e''\omega_e''$ are not expected. It is therefore quite certain that system δ does not share any of the levels of system A, and it is also unlikely that it is due to transition involving levels independent of those giving rise to the system A. If there were any such levels, intercombination should be very certain, giving rise to singlet systems in the neighbourhood. No such systems are known.

Systems β of TiO also consists of four double headed bands, representing a (0,0) sequence at λ5597.85. No bands of any other sequence are known. That system β of TiO is due to a $^1\Sigma - {}^1\Pi$ transition is likely, as it is very difficult to relate

it to the triplet levels. The four double headed bands of the β system of TiO are evidently the (0,0), (1,1), (2,2) and (3,3) R and Q heads.

But an analogy between the system β of TiO and the δ system of ZrO will be misleading. While in the β system of TiO the intensity falls regularly from (0,0) to about one third in (3,3) band, all the three double headed bands of system δ have almost equal intensity. Furthermore, if they were the bands from different vibrational levels, other bands from higher vibrational levels would be expected before the sequence fades out. But there are only three double heads of equal intensity. All these considerations rule out the possibility of the system δ of ZrO being a singlet system. That only three double heads appear has its own significance. There must be the three R heads (with three Q heads) of the (0,0) band of a triplet system, other bands being too faint to be photographed. The classification of bands in system is as follows:-

3472.39	(3)	28790.5	$(0,0)R_a$
3473.62	(1)	28780.3	$(0,0)Q_a$
3491.80	(3)	28630.4	$(0,0)R_b$
3493.06	(1)	28620.1	$(0,0)Q_b$
3506.30	(3)	28512.0	$(0,0)R_c$
3507.56	(1)	28501.7	$(0,0)Q_c$

If these considerations are not wrong, the question arises what are the levels responsible for this system δ. The lower level is likely to be the $X\,^3\Pi$ ground state of ZrO, but there is

always the possibility that the final level of system δ may be an excited state. If from any initial level transitions are possible to this final excited state, transitions from that level should also be possible to the X $^3\Pi$ ground state, giving a system towards the ultra-violet. The only system towards the ultra-violet of System δ is the system ϕ. If its initial level E $^3\Pi$ is supposed to be the initial levels of both the system δ and the system ϕ (system ϕ to X $^3\Pi$ ground state) then the multiplet separations in the final level of system δ can easily be evaluated. For δ system we know that

$$R_a - R_b = 160.1 \quad cm^{-1}$$

$$R_b - R_c = 118.4 \quad cm^{-1}$$

and corresponding multiplet separations in supposed initial E $^3\Pi$ levels are

$$^3\Pi_2 - {}^3\Pi_1 = 110.8 \ cm^{-1}$$

and

$$^3\Pi_1 - {}^3\Pi_0 = 186.8 \ cm^{-1}$$

then multiplet separations in the final level of system δ should be 229.2 and 346.9 or - 49.3 and 68.4 cm^{-1} the multiplet separations according to former set of values suggest a $^3\Pi$ state and according to the latter, a $^3\Sigma$ state, which should not possess negative separations, or separations of such large magnitude. A $^3\Sigma$ final level is not possible, therefore, for the reasons already described while the suggested $^3\Pi$ level with 229.2 and 346.9 cm^{-1} separations is also not possible, because transitions between $^3\Pi$ and $^3\Pi$ states do not give Q branches.

It is, therefore, not beyond reason to conclude that the initial level of system δ is not the same as that of the system ϕ; and it becomes all the more unlikely that any other levels other than those giving rise to system ϕ are involved.

The only logical possibility left, is to conclude that system δ has the $X\,^3\Pi$ ground state of ZrO as its final level. The presence of Q heads suggests that the upper level is neither $^3\Delta$ with multiplet separations of 195.0 and 132.0 cm^{-1} or a $^3\Delta$ state with multiplet separations of 473.6 and 410.8 cm^{-1} respectively.

Since $^3\Sigma$ states cannot possess such large separations the upper level is perhaps the $D\,^3\Delta$ state of ZrO. This demands that the three sub-levels of $D\,^3\Delta$ state should be roughly at 28512.0, 28922.8, 29396.4 cm. or 28780.3, 28912.3, 29107.3 cm^{-1} from the $X\,^3\Pi_0$ ground state of ZrO.

In the letter, "Band system of Zirconium Oxide (ZrO) in the Ultra-violet", by the author, in Nature, 164, 752 (29 Oct. 1949), the splittings in the $B\,^3\Delta$ state were tentatively assumed to be 473.6 410.8 cm. respectively. However the smaller separations of 195.0 and 132.0 cm. appear to be more likely.

It should be noted that the three R heads of this system were also observed and measured by Miss Lowater.

SINGLET SYSTEM "A" OF ZnO.

INTRODUCTION:

This is the only singlet system which has been reasonably well established for ZrO. In fact the existance of a singlet system for ZrO lends weight to the conclusion that system β of TiO is also a singlet system.

Recently Herbig[19] measured the rotational lines in the band at λ3682 (which has now been established to be the (0,0) band of the system), and after arranging all the measured lines in two R and P branches came to the conclusion that this band is due to a $^1\Sigma - ^1\Sigma$ transition, which in the opinion of the author is quite likely though not final. Since this system was also observed in absorption in stellar spectra, Herbig concluded that the $^1\Sigma$ state (or other singlet state, involved in this system) could be the ground state of ZrO instead of $X\ ^3\Pi$. Our objections to his deductions have been expressed in the beginning and, while considering the theoretical energy levels of the oxides of Ti sub-group on the one hand, and of the oxides of the C sub-group on the other. Theoretically a singlet level can not possibly be the ground state of ZrO or TiO or the like; and the absorption of λ 3682 band can easily be understood if its lower level be supposed to lie very little above the ground state, $X^3\Pi$, of ZrO. The singlet levels involved in this system "A" are likely to be excited states.

Now triplet levels are known for molecules like CO, though the ground state and most of the more prominent levels are singlets.

The converse is true for the oxides of the Ti sub-group. Here the more prominent levels, including the ground state are triplets, while singlet levels also appear to exist. As the singlet systems are the main feature of the CO molecule, with weaker triplet systems, so the triplet systems are the chief feature of TiO and ZrO with weaker singlet systems.

Returning to our description of the spectrum, it will be noted that Miss Lowater measured two bands of this system at λ 3682.43 (6) and at λ 3589.81 (3). The former is the (0,0) and the latter the (2,1) band of System A. Another strong band of System A, viz. the (1,0) band at λ3571.96, might easily have been located, if its head had not been concealed by the strong Zr line at λ3572.47 in Miss Lowater's spectrograms.

OBSERVATIONAL DATA: In the table on the next page are shown the wavelengths of the bands of System A. The first column gives the wavelength in air, the second the intensity, the third wave-numbers in vacuum, the fourth the vibrational classification, and the fifth column gives the difference between the observed and the calculated wave-numbers of the band-heads as calculated from the formulae developed.

THE VIBRATIONAL CONSTANTS: Consider the differences $\Delta'(v'+\frac{1}{2})$ and $\Delta''(v''+\frac{1}{2})$. The gradual variation in both of them in the same column or row, suggests that θ has an appreciable magnitude. Here θ is a constant which enters the formulae, when band-heads instead of the band origins of a system are represented.

Since $\nu_h - \nu_o = -\frac{B' + B''}{4(B' - B'')} = -\frac{((B_o' + B_o'') - (\alpha'v' + \alpha''v''))}{4(B_o' - B_o'') - 4(\alpha' v' - \alpha'' v'')}$

or $= -\frac{B_o' + B_o''}{4(B_o' - B_o'')} - \{\zeta' v' - \eta' v'^2 + \ldots\} - \{\zeta'' v'' - \eta'' v''^2 + \ldots\} + \Theta v' v''$

Here ζ, η and Θ are functions of B_o', B_o'', and α', α''

The formulae representing the band origins is

$$\nu_o = \nu_e + \left[\omega_e'(v'+\tfrac{1}{2}) - x_e'\omega_e'(v'+\tfrac{1}{2})^2\right] - \left[\omega_e''(v''+\tfrac{1}{2}) - x_e''\omega_e''(v''+\tfrac{1}{2})^2\right]$$

when the heads are taken in account, the formulae becomes

$$\nu_h = \nu_o + (\nu_h - \nu_o)$$

Introducing ν_o and $\nu_h - \nu_o$

$$\nu_h^{v',v''} = \nu_e^* + \left[\omega_e'^*(v'+\tfrac{1}{2}) - x_e'\omega_e'^*(v'+\tfrac{1}{2})^2\right] - \left[\omega_e''^*(v''+\tfrac{1}{2}) - x_e''\omega_e''^*(v''+\tfrac{1}{2})^2\right] - \Theta v' v''$$

Here ω_e^* and $x_e\omega_e^*$ are slightly different from the corresponding ω_e and $x_e\omega_e$

λ air	I	ν_{vac}	Vibrational Classification, System "A"	O - C
3390.05	(1)	29489.7	A, (4,1)	0.8
3407.89	(0)	29335.3	A, (5,2)	- 1,0
3425.92	(0)	29180.9	A, (6,3)	- 2.9
3468.90	(1)	28819.4	A, (2,0)	0.6
3486.71	(2)	28672.2	A, (3,1)	0.5
3504.22	(1)	28528.9	A, (4,2)	2.8

λ_{air}	I	ν_{vac}	Vibrational Classification, System "A"	O - C
3571.96	(8)	27987.9	A, (1,0)	- 0.1
3589.87	(6)	27848.3	A, (2,1)	0.1
3607.61	(2)	27711.4	A, (3,2)	1.6
3682.07	(10)	27151.0	A, (0,0)	0.0
3700.11	(2)	27018.6	A, (1,1)	0.1
3754.72	(1)	26625.6	A, (4,4)	- 0.5
3772.9	(0)	26497.4	A, (5,5)	0.4
3791.6	(0)	26366.7	A, (6,6)	- 0.0.
3818.32	(4)	26182.2	A, (0,1)	- 0.1
3836.38	(1)	26059.0	A, (1,2)	0.9
3854.18	(0)	25938.5	A, (2,3)	2.9
3981.45	(3)	25109.4	A, (1,3)	1.8
4000.72	(0)	24988.4	A, (2,4)	- 3.3

DESLANDRES TABLE FOR SYSTEM "A" OF ZrO

v'\v''	0	$\Delta''_{\frac{1}{2}}$	1	$\Delta''_{\frac{3}{2}}$	2	$\Delta''_{\frac{5}{2}}$	3	$\Delta''_{\frac{7}{2}}$	4	5	6
0	27151.0	(968.8)	26182.2								
$\Delta'_{\frac{1}{2}}$	(836.9)		(836.4)								
1	27987.9	(969.3)	27018.6	(959.6)	26059.0	(949.6)	25109.4				
$\Delta'_{\frac{3}{2}}$	(831.5)		(829.7)				(829.1)				
2	28819.4	(971.1)	27848.3				25938.5	(950.1)	24988.4		
$\Delta'_{\frac{5}{2}}$			(823.9)								
3			28672.2	(960.8)	27711.4						
$\Delta'_{\frac{7}{2}}$			(817.5)		(817.5)						
4			29489.7	(960.8)	28528.9				26625.6		
$\Delta'_{\frac{9}{2}}$					(806.4)						
5					29335.3					26497.4	
6							29180.9				26366.7

It will almost at once become evident that $\Delta'(v'+\frac{1}{2})$ decrease regularly with increasing v'' and $\Delta(v''+\frac{1}{2})$ increase with increase in v' in the same row and column or row respectively. This, at once suggests an appreciable value of θ By usual evaluation, it was found that has widely different values for different bands, though of appreciable magnitude and negative in all cases. An average value of θ equal to 0.90 cm^{-1} was adopted, as most suitable. After deducting the term $\theta v'v''$ from the wave numbers of the band-heads the reconstructed table showed greater regularity, as shown in the table following.

v' \ v''	0	$\Delta''\frac{1}{2}$	1	$\Delta''\frac{3}{2}$	2	$\Delta''\frac{5}{2}$	3	$\Delta''\frac{7}{2}$	4
0	27151.0	(968.8)	26182.2						
$\Delta'\frac{1}{2}$	(836.9)		(837.3)						
1	27987.9	(968.4)	27019.5	(958.7)	26060.8	(948.7)	25112.1		
$\Delta'\frac{3}{2}$	(831.5)		(830.6)				(831.8)		
2	28819.4	(969.3)	27850.1				25943.9	(948.3)	24995.6
$\Delta'\frac{5}{2}$			(824.8)						
3			28674.9	(958.1)	27716.8				
$\Delta'\frac{7}{2}$			(818.4)		(819.3)				
4			29493.3	(957.2)	28536.1				
$\Delta'\frac{9}{2}$					(808.2)				
5					29344.3				

From the preceding table it will perhaps be noted that the evaluation of a very accurate value of θ is impossible. Still the adopted average value of θ viz. -0.90 cm^{-1} has regularised the differences to a great extent. The rest of the vibrational constants were calculated for the upper and lower state of the system by usual methods.

UPPER STATE.		LOWER STATE.	
ω_e' =	843.75 cm^{-1}	ω_e'' =	973.07 cm^{-1}
$x_e'\omega_e'$ =	3.15 "	$x_e''\omega_e''$ =	5.04 "
$y_e\omega_e'$ =	0.000 "	$y_e\omega_e''$ =	0.072 "

$$\nu_e = 27217.92 \ cm^{-1}$$

and $\theta = -0.90$ "

It should be worth while to note that the magnitude of θ is appreciable, so that ξ', ξ'', η' and η'' will also be appreciable. The latter are included in the vibrational constants, as corrections, when wave-numbers of band heads instead of the origins are used to construct the usual formulae for a system. The true ω_es and $x_e\omega_e$s will, however, not be very different from the above. The formula for the band-heads of System A eventually is,

$$\nu_k^{v',v''} = 27217.92 + \{843.75(v'+\tfrac{1}{2}) - 3.15\,(v'+\tfrac{1}{2})^2\} - \{973.07(v''+\tfrac{1}{2}) - 5.04(v''+\tfrac{1}{2})^2 + .072(v''+\tfrac{1}{2})^3\} - 0.90(v'+\tfrac{1}{2})(v''+\tfrac{1}{2})$$

The bands having a deviation of more than a cm^{-1} from this formulae are those, which are very weak, and whose heads are difficult to assess accurately. The maximum deviation however does not exceed more than 3 cm^{-1} except for the λ4000.72 band, which is overlapped by many weak lines.

THE INTENSITY DISTRIBUTION IN SYSTEM "A":

The distribution of intensity amongst the various bands in the system is according to general expectations. There is a continuity, which inspires confidence, and there are no abrupt breaks or gaps such as are shown in the analysis which has been put forward for other systems of ZrO or TiO. The condon parabola is a narrow one, with its vertex at the 0,0 band but shifted slightly to (1,0) band. There are three bands at (4,4), (5,5) and (6,6) whose existence is beyond doubt. Undoubtedly, they fall on the axis of the secondary parabola.

ROTATIONAL STRUCTURE OF THE (0,0) BAND OF SYSTEM "A".

Efforts have been made by the author to photograph the (0,0) band of System A at λ 3682, on larger dispersions with sufficient resolution to reveal the structure of the band near the origin and make possible the identification of the branches in the band. This band is very weak. In fact System A itself is one tenth as strong as the strongest System γ of ZrO. Very long exposures and careful control of temperature of the spectrograph were required.

Photographs of the band were obtained in the second order of the 20 ft. grating with 11000 lines/inch and five inches of ruled surface. The theoretical limit of resolution can be reached on the plates. Exposures of five to six hours failed to obtain the spectrum with any intensity. The lines were too faint at the origin to be identified, but away from the origin, two branches could easily be traced. These were the P and R branches of the

band.

A five hour exposure with the ZrO arc as the source (by far the strongest source for ZrO) proved sufficient for photographing the λ3682 band in the second order of the 20 ft. grating with 30000 inch/line giving a dispersion of 0.59A/m.m. Unfortunately a strong background and intense atomic spectrum reduced the definition very much. Still it is the best large dispersion photograph of this band, of which the author is aware; lines have been resolved clearly down to 3682.2. A But the branches remain generally faint.

While carrying out this work, the author came across the contribution by Herbig[19] on the fine structure of λ3682 band of ZrO. In his efforts to identify the absorption lines of the stellar absorption band at λ3682, Herbig measured about 130 lines of the ZrO band at λ3682, and showed that the stellar band lines and the band-head, as measured by Merrill, agreed with the laboratory data for the λ3682 band of ZrO. The spectrum of ZrO employed in his laboratory measurements, was obtained by Dr. A. S. King in the first order of a 20 ft. grating, giving a dispersion of 3.7 A/m.m., using the carbon arc in air, charged with ZrO as the source of the spectrum.

About 130 lines of this band were arranged into two branches by Herbig, a P and an R. He therefore postulated that the λ3682 band was the (0,0) band of a system arising from a transition $^1\Sigma - ^1\Sigma$.

In the following table we reproduce the wave-numbers of some of the lines measured and arranged by Herbig in λ3682 band. No evaluation of rotational constants is possible as the numbering

cannot be carried down to the origin.

R.branch	I	R.branch	I	P.branch	I	R.branch	I	P.branch	I
3682.877	3	2686.067	3	2686.198	1	3694.334	3	3694.439	2
82.989	4	86.334	3	86.443	1	94.292	3	94.389	2
83.108	4	86.585	4	86.707	2	95.243	3	95.332	2
83.357	3	86.823	3	86.964	2	95.627	3	95.786 96.255	3 3
83.491	4	87.124	4	97.251	2	96.646	3	96.743	3
83.644	3	(87.41)	-	(87.53)	-	97.186	4	97.186	4
83.815	3	87.701	4	(87.820)	2	97.617	3	97.692	3
83.968	3	87.992	3	88.129	2	(98.12)	-	(98.20)	-
84.158	3	88.301	3	88.427	2	98.612	3	98.701	3
84.340	3	88.617	3	88.755	2	99.173	3	99.173	3
84.515	3	88.937	3	89.079	2	99.713	3	99.713	3
84.712	3	89.272	3	89.399	2	3700.223	5	3700.223	5
84.927	4	89.622	3	89.741	2	00.774	4	00.774	4
85.148	3	89.950	3	90.098	2	01.340	4	01.340	4
85.356	3	90.318	3	90.456	2	01.894	4	01.894	4
85.580	3	90.694	3	90.821	2	02.456	4	02.456	4
85.940	4	91.059	3	91.189	2	03.026	6	03.026	6
		91.435	3	91.550	2	03.614	6	03.614	6
		91.826	3	91.952	2	04.213	5	04.213	5

continued.....

R.branch	I	R.branch	I	P.branch	I	R.branch	I	P.branch	I
92.228	3	92.339	2	04.824	5	04.824	5		
92.633	3	92.752	2	05.430	6	05.430	6		
93.039	3	93.151	2						
93.467	3	93.568	2						
93.880	3	94.014	2						

Bracketted lines are computed wavelengths, the region being overlapped by atomic line. The molecular lines which have been underlined have been identified in Stellar spectra, eg, O. Cet. and R Andromedae.

THE POSITION AND NATURE OF THE LEVELS OF THE SYSTEM "A":

To continue the discussion on the nature of energy levels involved in the system "A", it will be noted that Herbig postulated that the λ3682 band of ZrO was the (0,0) band, because of failure to observe any isotopic shift, and classified it a $^1\Sigma - ^1\Sigma$ system, since only one R and one P branch could be located in the band structure. He did not observe any other band belonging to this very system in the laboratory, but in stellar spectra he noted that an absorption feature at λ3571 generally accompanied the absorption of the λ3682 band. Unfortunately he identified the former with the OH^+ band in the same wavelength, not being aware of the existance of any ZrO band at λ3571. From the present analysis by the author, it is apparent that the stellar absorption at λ3571 is clearly the absorption $1 \leftarrow 0$ in singlet system A of ZrO.

That the system A is due to a $^1\Sigma - ^1\Sigma$ transition is quite plausible, though there is always the possibility that in weakly photographed spectra, the relatively faint Q branch in a $^1\Pi - ^1\Pi$ transition may not be observed. Both the spectra obtained by us, and the print of the spectrogram published by Herbig, are so weak that they can hardly inspire confidence in the conclusion that a Q branch is definitely absent. (At this point it should be mentioned that Miss Lowater failed to observe a Q branch for $^3\Pi_1 - ^3\Pi_1$ band in system α of ZrO, though the relative intensity of R branch to Q branch will be about the same as in a $^1\Pi_1 - ^1\Pi_1$ transition. In Miss Lowater's photographs the branches are several times as intense as in Herbig's or ours). This consideration makes the transitions $^1\Sigma - ^1\Sigma$ or $^1\Pi - ^1\Pi$ equally possible for the system A, though there is always a little greater probability of a $^1\Sigma - ^1\Sigma$ transition. The upper and the lower levels of system A are either both $^1\Sigma$ levels, or both $^1\Pi$ levels. But tentatively, we will suppose that the system A arises from a $^1\Sigma - ^1\Sigma$ transition, until the contrary is proved to be the case.

Because the λ3682 (0,0) band of system A was observed in absorption along with systems α, β and γ of ZrO, whose lower level is X $^3\Pi$ Herbig raised the question as to which of the two levels X $^3\Pi$ and $^1\Sigma$ was the ground state of ZrO. In our opinion, there can be little doubt that X $^3\Pi$ is the ground state, and that $^1\Sigma$ is a low excited state. All the lower levels of the systems observed in absorption are not necessarily the ground states of molecules. At temperatures of 2500° enough molecules of ZrO

may be thrown into the low excited $^1\Sigma$ level to make a faint absorption possible. That the absorption in λ 3682 is very weak compared with absorption in α, β and γ supports this hypothesis. To determine its position roughly, let us take into consideration the fact that the multiplet splitting in the ^3F ground state of Zr^{++} is 804.3 and 682.5 cm^{-1} respectively. Assuming that there is a correspondence between ZrO levels and Zr^{++} levels, the multiplet separations in the $X\,^3\Pi$ ground state of the former are 313.4 and 292.1 cm^{-1}. These are roughly in a ratio of 2.57 and 2.34 respectively. Expecting this ratio to hold further, approximately, we note that three singlet levels ^1G, ^1D and ^1S fall next to ^3F ground state of Zr^{++} at 2534, 3392, 3835 cm^{-1} If these levels correspond with $^1\Sigma$ level of ZrO, the position of $^1\Sigma$ level with respect to $X\,^3\Pi_0$ ground state of ZrO will be between

$$\frac{2534}{2.57} = 986 \text{ cm}^{-1}$$

and

$$\frac{3835}{2.34} = 1639 \text{ cm}^{-1}$$

Taking an average position for $a^1\Sigma$ level of ZrO, it is found that the lower state of System A lies near about 1310 cm^{-1} above $X\,^3\Pi_0$ ground state of ZrO. Absorption is clearly possible from $a\,^1\Sigma$ state. The upper $b^1\Sigma$ level of the system A is at (1310 + 27151.00) or roughly at 28461 cm^{-1}.

As has already been mentioned, adoption of the $^1\Sigma$ levels for the singlet system A is provisional. If it is proved that states other than $^1\Sigma$ are involved, the levels $^1\Sigma$ should be altered accordingly.

EXTENSION OF SYSTEM α

In describing the work of Miss Lowater, on the analysis of ZrO bands in the visible, it has been mentioned that system α was somewhat incomplete. The Deslandre's Table of System α produced on the pages previously, was constructed by Miss Lowater. Though the analysis of the system was no doubt correct, it was thought worthwhile to try to complete it, and to remove serious gaps and discontinuities if possible.

Very satisfactory spectrograms of the triplet systems of ZrO, α, β and γ in the visible were obtained, both on the ten ft. grating, and the Large Littrow. The best source of the spectrum was the flame shooting from the anode cup of the Zr Arc in moist Hydrogen, but the ZrF_4 unsteady, rapidly oxidising arc proved almost as satisfactory. In both these sources, the atomic spectrum of both the electrode material and Zirconium itself, was suppressed so much that comparatively few atomic lines could be traced in the spectrograms. This helped in deciding the shape and character of doubtful heads; and allowed weaker bands to become conspicuous.

A few bands found in front of (0,1) R_a and (0,1) R_c heads were classified by Miss Lowater as for (8,8)R_a, and (8,8)R_c heads respectively. We have also observed a few heads displaced roughly by the same amount. The theoretically expected displacements for the $Zr^{94}O^{16}$ isotopic heads compared with the known $Zr^{90}O^{16}$ heads are about 3.1 cm^{-1} in (0,1) bands. It will be found that the order of the displacement of these heads suggests that they in

reality are the isotopic heads belonging to $Zr^{94}O^{16}$ molecule. The reason that isotopic heads to other bands could not be discovered, is that either the bands are too weak, or the displacements too small to become observable, or else that the isotopic head falls within the main bands.

Furthermore, we have come to the conclusion that all the bands of system α classified as (0,4) by Miss Lowater do not belong to this system.

DISLANDER TABLE FOR THE BANDS IN SPECTRA.

v''		0	Δ''½	1	Δ''1½	2	Δ''2½	3	Δ''3½	4
0	a	21640.3	(931.2)	20709.1	(923.5)	19785.6	(916.7)	18868.9		
	b	21556.4	(931.4)	20625.0	(921.9)	19703.1	(918.5)	18784.6		
	c	21543.7	(930.9)	20612.8	(922.9)	19688.9	(———)	———		
	Δ'½	(814.2) (813.1) (814.2)		(814.9) (814.5) (814.3)		(———) (809.6) (814.2)		(———) (———) (———)		
1	a	22454.7	(930.7)	21524.0	(———)	———		———		
	b	22369.5	(930.0)	21439.5	(926.8)	20512.7		———		
	c	22357.9	(930.8)	21427.7	(924.0)	20503.1		19587.6 ■		
	Δ'1½	(803.4) (808.1) (807.5)		(———) (807.4) (807.7)		(———) (———) (803.7)		(———) (———) (805.1)		
2	a	23253.1	(———)	———	(———)	———	(———)	———		
	b	23177.6	(930.7)	22246.9	(———)	———	(———)	20404.7		
	c	23165.4	(930.6)	22234.8	(927.9)	21306.8	(914.1)	20392.7		
	Δ'2½	(———) (802.9) (———)		(———) (801.6) (802.1)		(———) (———) (805.4)		(———) (———) (801.9)		
3	a	———	(———)	———	(———)	———	(———)	———	(———)	———
	b	23980.5 ■	(932.8)	23048.5	(926.3)	22122.2	(———)	———	(———)	20294.8
	c	———	(———)	23036.9	(924.6)	22112.3	(917.7)	21194.6 ■	(912.2)	20282.4
	Δ'3½			(———) (———) (789.9)		(———) (796.9) (794.7)		(———) (———) (794.2)		
4	a			———	(———)	———	(———)	———		
	b			———	(———)	22919.1	(918.2)	22000.9		
	c			23826.8	(919.6)	22907.0	(918.2)	21988.8		
	Δ'4½					(———) (787.8) (788.7)		(———) (788.4) (788.6)		
5	a					———	(———)	———		
	b					23706.9	(917.6)	22789.3		
	c					23695.7	(918.3)	22777.4		

■ Bands observed by Johnson but not by us.
✓ do do do Lowater do do do do.

λ 8192 BAND OF ZrO.

The band spectrum though fairly continuous in the infra-red is generally very weak. As the γ system of ZrO fades out on the longer wavelength-side, a few weaker bands become conspicuous in this near infra-red region; but none of these appears to fit in the γ system. This region of the bands is such that all the prominent and a very great majority of the weaker bands have been assigned to the γ system of ZrO. The weak bands at λ 7426(2), λ 7454(3) and λ7541(4) are the only unassigned ones. Their general weakness makes it difficult to ascertain whether they are in reality three bands of the same sequence (with $\nu^{v',v''} - \nu^{(v'+1)(v''+1)} = 104\ cm^{-1}$)

Spectrograms of the region $\lambda\lambda$7600-9000 were obtained in the first order of the 10 ft. grating with ZrO arc in air as the source, in the hope of discovering other sequences of ZrO bands related to the above bands, and thereby ascertaining the nature of the system and its constants. The experiment appeared to be hopeful, because the γ system of ZrO fades out completely in this region leaving little complicated background. The author failed to discover such bands, but instead observed the fine band structure to extend from λ7600 to λ7900 without trace of any conspicuous heads. Finally there appeared a relatively strong band at λ8192, which was fairly well resolved in the spectrogram; and of which the band lines could easily be traced right to the head. The band must be about one tenth as strong as the $(0,0)R_e$ band of system γ , though much stronger than the general ZrO spectrum in the $\lambda\lambda$ 8500-8900 region. In appearance this band seemed to be of very simple structure,

apparently a P and an R branch superposed on each other, making it impossible to locate the origin, there being no Q branch. As this band does not appear to belong to either system γ or the infrared system "I" of ZrO, it should belong to a new system. If this is supposed to be a triplet system the remaining two heads should be located within 600 and 1200 cm^{-1}. Apparently there is no other band resembling in general features the band at λ8192, within the regions mentioned. It is therefore unlikely that this band is due to a triplet system. The possibility of quintet systems is farther remote. The band can therefore be due to a singlet system. The presence of a P and an R branch and a definite absence of Q branch suggests a $^1\Sigma \rightarrow {}^1\Sigma$ transition. The band may very well be the (0,0) band of this system. This is confirmed by the consideration of the isotopic displacements. Near the head, the branches within the band are sharp, showing that the isotopic displacements due to $Zr^{92}O^{16}$ and $Zr^{94}O^{16}$ are small and unresolved from the main branches. As one traces the branches farther towards the tail, it is noted that the branch-lines begin to become diffuse on the shorter wavelength-side, and at λ8350 they definitely split into three components. The weaker two on the shorter wavelength side of the main and strong branch line are due to $Zr^{92}O^{16}$ and $Zr^{94}O^{16}$ respectively. The isotopic displacement due to the rotational term ... ($\Delta\nu_r$=180 cm^{-1}) should become considerable in this region and be strengthened by displacement in the vibrational term. Other bands of this system might have been expected in the regions λ7600 and λ8800; but as both these regions are occupied by other spectral features of

ZrO, it is likely that they would be masked by more conspicuous band-features. Within the sequence it is difficult to discover the far weaker (1,1) (2,2) bands etc., as they fall on the strong (0,0) band. However, there appears to be a faint band-head at 8210A. This may very well be the (1,1) band of this system.

INFRA-RED SYSTEM "I" OF ZrO.

There is a further system, in the infra-red, of very complicated structure. Though it has been possible to discover some relationships between the bands and construct what looks like the Deslandres's Table for the new system, the analysis remains extremely doubtful.

Attention was first drawn to the bands of ZrO in the infra-red, by Meggers and Keiss[18] King's publication of the wavelengths of the bands of ZrO in the infra-red region λλ 9200-9500. The bands had a very complicated structure, and were very weak. It was impossible to identify the triplets, which can be expected for ZrO spectra.

Photographs of the ZrO spectrum in the region λλ7600 - 9000 were obtained by the author in the first order of a ten ft. grating on I.R.E.R. plates, with ZrO arc (a) in air, giving exposures of 10-20 minutes. A faint and complicated system of bands was observed between λλ 8500-8950, and it was assumed that this new group of bands formed a part of the system mentioned by Meggers and Keiss King. Actually, it was possible to assign Meggers' and Keiss King's group of bands in the region λλ 9200-9500, to the (0,0) sequence of the system, and the new group of bands discovered by the author at λλ8500-8950 to the (1,0) sequence. It appears that there are

five heads to each band. This does not necessarily mean that the levels involved in this system are quintets, though they may exist for ZrO. However, some systems of CO, like the third positive are known to possess five heads, although the levels involved are only triplets. Much inference about the multiplicity of the levels involved in this system "I" of ZrO can hardly been drawn.

With the observational data available, little can be postulated with confidence, except that these complicated bands of ZrO belong to a new system or systems of ZrO, perhaps involving more complicated levels, than hitherto observed for this molecule. Below, suggested Deslandres's table for the ZrO system "I" is shown. Too much stress cannot be laid on the accuracy of the analysis at this stage.

		0	1	$\Delta^{N\frac{3}{2}}_{\frac{1}{2}}$	2
	a	10750.3			
	b	10731.4			
0	c	10715.3			
	d	10700.1			
	e	10685.3			
$\Delta'\frac{1}{2}$					
	a		10668.6		
	b		10649.8		
1	c		10632.2		
	d		10621.8		
	e		10599.6		
	a		(828.8)		
	b		(829.0)		
$\Delta'\frac{3}{2}$	c		(830.8)		
	d		(834.6)		
	e		(833.5)		
	a		11497.4 (911.5)	10585.9	
	b		11478.8 (-----)	-------	
2	c		11463.0 (913.6)	10549.4	
	d		11446.4 (-----)	-------	
	e		11433.1 (-----)	-------	

continued....

0		1 $\Delta''\frac{3}{2}$	2 $\Delta''\frac{5}{2}$	3
	a		(814.5)	
	b		(-----)	
$\Delta'\frac{5}{2}$	c		(-----)	
	d		(-----)	
	e		(-----)	
	a		11400.4	
	b		11380.0	
3	c		-------	
	d		-------	
	e		11334.2	
	a			-------
	b			11286.8
4	c			11272.2
	d			11256.6
	e			11242.5

Many bands observed in the Infra-red, remain unassigned. The majority of these unassigned bands are about as weak, and fall in the same region as the system "I". In general appearance, as well, they are like the bands that have been systematised. Further these are bands in the same region, though somewhat weaker, which degrade towards the shorter wavelength. (It will be not irrelevant to point out that there were similar weak bands, degrading to the

shorter wavelength, in the Infra-red system of TiO, analysed by Dobroneravin). All these facts make the analysis more uncertain. However, as has already been suggested, present efforts haveborne fruit only in discovering a relationship between various bands which can scarcely be said to be an analysis.

The tentative formula representing the system is:-

$$\nu_k^{v'v''} = \left\{\begin{array}{l} 10790.8 \\ 10771.9 \\ 10756.3 \\ 10742.6 \\ 10727.8 \end{array}\right\} + \left\{862.9(v'+\tfrac{1}{2}) - 8.8(v'+\tfrac{1}{2})^2\right\} - \left\{945.4(v''+\tfrac{1}{2}) - 8.6(v''+\tfrac{1}{2})^2\right\}$$

$\omega_e' = 862.9$ cm^{-1} $\qquad$ $\omega_e'' = 945.4$ cm^{-1}

$\chi_e'\omega_e' = 8.8$ cm^{-1} $\qquad$ $\chi_e''\omega_e'' = 8.6$ cm^{-1}

The values of $\chi_e\omega_e$'s are unreliable, though there is greater accuracy in the calculated values of ω_e' and ω_e''. The former vary from 861.4 to 864.4 cm^{-1} and the latter from 942.5 to 948.1 cm^{-1} for the five sub-heads. The ω_e'' in the final level of the System "I" is very nearly the same as the value of ω_e'' in the ground level $X\ ^3\Pi$ of ZrO. But it does not prove that $X\ ^3\Pi$ is involved in the System "I", due to the general unreliability of the calculated values for ω_e's and $\chi_e\omega_e$'s.

ENERGY LEVELS OF ZrO

EXPECTED GROUND STATE OF THE OXIDES OF Ti SUB-GROUP.

In the following we present a table showing the electronic configurations in the ground state of the elements of Group IV of the periodic table.

Element	A	N	Electronic configuration	The State
Carbon	6		$(2s)^2\,(2p)^2$	$^3P_0$
Silicon	14		$(3s)^2\,(3p)^2$	$^3P_0$
Titanium	22		$(3d)^2(4s)^2$	$^3F_2$
Germanium	32		$(4s)^2\,(4p)^2$	$^3P_0$
Zirconium	40		$(4d)^2(5s)^2$	$^3F_2$
Tin	50		$(5s)^2\,(5p)^2$	$^3P_0$
Hafnium	72		$(5d)^2\,(6s)^2$	$^3F_2$
Lead	82		$(6s)^2\,(6p)^2$	$^3P_0$
Thorium	90		$(6d)^2\,\,(7s)^2$	$^3F_2$?

It will be evident from the above table that the elements C, Si, Ge, Sn and Pb can be grouped together while Ti, Zr, Hf and Th fall in a separate group. For brevity's sake we will refer to the two groups as the C sub-group and the Ti sub-group respectively.

It will be observed that the ground state of the oxides of the C sub-group is $^1\Sigma$ while that for the oxides of Ti sub-group has not been established with certainty. Since the electronic configuration in the two sub-groups is different, it can easily be concluded that they may in all probability

not possess similar ground states. As we already know the combination of two atoms in ^3F and ^3P states (Oxygen atom) is expected to give several possible energy levels, such as

$^1\Pi$, $^1\Sigma$, $^1\Delta$, $^1\Phi$, $^3\Sigma$, $^3\Pi$, $^3\Delta$, $^3\Phi$, $^5\Sigma$, $^5\Pi$

etc. Any of these could be the ground state of the oxides of the Titanium sub-group. Since, singlet and triplet levels have so far been identified for the TiO and ZrO molecules, from both of which absorption takes place in stellar atmospheres, considerable doubts have arisen as to the true nature of the ground state of these molecules.

Before the energy levels of the Ti, Zr or Hf atoms had been observed and the electronic configuration determined, Miss Lowater analysed the β and γ systems of TiO. She found that while the α and γ systems of TiO were due to transitions $C\,^3\Pi \rightarrow X\,^3\Pi$ and $B\,^3\Sigma \rightarrow X\,^3\Pi$, the levels involved in system β were presumably $^1\Pi$ and $^1\Sigma$. To establish which of these $^1\Pi$, $^1\Sigma$ or $X\,^3\Pi$ states was the ground state of the molecule, she postulated an an analogy between TiO and Ca. Her reasons were as follows. The Oxygen atom requires two more electrons in (2p) states to complete the shell and make it inactive like Ne (with S:O and L:O). The Titanium atom in the oxide may be supposed to be deprived of the two least strongly held electrons, to complete the oxygen shell. An atom of Titanium deprived of the two electrons, was supposed to resemble Ca with two less electrons. (We know now that this is not true). As the energy levels in

Ca were in the order ^1S, ^3P, ^1P, ^3S and ^3P, the corresponding energy levels in the TiO in the same order will be $^1\Sigma$, $^3\Pi$, $^1\Pi$, $^3\Sigma$ and $^3\Pi$ as the Oxygen atom is in-active. Miss Lowater consequently constructed a diagram of the energy levels of the TiO molecule, wherein a $^1\Sigma$ state was supposed to be the ground state of TiO.

Quite recently Herbig[19] has made similar suggestion for the ZrO molecule. Hitherto only triplet states were known for this molecule. Herbig studied the fine structure in the λ3682 band of ZrO to establish the identity of the absorption feature at the same wavelength in some of the S and M type stars. He measured about 130 lines in this band, which had been photographed in the first order of a 20 ft. grating, giving a dispersion of 3.7 A/m.m. Herbig arranged these into a P and an R branch. Due to the absence of a Q branch - not proved conclusively - he came to the conclusion that the band was due to a $^1\Sigma - {}^1\Sigma$ transition. As this band had already been observed in stellar absorption, he was in doubt, whether the new $^1\Sigma$ or the old $X^3\Pi$ (final level of system α, β and γ) was the ground state of the ZrO molecule.

Some of the confusion in this field can perhaps be cleared by theoretical considerations. Keeping to the idea advanced by Miss Lowater, that the shells of the Oxygen atom in TiO and similar molecules are closed by the inclusion of two more electrons in its (2p) shell, whereby it becomes inactive like Ne (SrO, LaO), and the Ti atom (or any other atom of the same

group) resembles in electronic configurations its own doubly ionised atom, we find that the ground state of the doubly ionised atoms of the Ti sub-group is $^3F_2$; or the only contribution to λs and Σs of the TiO (and the like molecules) will be coming from the $^3F_2$ term, oxygen atom being already inactive. This will demand that,

$S = 1$ and $L = 3$,

Therefore $S = 1$ and $\lambda = 3, 2, 1$ and 0

The only states possible for TiO (and the like molecules) from this angle are all triplets, either $^3\Sigma$, $^3\Pi$, $^3\Delta$ and $^3\Phi$

Further, without changing the electronic configuration, but altering spin orientation of the electrons to obtain singlet states for the doubly ionised Ti^{++} atom, we observe that these state lie slightly above the triplet ground state. We may therefore assume that the singlet states of the TiO and ZrO molecules will also lie slightly above their triplet ground state. We know that $X\,^3\Pi$ is the only triplet level, which has been identified to be the lower one in all the triplet systems of TiO and ZrO molecules; and it should therefore be the ground state of these molecules.

A further point of interest is the variation of constants of the oxides of Gr.IV in their ground state. Whereas the variation for the oxides of the C sub-group is uniform, it does not appear to hold for those of the Ti sub-group. Here the ω_e and $x_e\omega_e$ decrease according to expectation from TiO to ZrO (we may suppose that they will be further smaller

for HfO and ThO), but B_s increase from TiO to ZrO. This increase is very prominent. The author is not aware, where within a group, ω_e and B_e for similar molecules have shown tendencies of variation in opposite directions. They are known to increase or decrease together. As ω_e's are accurately known, it raises some doubts about the B_e's as evaluated for TiO and ZrO. So far as the B in the ground state of ZrO is concerned, the author is convinced that it has been accurately determined and also confirmed independently. This leaves some doubt about the true value of B for the TiO molecule. Birge and Christy had analysed the system α due to $C\,^3\Pi \rightarrow X\,^3\Pi$ transition and obtained the B, D and α constants in the $X\,^3\Pi$ and $C\,^3\Pi$ states from rather large J values. Their work has not so far been confirmed by any other worker.

If we adopt the idea that the vibrational and rotational constants of TiO and ZrO have both been determined with reasonable accuracy, we shall have to accept a striking characteristic for the oxides of the Ti sub-group, and that is, B_s and ω_s vary manifestly in opposite directions, the former increasing and the latter decreasing with increasing atomic weight. This phenomenon, if true, will be the only example of its kind.

MOLECULAR CONSTANTS OF THE OXIDES OF ELEMENTS IN THE Gr III

At.Wt.	Mol.	Gr. St.	ω_e $c\bar{m}^{-1}$	$x_e\omega_e$ $c\bar{m}^{-1}$	B_e $c\bar{m}^{-1}$	α_e $c\bar{m}^{-1}$	r_e A°
12	CO	$^1\Sigma$	2167.4	12.7	1.85 *	---	1.15 *
28	SiO	$^1\Sigma$	1240.5	5.95	0.7215	0.005	1.505
48	TiO	$^3\Pi$	1008.1	4.52	0.5352	0.0028	1.618
74	GeO	$^1\Sigma$	985.7	4.30	0.4704	0.0029	1.647
90	ZrO	$^3\Pi$	937.20	3.35	0.6189	0.0038	1.412
128	SnO	$^1\Sigma$	821.9	3.6	0.3488	---	1.832
180	HfO	$^3\Pi$?	----	----	----	----	----
208	PbO	$^1\Sigma$	722.3	3.73	0.3073	0.0019	1.90
232	ThO	$^3\Pi$?	----	----	----	----	----

* For CO Be and r_e are B_e and r_o respectively.

ENERGY LEVELS OF ZrO.

Enough has been said about the ground level of ZrO. It is now clear that it is the X $^3\Pi$ final level of the α, β and γ systems. This is supported both by theoretical considerations and by observational data. Next above it is the $^1\Sigma$ or $^1\Pi$ lower level of the system A. The upper levels of systems α, and γ have been proved to be C $^3\Pi$ and A $^3\Sigma$ levels respectively. Next come the upper levels of system δ and system ϕ both of which share the X $^3\Pi$ state as their final level. About the β system, there are still some doubts in the mind of the author. Miss Lowater[5] thought that the β system arose from a B $^3\Sigma \rightarrow$ X $^3\Pi$ transition. This demanded that the B $^3\Sigma$ multiplet separations should be 36.7 and 44.9 cm^{-1} respectively, and these are very large indeed. Miss Lowater was conscious of this defect in the diagram which she had constructed, for she said, "It would have been more in conformity with other band spectra, had the separations in the upper $^3\Pi$ state (viz. C $^3\Pi$) been more nearly equal to one another, and had those in the upper (B $^3\Sigma$) state of system β been still smaller." System β could also arise from an upper triplet level with 5,606 and 559.8 cm^{-1} separations ending on the X $^3\Pi$ ground state of ZrO. The upper sub-level of R_a band of system lies about 1120.4 cm^{-1} and that of R_b about 559.8 cm^{-1} above the lowest sub-level of the upper triplet state, from which originates the R_a head. This will demand that the intensity

in R_b heads be much smaller than in R_c heads, while the intensity in R_a heads should be still smaller. If the multiplet separations in the upper triplet level of system were only 36.7 and 44.9 cm^{-1} the three R_a, R_b and R_c heads should be of about equal intensity, though R_c head should be slightly weaker of the three. (This appears to be the case with system γ, $A\ ^3\Sigma \rightarrow X\ ^3\Pi$). But contrary to this, we find that the R_a heads are about half as intense, and R_b heads about three quarters as strong as the R_c heads in system β . This supports the hypothesis that the multiplet separations in the upper triplet level of system β are 560.8 and 559.8 cm^{-1} respectively. $^3\Delta$ levels of ZrO may be supposed to possess such large splittings. The appearance of X heads behind the R heads in system β provides further support to the idea. If they are the Q heads, then they are in accordance with the theoretical demands. The transition responsible for the System β appears to be $B\ ^3\Delta \rightarrow X\ ^3\Pi$. This is also supported by Johnson's[4] observations. He notes several weaker heads to Principle R heads, which may be sattelites.

A table of various molecular constants, for the identified energy levels of ZrO is given below, in order of their occurrence. On the next page is the Energy level diagram.

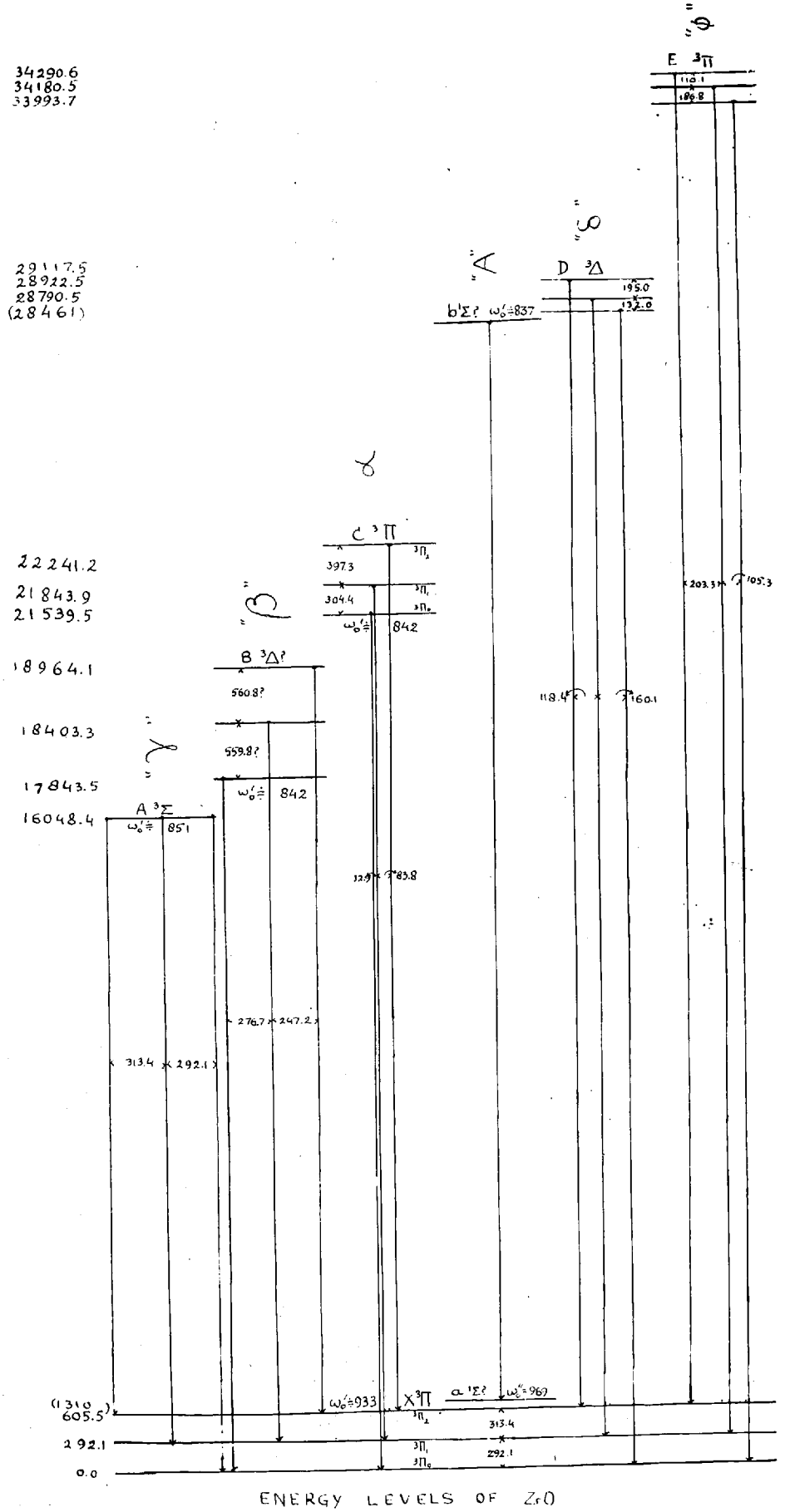
P.S:-

Since this manuscript has been written, the auther has come across a contribution by Richard, Barrow, and Lagerqvist* on a "New ultra-violet Band systems of GeCl" ($^2\Delta \rightarrow {}^2\Pi$), where the splittings in the upper $^2\Delta$ state have been found to be one sixteenth of that in the $^2\Pi$ state. If it were assumed that Zr and Ti spectra show the same regularity as Ge, the upper $B^3\Delta$ state of the β system of ZrO may very well possess splittings of 26.7 and 44.9 $cm.^{-1}$

* Arrirk För Fysik, Band 1, nr 8, p. 221. (1949)

STATE	ν_o	ω_e	$x_e\omega_e$	B_e	α_e	$-D_e$
$X\,^3\Pi$	0	937.20	3.346	0.6189	0.0045	1.413 x 10
$a\,^1\Sigma$ x	(1310)	978.07	5.04	---	---	---
$A\,^3\Sigma$	16048.4	856.97	3.373	0.5658	0.0077	1.477 x 10
$B\,^3\Delta$?	17483.5	846.28	3.409	---	---	---
$C\,^3\Pi$	21599.5	820.58	3.306	0.5333	0.0123	1.521 x 10
$b\,^1\Sigma$ x	(28461)	843.75	3.15	---	---	---
$D\,^3\Delta$	28912.5	---		---	---	---
$E\,^3\Pi$	33993.7	---		---	---	---

x These singlet levels may well be $^1\Pi$ or $^1\Delta$ instead of


34290.6
34180.5
33993.7
E ³Π
29117.5
28922.5
28790.5
(28461)
D ³Δ
195.0
132.0
b¹Σ? ω'e=837
22241.2
21843.9
21539.5
c ³Π
397.3
304.4
ω'e= 842
18964.1
B ³Δ?
560.8?
18403.3
559.8?
17843.5
ω'e= 842
16048.4
A ³Σ
ω'e= 851
118.4
160.1
203.3
105.3
133.9
85.8
276.7
247.2
313.4
292.1
(1310)
605.5
ω'e=933
X ³Π
a ¹Σ? ω'e=969
313.4
292.1
2 92.1
0.0
ENERGY LEVELS OF ZrO

ZrO in STELLAR SPECTRA.

Merrill[2] identified ZrO in late type Stellar spectra, in the year 1922, by comparing the absorption features with laboratory spectrograms of Zirconium Oxide. The long period variables investigated by Merrill differed from the stars of class M, since they did not show the characteristic TiO bands. He thought that these stars formed a third branch of the giant sequence BAFG, and were related to class M rather than to class N. There was a very interesting analogy between the two. Zirconium and Titanium both belong to the same group in the periodic table, while the Titanium Oxide bands predominated in stars of class M, the bands of Zirconium Oxide appeared to be characteristic of the new class of stars, later designated as S.

Stars in which Merrill discovered conspicuous absorption by Zirconium Oxide were

R Andromedae
T Camelpardalis
R Lyncis
T Sagittari
and R Cygni

Merrill says[22] "In many S type variables TiO bands are present during part or all of the light cycle. In the blue green portion of the spectrum they may become prominent, and make the ZrO bands difficult to recognise. Sometimes, as in χ Cygni, the chief reminder of the presence of ZrO is an

apparent decrease of about 7 A° in the wavelength of the TiO band at λ4626 caused by the ZrO head at λ4619. This might be overlooked in general examination of small scale spectra."

The above shows clearly that TiO is not excluded from the S type stars. Even peculiarly characteristic S type stars show weak absorption in TiO.

Systems γ, α and β of ZrO have been observed to cause strong absorption in S type stars.

The author has examined a large dispersion spectrogram of R Andromedae, a typical S type star. While the absorption in the α system is mainly confined to the $v''=0$ progression (viz absorption is $v' \leftarrow 0$), (0,0) R_a, (0,0)R_b and (0,0)R_c bands appearing conspicuously, a weaker absorption from the $v''=1$ level is also beyond doubt, the bands appearing most strongly being the (2,1)R_b and (2,1)R_c. This shows that the temperature in S type stars corresponds to such magnitudes that quite an appreciable fraction of ZrO molecules are maintained in the $v''=1$ level, which is about 937 cm^{-1} above the $v''=0$ level of the ground state of ZrO.

Many unclassified bands also appear in absorption. An example is a single ZrO band at λ4736.9, whose assignment has not yet been possible. The strong absorption in this band suggests that it arises from absorption by the ground state of ZrO. That other bands of the triplet cannot be found in the neighbourhood of λ4736.9 band, might be due to upper levels of the band being inverted, which will cause large separations

in the bands arising from different levels. This may provide a clue which will unlock the mystery of the unassigned bands, and help systematise them.

In 1933, Richardson[23] tried to provide a theoretical background for understanding the differences in the S and the M type stars. Using Saha's equation for dissociative equilibrium he tried to determine the relation between the temperature and pressure of the stellar atmosphere, and the absorption by the molecules of TiO and ZrO; the equation he used was

$$\text{Log } K = \frac{-5041\,D}{T} + \frac{3}{2}\log T + \frac{3}{2}\log M + \log G + \log\left(1 - e^{-\frac{h\nu}{RT}}\right) - \log I - 39.688$$

where $K = \frac{P x^2}{1-x^2}$ (x fraction of dissociated molecules)

D = Heat of dissociation 7.5 V for ZrO and 6.55 for TiO.

$M = \frac{M_{Zr}\, M_O}{M_{ZrO}}$, $\frac{M_{Ti}\, M_O}{M_{TiO}}$

$G = \frac{g_{Zr}\, g_O}{g_{ZrO}}$ or $\frac{g_{Ti}\, g_O}{g_{TiO}}$

$I = \mu\, r_e^2$

and $\nu = \omega_e c$

Whereas the moment of inertia of TiO was known to Richardson by Christy's work, no such data were available to him for ZrO. Morse relation, viz

$$r_e^3\, \omega_e \sim \text{constant}$$

holds fairly well for a wide variety of electronic states, even of different molecules. Richardson computed values of $r_e^3\, \omega_e$ for all the metallic oxides for which these

quantities were known. By plotting these results against the logarithms of the At. Wt. of the metals, a roughly linear relation was obtained. This process gave for ZrO

$$\pi e^2 \mu_e^2 \sim 4.5 \times 10^{-21} \text{ cm}^{-1}$$

$$I \sim 64 \times 10^{-40} \text{ gm cm}^2$$

It will be found that this computed value for the moment of Inertia of ZrO is widely different from the experimentally determined value of "I" which is only 44.717×10^{-40} gm cm^2

However, the chief determining factor in the equation of dissociative equilibrium is the energy of dissociation.

The results obtained by Richardson may be summarised as follows:-

"The temperatures of the M and S stars probably overlap. Several lines of inquiry indicate that S type stars are probably lower in density than those of class M.

For a constant pressure of 10^{-6} atmospheres, TiO is rapidly dissociated and disappears from the spectra at 3000° while ZrO is only 60% dissociated. Similarly, TiO is found to be much more sensitive to pressure changes than ZrO, and can not exist at a temperature of 2500° if the pressure falls below 10^{-8} atmospheres.

The fact that TiO alone is found in M type stars can be explained if their density is greater than stars of class S, as indicated by observations."

Somewhat analogous results were obtained by Miss Cambresier

and Rosenfeld[24].

Bobrovnikoff[25] has however shown the existence of Zirconium Oxide bands in almost all the M type stars, with varied intensities. It is observed that the abundance of Oxygen, Titanium and Zirconium in the atmosphere of the sun is of the order of 100,000; 100:1; and that in most of M type stars the Ti lines of low excitation potential are among the strongest in the spectrum, whereas analogous Zr lines are hardly noticeable. This shows that the abundance of Zr in M type stars is very small indeed. Therefore the relative intensities of the TiO and ZrO bands in red stars depend primarily on the variation in the relative abundance of Ti and Zr, rather than on that of Oxygen.

Searching for the bands of the γ system of ZrO in the M type stars, he definitely concluded that this molecule was present in M type stars, though the absorption was very weak compared with the corresponding absorption by TiO. Comparing the intensity of the ZrO $\lambda 6473.7$, $(0,0)R_e$ head of System γ whose intensity on the laboratory spectrogram is (20), with the TiO band $\lambda 6483.6$, $\gamma(4,2)\,Q_c$ whose intensity on laboratory spectrogram is only (2), the following relation is obtained.

STARS	T	CLASS	R(O=1)	INTENSITY TiO	INTENSITY ZrO	ZrO / TiO
α Ori ---	3200°	M2	300	2	2	1.0
α Sco ---	3100	M1	450	5	1	0.2
β Peg ---	3100	M2	40	2	10	5.0
α Her ---	2650	M5	400	10	7	0.7
ρ Per ---		M4		6	10	1.2

The above table shows that variations in the strength of ZrO are not so much dependent on the density (α Her has seven times the intensity of ZrO absorption compared with α Sco which has about the same density) or the temperature as on the relative abundance of Zirconium itself. To quote Sobrovnikoff, "it seems that the variation of the two parameters T and g does not explain the behaviour of ZrO in stars. There seem to be M type stars especially rich in ZrO, among which β Pegasi is the most remarkable.--------It appears that Zr is wholly oxidised in the atmosphere of β Pegasi, in contract to Ti in the same star."

ABSORPTION IN NEW SYSTEMS OF ZrO.

Miss Lowater had measured a band of ZrO at λ 3682.4 which is rather weak compared to other prominent bands of ZrO in the visible. This band was postulated to be the (0,0) band of a $^1\Sigma - {}^1\Sigma$ system by Herbig[19], when he identified the

band in M and S type stellar spectra. The existence of an unidentified band was known for long in the stellar spectra at λ 3682. This band could not probably be identified with the ZrO band at the same wavelength, because the wavelength of the band head of ZrO as given by Miss Lowater appeared to be half an angstrom to the longer wavelength. Unfortunately, due to some mistake, Miss Lowater gave a wavelength for this band which was wrong by about the same amount. It has now been established that the band head is at λ 3682.1 and not at λ3682.4Å. Merrill[26] was the first to mention a well marked molecular band at λ3682 in the spectra of S and late M type stars, in his description of R Andromedae. He later published the wavelengths of the band heads and about thirty band lines.

Obtaining some large dispersion stellar spectra, and a spectrogram of the 3682Å ZrO band taken in the 1st order of a 20 ft. grating, by Dr. A. S. King, Herbig identified all of the thirty band lines published by Merrill along with the band head, with the ZrO band at λ3682.

He also observed an absorption feature at λ 3571 accompanying the absorption of the λ3682 band of ZrO in stellar spectra. He identified this absorption with OH^+, but suggested that 3682 was perhaps the (0,0) band of a $^1\Sigma - ^1\Sigma$ system of ZrO. This system has now been produced by the author in the Laboratory. It will be found that the λ 3571 stellar absorption feature corresponds with λ 3571.9 (1,0) band of ZrO of the same system A. This seems preferable to the

possibility of absorption of OH^+. Both bands at λ 3682 and λ 3571 are in the $v'' = o$ progression of the system A of ZrO. Below a table of stars in which λ 3682 and λ 3571 were observed by Herbig is reproduced.

Star.	Type.	Estimated λ3682	Strength of λ3571.
β Peg	M2	Absent	------
α Her	M5	Weak	------
R Hya	M6e	Weak	Invisible
O Cet	M6e	Variable	Weak
R Cas	M7e	Medium	------
R Ser	M7e	Medium	------
R Aql	M7e	Very weak	Very weak
R Ori	M8e	Very weak	------
R Leo	M8e	Very weak	Weak
X Cyg	M6e Se	Very strong	Medium
R And	Se	Strong	Weak.

The author has examined a large dispersion spectrogram of R Andromedae. λ 3682 (0,0)A, and λ3571 (1,0)A are quite strong, as mentioned by Herbig. Other bands of the system A which also seem to be present are:

λ 3571.9	(8)	(1,0)A	Conspicuous absorption.
λ 3589.9	(6)	(2,1)A	Faint absorption.
λ 3682.1	(10)	(0,0)A	Conspicuous absorption
λ 3700.1	(1)	(1,1)A	Less conspicuous absorption
λ 3818.3	(4)	(0,1)A	Less conspicuous absorption.

Unfortunately the region $\lambda\lambda$ 3450-3520 of the R And. spectrum is not available, and so it is not possible to decide about absorption of system δ . If absorption were observed, it would perhaps provide a clue to the lower level of System δ.

ZIRCONIUM FLUORIDE

ZIRCONIUM FLUORIDE.

Introduction:

Having explored the various systems originating from ZrO, an effort will be made to describe a band system due to ZrF, which in its general appearance is so complicated that there is little hope of a successful analysis. So far as the present author is aware, no band spectrum has hitherto been reported for ZrF. Before proceeding to describe the system, it will be relevant to survey the spectra of the corresponding fluorides in Gr IV. Since the only fluoride spectra so far reported or analysed belong to those of the C sub-group, we are obliged to give a brief description of the spectra of molecules like SiF, SnF and PbF, although the corresponding fluorides of the Ti sub-group will essentially be different.

FLUORIDES OF THE C SUB-GROUP.

Several systems, many of them very extensive, are known for the fluorides of this sub-group, the only exception being C and Ge, for whose fluorides no band spectrum has been reported. For SiF three well developed systems have been observed and analysed by Asundi and Samual[27]. Two of these SiF systems were rotationally analysed by E. H. Eyster[28]. For SnF six systems have been reported, of which two still remain unanalysed, while the rest have been analysed by Jenkins and Rochester[29]. Below, we reproduce the table of vibrational constants in the ground state of the fluorides of the C sub-group.

TABLE OF THE VIBRATIONAL CONSTANTS IN THE GROUND LEVEL OF THE FLUORIDES.

MOLECULE	PROBABLE STATE	ω_e cm^{-1}	$x_e\omega_e$ cm^{-1}	B_e cm^{-1}	r_e A
SiF	$X\ ^2\Pi$	865.7	4.7	0.5795	1.599
SnF	$X^2\Pi$	582.9	2.69	---	---
		587.6	2.65	---	---
PbF	$^2\Pi$?	507.2	2.30	---	---

If the vibrational constants in the Fluorides of the Ti sub-group also follow the same relation it might be deduced that the expected magnitudes of ω_e for ZrF will be between 600-640 cm^{-1} and for TiF between 700-750 cm^{-1}. But there is no reason to conclude that the relation holding good for the fluorides of the C sub-group will hold accurately for the Ti sub-group. In the case of Oxides this relationship is very loose.

TITANIUM CHLORIDE SPECTRUM.

The molecules which might have been expected to have a spectrum analogous to that of ZrF are TiF, HfF and ThF. No spectra have so far been reported for either of these. It will be reasonable to assume that the halide spectra of the same element will exhibit similar characteristics, viz TiF in general characteristics will be very similar to TiCl and so Ti Cl will exhibit characteristic similar to ZrF as well.

This is the nearest molecule known whose spectrum could be described to be of the same type as ZrF.

The spectrum of Ti Cl has been known for a long time. Fowler[30] as early as 1907, reported three bands of this molecule at λλ4199.5, 4192.7 and 4188.0. Later Christy[6] also observed the spectrum in a discharge tube, under similar conditions. In 1937, Parker and More[31] photographed the spectrum of this molecule on large dispersion. The source they used was a high voltage low current arc, in a vacuum tight flask, in which was placed liquid $TiCl_4$. The vapour pressure of $TiCl_4$ in the flask corresponded with the room temperature. The other source was a discharge tube of external electrode type, wherein the pressure of flowing $TiCl_4$ vapour could be adjusted according to requirements.

DESCRIPTION OF THE SPECTRUM:- The region of the strongest bands was between λ4150 and λ4200; and it was found that six sequences of bands, with similar spacings between consecutive heads for corresponding bands overlapped over each other in this region. The sequence lying to the extreme red was the weakest, and only one band could be traced for it. The next sequence was the strongest of all, and the band heads in this sequence were supposed by Parker and More to form either in the P_1 or in the P_2 branch. (They supposed the transition involved was $^2\Pi - {}^2\Delta$ or $^2\Delta - {}^2\Phi$ consequently two P branches).

All six sequences were supposed to originate from $v' = v''$

transitions, viz each main band of the (0,0) sequence was supposed to have six sub-heads. Other sequences of Ti Cl are extremely weak. Bands due to $v'' = v' + 1$ cannot be traced, while only one band head each is known for the (1,0) and (2,1) bands (of twelve band heads for two main bands). These were supposed to belong to the P_{1-2} heads. Many weak bands have been left unclassified in the region of the (1,0) and (2,1) bands, whose wavelengths or wave-numbers have not been reported. The assignment of the (1,0) and (2,1) bands was decided upon because they occupied positions whereby the ω'' for Ti Cl came to 456 cm^{-1}. The expected magnitude according to Parker and More was between 420 and 480 cm^{-1}.

The formulae relating the strongest sub-heads in P_1 or P_2 branches is given by Parker and More as follows:-

for P_1 or P_2 band heads. $\nu^{v',v''} = 23820.0 + [503.4(v'+\frac{1}{2}) - 2.5(v'+\frac{1}{2})^2] - [456.4(v''+\frac{1}{2}) - 6.3(v''+\frac{1}{2})^2]$

TiCl Spectrum

as analysed by Parker and Nore.

v',v''	P_1 or P_2					
0,0	23805.6 (1)	23844.5 (10)	23864.8 (4)	23871.3 (8)	23890.8 (6)	23906.4 (5)
1,1		23899.1 (9)	23920.5 (4)	23930.8 (8)	23946.3 (5)	23965.4 (3)
2,2		23961.3 (9)	23983.4 (4)	23995.6 (7)	24013.2 (5)	24033.7 (b1)
3,3		24030.1 (6)	24057.4(b1)	24069.5 (5)	24070.0(b1)	24112.7 (1)
4,4		24106.8 (3)	24136.3 (3)	24147.4 (2)	24178.3 (1)	24206.3 (0)
5,5		24191.7 (b1)	24225.2 (1)	24233.4 (0)	24274.6 (0)	
1,0		24342.8 (3)				
2,1		24392.3 (2)				

Parker and More, after carrying out this analysis concluded that the strong sequence was perhaps due to P branches the weaker bands were due to head formation in Q branches, while the faint 23805.6 cm^{-1} head was perhaps due to a sattelite branch. They therefore postulated that the transition responsible for this system may well be a $^2\Pi - ^2\Delta$ or $^2\Delta - ^2\Phi$, both of which have not very strong Q branches, but prominent sattelites. Our objection is to the expected multiplicity of the levels involved. Theoretical considerations demand quartet levels. The complicated nature of the spectrum is perhaps due to this high multiplicity.

SPECTRUM OF ZrF.

EXPERIMENTAL:- A complicated band structure in the region λλ4900-5100 was observed in the ZrF_4 arc which could not be attributed to ZrO. The conditions of excitation, and the nature of the spectrum all suggested that the spectrum was due to ZrF. The source of the spectrum was an arc in air containing ZrF_4 running at 4 - 5 amps with 110 volts D.C. This arc has already been described under the heading "Source (b)I: The steady and colder ZrF_4 arc." The electrodes were of copper. The lower one had been shaped into a cylindrical cup with walls of about 0.5 m.m. thickness, and 1 cm of depth. The cup was supported on the pole by a copper rod (forming a neck to reduce heat conduction) about half a cm in length, and about a m.m. in thickness. The upper electrode was rather thicker to facilitate rapid conduction of heat from it; and

this formed the cathode. The anode cup was filled with ZrF_4 + KF + mH_2O (water present due to hydrate formation). The arc, initially struck between copper surfaces, heated this mixture in the anode cup, H_2O and KF were the first to vapourise. Later when most of these had escaped, the temperature showed signs of increasing, and the solid material melted into a red hot liquid in the anode cup. This evidently was molten ZrF_4. As the temperature increased, more and more vapours rose from the cup, and condensed on the anode-cup walls and on the cathode, forming a protective coating of ZrF_4 and ZrO_2 on the Copper surfaces. Being hot they remained conducting and maintained the arc. This suppressed the spectrum of the Copper vapours appreciably. At this stage the current in the arc had to be adjusted very carefully. If the temperature of molten ZrF_4 reached a critical value a rapid oxidisation set up in the cup itself, burning the whole of the fluoride in a matter of 30-50 secs., and raising the temperature very greatly. The critical temperature evidently was the "Ignition temperature of ZrF_4." The anode cup had to be kept below this temperature, otherwise the oxidisation of ZrF_4 left no trace of the fluoride, and one failed to observe the complicated ZrF bands in $\lambda\lambda$ 4900-5100 region, in the arc. In the cold and steady arc the vapours of ZrF_4 rising above the molten ZrF_4 were excited in the arc, and were gradually oxidised on their journey upward. Consequently ZrF bands come up most strongly from the central arc above the anode cup,

those due to ZrO being much weaker; and as one photographs the spectrum higher and higher above the anode cup, the ZrF become predominant until just below the cathode, ZrF fades out leaving an almost pure spectrum of ZrO.

The arc was also run in atmospheres of Hydrogen and Nitrogen. Unfortunately the arc could not be manipulated as before and the atomic spectrum, masked the spectra of both ZrF and ZrO. The latter were evidently due to impurities of Oxides in the ZrF_4 mixture.

Effort was also made to excite the ZrF spectrum in the discharge tube. For this purpose a small quantity of ZrF_4 mixture was placed in a constricted quarts capillary, of a high current discharge tube, used by Prof. Pearse and Dr. Gaydon[32] to bring up the hydrides of heavy metals. The tube was evacuated and the discharge was run in atmosphere of H_2. It appears that ZrF_4 attacks the quarts, because whereas SiF shows up at low temperatures, no trace of ZrF is found; at high temperatures vapourisation of quarts is evidenced by the presence of strong SiO bands.

The spectrograms on which measurements have been taken, were obtained on a Large Littrow spectrograph with a 30^0 dense glass prism. The dispersion ranged from 5.01 A/m.m. at λ4850 to 5.76 A/m.m. at λ5100.

On the next page are tabulated the wavelengths and wave-numbers of the band heads, observed in a ZrF_4 arc, and attributed to ZrF. A spectrogram of the ZrF spectrum will be found

in Table III at the end of the thesis.

OBSERVATIONAL DATA

BANDS OF ZrF

λ_{air}	I	ν_{vac}	REMARK
4897.25	(0)	20414.0	
4897.88	(0)	20411.3	
4899.24	(0)	20405.7	
4906.28	(2)	20376.8	
4911.37	(2)	20355.2	
4914.76	(2)	20341.2	
4916.33	(3)	20334.7	
4920.22	(2)	20318.6	
4921.58	(5)	20313.0	
4926.88	(4)	20291.2	
4932.12	(5)	20269.6	
4933.38	(4)	20264.5	
4933.95	(4)	20262.1	
5026.15	(0)	19890.4	Doubtful
5034.16	(0)	19858.8	Doubtful
5044.08	(1)	19819.7	Line like heads
5052.27	(2)	19787.6	Line like heads
5061.18	(3)	19752.8	Line like heads, spurious

D I S C U S S I O N

From the previous table it will be found that the bands are extremely difficult to analyse. This will also be evident from the appearance of the bands, whose photograph can be examined on Plate III. In two or three cases where differences show some regularity, this appears to be due to chance rather than representing a sequence, because many strong bands cannot be related to these differences. The structure of this system may be revealed when spectrograms of better definition and free from overlapping ZrO bands have been obtained.

Further, it is also possible that there are two overlapping systems in the same region. There are bands which are closely double headed with small separations, while other bands are sharp and single headed.

It is hard to guess the nature of the levels involved in this system. The complicated nature of both ZrF and Ti Cl spectrum suggests that transitions more complicated than $^2\Pi - {}^2\Delta$ or $^2\Delta - {}^2\Phi$, as suggested by Parker and More[31], are involved. We can make some guess about the nature of the ground state of ZrF. The ground states of the two atoms are $^3F_2$ and ^2P. A combination of these atoms will make possible states whose multiplicity will be 2 and 4 like $^1\Sigma, ^2\Pi \ldots {}^4\Sigma, {}^4\Pi$ etc. This shows that the ground state of ZrF could be either a doublet or a quartet. Further, if we suppose that one electron from the Zr atom goes over to close the Fluorine (2p) shell in the ZrF molecule to make it inactive (S_2O, L_2O) like Ne, then

the term nature of the remaining electronic configuration of the Zirconium atom is determined by $4F_{\frac{3}{2}}$ which is the deepest lying state of the $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$ $(3p)^6$ $(3d)^{10}$ $(4s)^2$ $(4p)^2$ $(4d)^2$ $(5s)$ configuration. The above configuration of electrons of the Zirconium atom contributes with $L=3$ and $S=\frac{3}{2}$. Since the only effective contribution towards λ_s comes from the electrons of the Zirconium atom those from the Fluorine being supposed to be balanced, it is evident that Λ will be either 3, 2, 1 or 0, since

$$\Lambda = L,\quad L-1,\quad L-2 \ldots 0$$

But since S is supposed to preserve in the molecular state, the deepest lying state will either be a $^4\Sigma, ^4\Pi, ^4\Delta$ or $^4\Phi$ This shows that the ground state of ZrF will presumably be a quartet. The same should be true of TiCl. The spectra of both these molecules are so complicated that it seems reasonable to assume that they originate from quartet levels, as doublet levels will fail to explain the many heads observed to each main band. This consideration appears to furnish a ready explanation of the complex nature of the spectrum of ZrF. For suppose the transition involved is $^4\Sigma - ^4\Pi$ then eight heads to each main band should be observed. If the eight (0,0) heads and eight (1,1) heads fall over one another, it will become extremely difficult to discover any regular differences corresponding to different vibrational levels, and hence the difficulty of classification. The complexity will be all the more troublesome if the different heads of the main band differ in their

intensity as well. It is the author's opinion that the ZrF bands which have been observed are in the resonance system of this molecule involving quartet levels.

ZIRCONIUM HYDRIDE.

ZIRCONIUM HYDRIDE.

Introduction.

Efforts have been made from time to time to obtain the spectra of the hydrides of titanium and zirconium. If there are any systems corresponding to these molecules, it is very probable that they are also present in stellar spectra. Titanium and Zirconium show up strongly in most of the late-type stars, both free and combined with Oxygen. It is not therefore unreasonable to expect that TiH and ZrH will also occur in stellar atmospheres. Not until their spectra have been produced in the laboratory, will it be easy to discover corresponding absorption in stellar spectra, which can be attributed to either of these hydrides. These considerations demand efforts to produce ZrH and TiH spectra in the laboratory. Many workers have tried to produce the spectrum of TiH, without success. Of the methods employed by them, the present author is ignorant, as no details seem to have been published.

EXPERIMENTAL PROCEDURE.

Three methods, already proved to be very efficient in exciting the hydrides of the heavy metals, were used. These can be described as

(1) Low voltage arcs in Hydrogen.

(2) High voltage arcs in Hydrogen.

(3) Heavy current discharge in Hydrogen.

The experimental details of the first two hardly need any detailed description, as they are of the very usual types

employed so frequently. The only thing worth being mentioned is that the arc was run between pure Zirconium electrodes, as well as between copper and carbon poles, the lower of which had been filled with Zirconium powder. Both the low and the high voltage arcs, fail to develop any conspicuous flame. With high voltage arcs the arc appeared to be unaffected by variation in pressure of Hydrogen. The pressure of Hydrogen was varied from a few m.m. to atmospheric pressure. Higher pressures of Hydrogen could not be tried, though perhaps this might be expected to help the excitation of ZrH.

The arcs showed up strong atomic lines, both due to Zr and Zr^+ with faint ZrO bands, which could not be completely eliminated. There was no structure visible, which might be attributed to ZrH.

(3) ZIRCONIUM IN DISCHARGE TUBE.

Having failed to excite Zirconium Hydride in these arcs, attention was diverted to a heavy current discharge tube. That used was a slightly modified form of the heavy current discharge tube (with constricted quartz capillary) used by Prof. Pearse and Dr. Gaydon[32] to vaporize metals like Chromium and Nickel. The essential features being the same, the modifications will be described briefly.

All rubber connections from the vacuum system were removed and replaced by glass and quartz. The chief modification was in the metal-ring support holding the constricted quartz capillary in the middle of the discharge tube. At first these

metal rings were replaced by funnel shaped pyrex tubes, sealed together. The funnel shaped tubes were of such dimensions that they left little space between the walls of the tube and their own external surface. They were however capable of smooth movement within the tube. The quartz capillary was held tightly between the funnel ends of these tubes, thus forcing the discharge to go through the capillary. It was however found that the funnel ends of the pyrex tubes got red hot and cracked after each operation. Further to the disadvantage of the experiment, strong impurities of Na, Mg and Pb were contributed from these funnel ends of the pyrex pieces.

Later on, considerable improvement was noted by the use of quartz rings, in place of the iron rings or the pyrex tubes. These rings were similar in their construction to the iron rings used by Prof. Pearse and Dr. Gaydon to hold the quartz capillary. Instead of being screwed together like iron-rings, the quartz rings used to be sealed together, after putting a new capillary between them.

The improvements noted could be described as follows. Whereas with the iron piece in the discharge tube, it was found that higher pressures of Hydrogen could not be used, as the discharge broke into two sections, no such difficulty was experienced when pyrex tubes or quartz rings were used. In fact the pressure of the gas could easily be increased by several m.m., once the quartz capillary had become red hot. The rise in pressure was accompanied by lowering of the current in

the tube, but the latter could always be adjusted by decreasing the resistance in the primary of the trans former. Currents of the order of 1.4 amps and 2.8 amps at 5000 and 2500 volts were passed through the quarts capillary at relatively high pressures of Hydrogen, in fact so high that it was impossible to re-start the discharge in the tube, once the quarts capillary had been cooled down. As higher pressure of Hydrogen in the tube is known to assist the maintenance of higher temperatures in the quarts capillary, it is reasonable to assume that the temperatures reached were higher than those hitherto obtained. This must have been further assisted by the drop in the conduction of heat along the quarts rings. However the limiting temperature should be determined by the vaporisation of the quarts capillary itself. This should keep the temperature down.

With the above modifications in use, powdered Zirconium was originally placed in the constricted portion of the quarts capillary. Even with very high currents through the quarts capillary, the author failed to find any trace of the Zirconium spectrum, which showed that Zirconium was not vaporising at all. The spectra of Si, SiO, SiO_2 and SiO^+ were manifestly very intense, showing that quarts was vaporising very rapidly. The boiling point of Zirconium is about 1000°C above that of quarts, and consequently the failure of the author to vaporise Zirconium in quarts capillary.

Prof. Pearse suggested that instead of putting Zirconium in the capillary, it would be better if the metallic powder

were packed through the quartz capillary, and a thin metallic wire drawn through this packed powder. This would give, for practical purposes, a Zirconium powder capillary of small bore, within the quartz capillary. As the heating is confined to the inner surface of the capillary, it was reasonable to assume that the inner surface of the Zirconium capillary might be heated above its boiling point, as there was little conduction of heat to the walls of the quartz capillary.

Several such capillaries were prepared; and the very first effort was crowned with success. The presence of the strong Zr and Zr^+ lines on the spectrum, provided the evidence that Zirconium was in fact vaporizing. This spectrum of Zirconium could in fact be maintained with relatively small currents through the Zirconium capillary. The impurities due to Si and SiO were relatively weak. Very long exposures could not be obtained, as the Zirconium capillary was vaporized in 10 - 15 m. exposing the surfaces of the quartz capillary, whence impurities of Si, SiO and SiO_2 marred the spectrum. One such spectrogram is shown in Plate III. Zirconium arc and spark lines have been marked by Zr and Zr^+ respectively. The latter appear to be more intense than the former.

However, no evidence of any structure, which could be attributed to ZrH, was found throughout the visible and the ultra-violet.

It will, therefore, be noted that all of these three methods failed to excite ZrH. It is possible that the use of

high pressures of Hydrogen might prove more favourable. This has not yet been tried by the author.

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DESCRIPTION OF PLATES.

PLATE I

(1) System ϕ ; Source ZrF_4 steady arc

(2) and (3) Systems δ and A; Source ZrF_4 steady arc.

(4) ZrO band at λ3682, Source, ZrO arc in air.

PLATE II

(1) ZrO spectrum, systems β and γ ; Source, Zirconium arc in moist Hydrogen.

(2) System α of ZrO; Source, ZrF_4 unsteady arc.

(3) System β ; source, ZrF_4 unsteady arc.

(4) λ 8192 band of ZrO; source ZrO arc.

(5) ZrO bands in 8600-8900A region; source ZrO arc in air.

PLATE III

(1) ZrF bands; Source ZrF_4 steady arc.

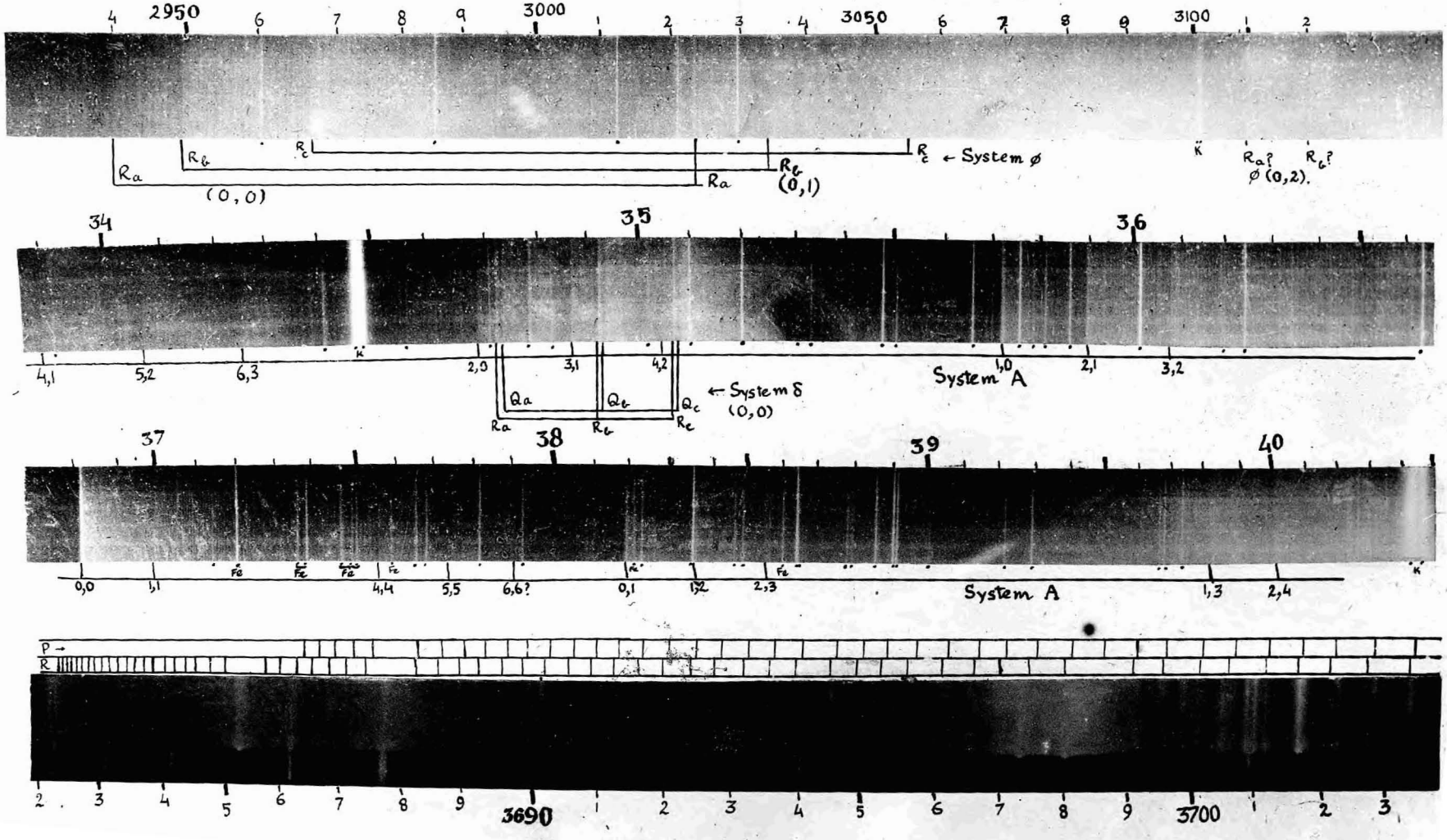
(2) Zr atomic spectrum as excited in a High current discharge tube.

On the preceding pages, the author has made an attempt to describe the experimental work undertaken by him, sometimes with success, sometimes with negative results, in order to study some molecules important for understanding the equilibrium in stellar atmospheres. All this work has been pursued under the kind guidance of Prof. R.W.B. Pearse, whose clear understanding of the subject, and a sympathetic disposition to help the author whenever in difficulty, has more than helped him. It has been an inspiration for which the author is deeply indebted, and expresses his deep sense of obligation towards him, whom he owes so much.

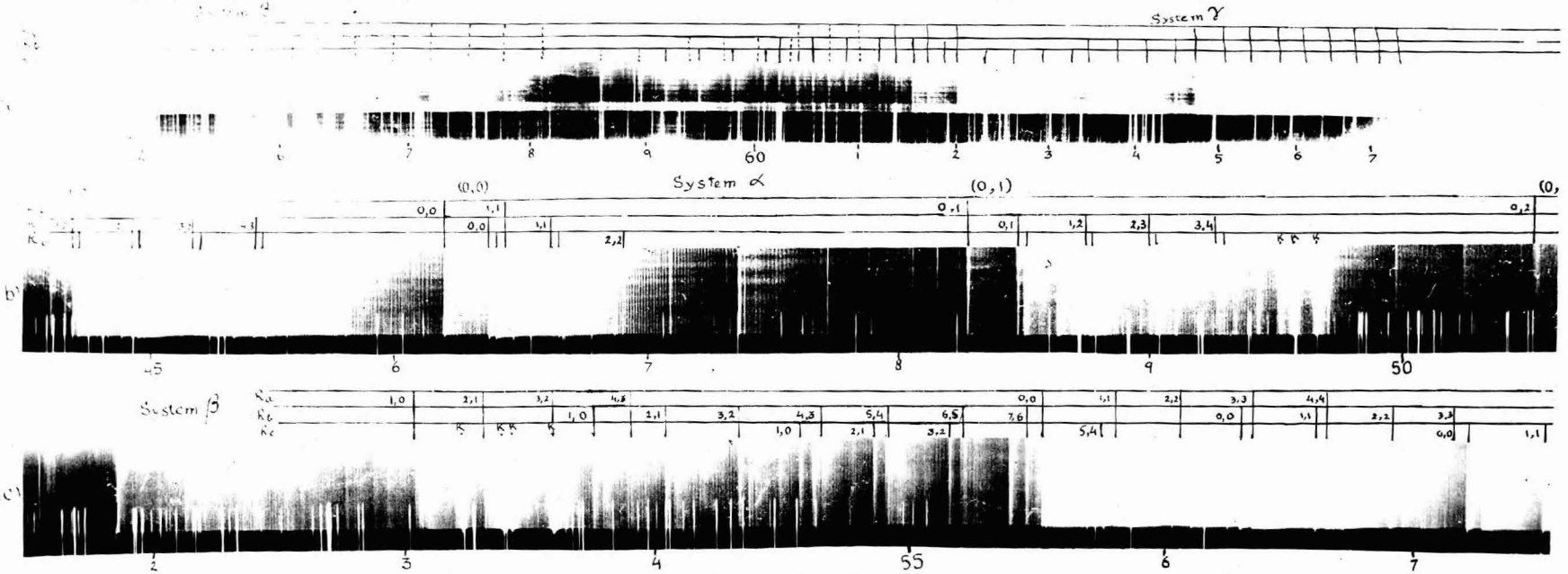
The author, further, expresses his gratitude to the "Sunni Central Board of Waqfs, Lucknow, (India), who financed the present work by awarding a scholarship to the author.

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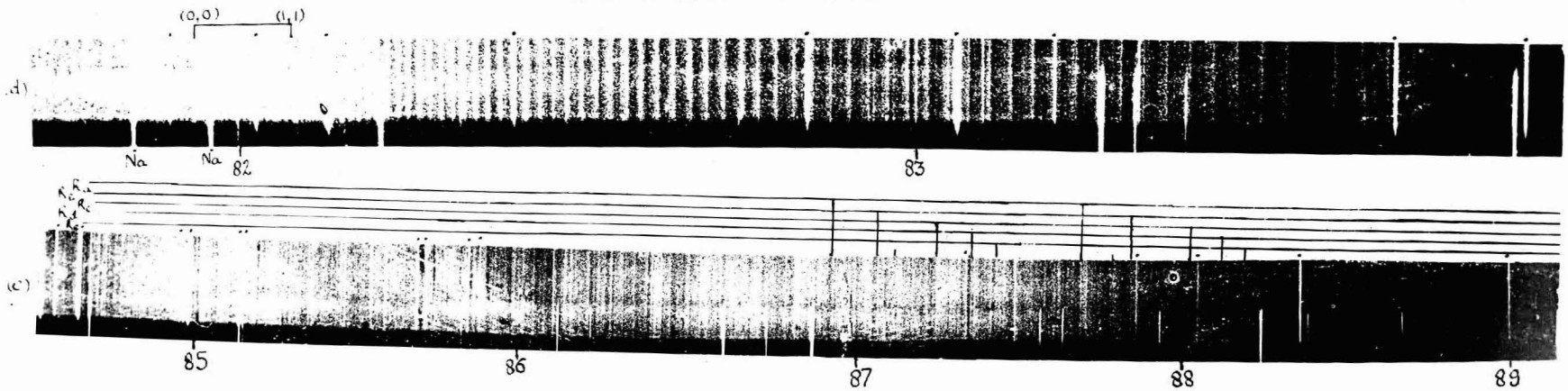
1. BANDS OF ZrO IN THE ULTRA-VIOLET



II. BANDS OF ZrO IN THE VISIBLE AND THE INFRA-RED

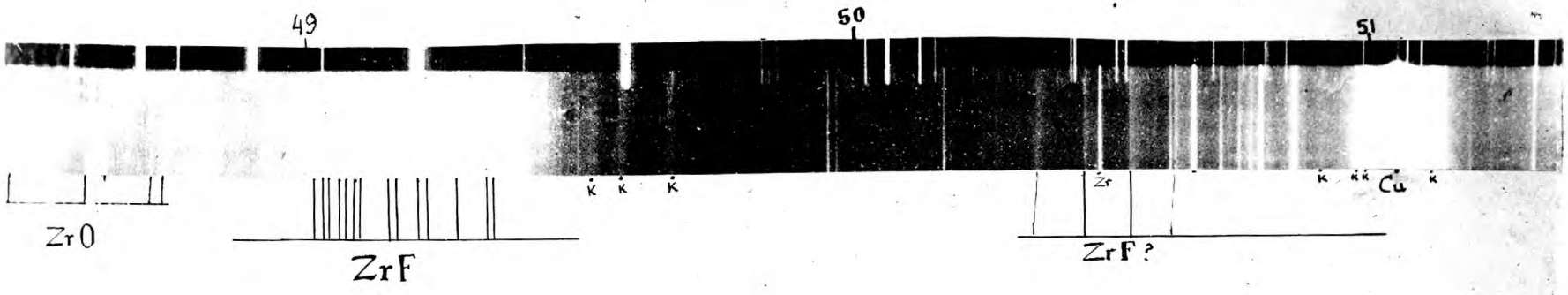


λ 8192 BAND OF ZrO



(a). Zirconium arc in moist Hydrogen ; (b) & (c), Rapid oxidising Zirconium Fluoride arc ; (d) & (e), Zirconium Oxide :

III. BANDS OF ZrF



Zr Vaporised and excited in Hydrogen filled Gaydon-Pearse discharge tube

