THE Ma X-RAY SATELLITES

OF YTTERBIUM AND HAFNIUM.

by

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TABLE OF CONTENTS

ABSTRACT

ACKNOWLEDGEMENTS

CHAPTER ONE : INTRODUCTION

X-ray Line Spectra 2
K Series Satellites 3
L Series Satellites 4
M Series Satellites 5
The Present Investigation 7

CHAPTER TWO : THEORIES OF SATELITE ORIGIN 8

Wentzel-Druyvesteyn Theory 9
Richtmyer Double Jump Theory 11
Coster-Kronig Theory 12
Origin of Low-Frequency Satellites 14
Other Theories 15

CHAPTER THREE : EXPERIMENTAL APPARATUS 21

Curved Crystal X-ray Spectrometry 22
Choice and Preparation of Analysing Crystal 24
The Two-Metre Spectrometer 27
   i) The X-ray Source 27
   ii) The Crystal Chamber 33
   iii) The Detector Chamber 34
   iv) The Proportional Counters 36
   v) Spectrometer Mounting and Vacuum System 36
   vi) The Vacuum Oven 39

Electronic Apparatus 42
<table>
<thead>
<tr>
<th>CHAPTER FOUR: EXPERIMENTAL TECHNIQUES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alignment of Analysing Crystal</td>
<td>45</td>
</tr>
<tr>
<td>Calculation of Dispersion</td>
<td>46</td>
</tr>
<tr>
<td>Preparation of Targets</td>
<td>47</td>
</tr>
<tr>
<td>Production of Line Profiles</td>
<td>48</td>
</tr>
<tr>
<td>Line Profiles obtained from Ytterbium Metal Targets</td>
<td>49</td>
</tr>
<tr>
<td>Experimental Errors</td>
<td>53</td>
</tr>
<tr>
<td>Analysis of Line Profiles</td>
<td>55</td>
</tr>
<tr>
<td>CHAPTER FIVE: EXPERIMENTAL RESULTS</td>
<td>59</td>
</tr>
<tr>
<td>The Ma Spectrum of Ytterbium Fluoride</td>
<td>61</td>
</tr>
<tr>
<td>The Ma Spectrum of Ytterbium Metal</td>
<td>82</td>
</tr>
<tr>
<td>Thickness of Ytterbium Targets</td>
<td>83</td>
</tr>
<tr>
<td>The Ma Spectrum of Hafnium Dioxide</td>
<td>86</td>
</tr>
<tr>
<td>Calibration of Power Supply</td>
<td>88</td>
</tr>
<tr>
<td>Tabulation of Results</td>
<td>97</td>
</tr>
<tr>
<td>CHAPTER SIX: DISCUSSION OF RESULTS AND CONCLUSION</td>
<td>101</td>
</tr>
<tr>
<td>Experimental Results</td>
<td>102</td>
</tr>
<tr>
<td>Instrumental Resolution</td>
<td>103</td>
</tr>
<tr>
<td>The Ma Line of Ytterbium Metal</td>
<td>106</td>
</tr>
<tr>
<td>The Ma Lines of Ytterbium in Ytterbium Fluoride and Hafnium</td>
<td>107</td>
</tr>
<tr>
<td>The M Spectra of the Rare-Earths</td>
<td>109</td>
</tr>
<tr>
<td>Application of Russell Theory to Present Case</td>
<td>112</td>
</tr>
<tr>
<td>Theory of Resonance Excitation</td>
<td>113</td>
</tr>
<tr>
<td>The Ma Satellites of Hafnium</td>
<td>118</td>
</tr>
<tr>
<td>Conclusion</td>
<td>120</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>122</td>
</tr>
</tbody>
</table>
ABSTRACT.

Modifications to an existing X-ray spectrometer are described which enable line profiles to be obtained undistorted by target ageing effects. Using the thin target technique, the M<sub>x</sub> spectrum of ytterbium fluoride was obtained and its dependence on exciting potential investigated. A similar investigation was made into the M<sub>x</sub> spectrum of hafnium dioxide. The profiles were analysed into Lorentzian components using a digital computer, and the M<sub>x</sub> satellites of ytterbium fluoride were found to attain a maximum integrated intensity of over 1100% of that of the parent line, whereas the M<sub>x</sub> satellites of hafnium dioxide attained a maximum integrated intensity of approximately 40% of that of the parent line.

A vacuum oven is described, which was used to prepare, in situ, X-ray targets of ytterbium metal, reasonably free from oxide content. A method is described by which the M<sub>x</sub> spectrum of ytterbium metal was obtained.

Comparisons are made between the M<sub>x</sub> spectra of hafnium dioxide, metallic ytterbium and triply ionised ytterbium, and the extraordinary magnitude of the M<sub>x</sub> satellites of triply ionised ytterbium is correlated with the presence of electron vacancies in the atomic core.

An explanation of the large intensity of M<sub>x</sub> satellites in triply ionised ytterbium is given, in which they are regarded as pseudo-satellites arising from electron transitions in ionised ytterbium atoms, the parent line arising from transitions in atoms in which electrons have been excited into the core vacancies. Suggestions for further work have been made, which would establish the validity of these processes in the emission spectra of other rare earth elements.

Also, it has been shown that the Coster-Kronig theory of the origin of the M<sub>s</sub> satellites of hafnium, proposed by Hirsh, cannot fully explain the observed facts, and a further suggestion has been made to explain their origin.
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CHAPTER ONE: INTRODUCTION.

X-Ray Line Spectra.
K Series Satellites.
L Series Satellites.
M Series Satellites.
The Present Investigation.
Bohr theory describes the atom as consisting of a heavy nucleus surrounded by concentric shells of orbiting electrons. The central, most tightly bound shell, is designated the K shell, the next most tightly bound shell is the L shell, and similarly there are the M, N etc shells, depending upon the particular element.

If an electron is removed from the atom by a suitable exciting agency, e.g. bombarding electrons, high energy protons, or photons of sufficient energy, the resulting ionised atom is raised in potential energy to a state depending upon the atomic shell from which the electron is removed. Thus an atom ionised in the K shell is raised into the K energy level, and similarly for the other shells. These energy states, resulting from single electron ionisation, may be represented on the conventional energy level diagram. The excess potential energy may be lost by transitions of the atom into successively lower energy states. An atom initially in a state of energy $E_1$, undergoing a transition into a state of energy $E_2$, radiates the excess as a photon, of energy equal to $E_1 - E_2$, $(E_1 > E_2)$.

By application of the quantum selection rules, various routes by which the excess energy may be radiated are allowed. These allowed transitions give rise to the characteristic X-ray line spectra containing K, L etc radiations depending upon the initial state of the atom. Such lines were first investigated by Moseley and are known as Diagram Lines or First Order Lines or Parent Lines.

In 1916 however, Siegbahn and Stenstrom, whilst investigating the spectra of some light elements, discovered a number of faint lines on the high frequency side of the K diagram lines. Since the energy of these lines cannot be expressed as differences of any of the terms in the conventional energy level diagram, they are known as Non-Diagram
Lines or Satellite Lines or Spark Lines. Long wavelength satellites have also been discovered. Ooster, in 1922 observed long wavelength satellites in the K spectra of elements Rb(37) to Lu(71), and more recently, Hulubei reported long wavelength satellites in the K spectra of elements As(33) to Br(35) and Rb(37) to Mo(42).

With refinements in technique, satellites have been discovered in the spectra of most elements, until now the number of known satellites greatly exceeds the number of diagram lines.

K Series Satellites.

Siegbahn and Stenstrom first reported the existence of satellites of the Kα lines in the spectra of the elements Na(11) to Zn(30) in 1916. Richtmyer and Taylor, in 1930, investigated the Kα,4 satellites of Cu(29) and reported that the group might contain more than two components, whereas a similar study of the K satellites of Ni(28) suggested a structure containing four components. Ford in 1932, made an extensive survey of Kα satellites for the elements Mg(12) to Ge(32), and also investigated the Kα satellites of Cl(17) to Cu(29), reporting several new lines. In 1936, Parratt reported that for elements 16 ≤ Z ≤ 28 there existed five components in the Kα,4 satellite group and four components for elements 29 ≤ Z ≤ 32. The wavelength, relative intensity and half-width of each component was measured. In the same year, Shaw and Parratt extended the survey of Kα satellites to investigate the spectra of the elements Zn(30) to Pd(46). Using a two-crystal spectrometer they discovered that the Kα,4 group contained four components for 30 ≤ Z ≤ 33, three components for 34 ≤ Z ≤ 40 and only two components for 41 ≤ Z ≤ 46.

A sharp and anomalous decrease in satellite intensity was also found in the region of Y(39). Curious variations in intensity between individual satellite components were also noted.
In 1948, Hulubei, Cauchois and Manescu, investigated the Kβ satellite structure for elements $Z = 30$ to $Z = 44$. In 1947, using a high frequency excitation method, Groven studied the K spectrum of As(33) in the vapour form, finding many new high and low energy satellites. The previous measurements, of Shaw and Parratt and Cauchois and Hulubei were confirmed for the high energy satellites and also agreement with Hulubei's low energy satellite measurements was obtained.

More recently, measurements have been made by Edamato in 1950, Hayasi in 1952 and Sawada in 1955. It should be mentioned that satellites have also been obtained in fluorescence by Tsutsumi in 1959, who succeeded in obtaining the Kαβ',4 and Kβ' satellites of the iron group. Most recently, Schölling in 1964 studied the Kβ1,3 lines of Sn(30) Cr(24) and V(23) using a flash X-ray tube, and noted the enhancement of the Kβ' satellite in this technique.

L Series Satellites.

Satellites of L series lines were first reported by Duyvesteyn in 1928, who noted their increased complexity as compared with K-series satellites. In 1929, F.K. and R.D. Richtmyer surveyed the Lα and Lβ1 & Lβ2 satellites for the elements Rb(37) to Sn(50). The satellite structure was found to be more complex than previously assumed including a continuous spectrum extending beyond the high energy limit of the satellites. The number of satellites was also found to depend on atomic number. Later (1931), R.D. Richtmyer reported the disappearance of Lβ2 satellites for elements heavier than $Z = 53$. In 1933, F.K. Richtmyer and Kaufmann examined the Lα satellite spectra of the elements $73 < Z < 92$, reporting rapid changes in intensity and appearance, even over short ranges of atomic number. The intensities of Lβ2 satellites relative to the parent line, were measured by Pearsall in 1934, for the elements $40 < Z < 53$. An integrated intensity of 4% was found for Nb(41), rising to 52% for As(47) and then falling to a value.
too small to be measured for Tp(52). In 1936, Parratt measured the line widths and the wavelengths of the \( \text{L}\alpha \) satellites of Ag(47). Later (1938) he made a further exhaustive study of 36 Ag L lines, including 21 satellites. Wavelengths, relative intensities, line widths and indices of asymmetry were measured, enabling the widths of the energy levels of silver to be calculated. Cauchois, (1936), investigated the L\( \alpha \) satellite spectra of the elements Sm(62) to U(92), noting four components over this range.

Richtmyer and Bamberger, in 1937, investigated the L\( \alpha \) and L\( \gamma_2 \) satellites of Au(79), measuring separations and relative intensities. In 1940, Randall and Parratt made a systematic study of L\( \alpha \) satellites for the elements Mo(42) to Ba(56), measuring integrated intensities and wavelengths.

Groven and Lagasse, in 1949, investigated the satellites of the L\( \alpha_1 \) line of Hg(60), using a high frequency excitation method. Approximately twenty long-wavelength and fifteen short-wavelength satellites were found. Also, in the L\( \beta \) spectrum, as many as five long-wavelength and ten short-wavelength satellites were reported. In 1951, Barriere, using a bombarding voltage of 400 Kv., or nearly forty times the excitation voltage, investigated the L\( \gamma_1 \) satellite structure of W(74). The L satellite spectra of the rare earths Ba(63) Cd(64) Tb(65) Ho(67) and Tm(69) were investigated by Sakellarides in 1953, who reported \( \gamma_8, \gamma_0, \gamma_7 \), and \( \gamma_4 \) components.

M Series Satellites.

M series satellites were first reported by Stenström in 1916. Hjalmar, in 1920, made an extensive study of M spectra and reported two satellites of M\( \alpha \) for elements Yb(70) to U(92), three satellites of M\( \beta \) for U(92) and one satellite of M\( \beta \) for elements Ho(67) to U(92). He also reported a satellite of M\( \gamma \) for elements W(74) to U(92).
Beuthe in 1928, investigated the M\(\alpha\) satellite spectrum of Re(75). Also in 1928, Lindberg studied the M spectra and found two satellites of M\(\alpha\) for elements Lu(71) to U(92), and one satellite of M\(\beta\) for the same elements. Later, in 1931, he surveyed the M spectra in the rare-earth region, giving wavelength values in agreement with earlier work carried out by Van der Tuuk. He reported a distinct change in the M\(\alpha\) line at Yb(70), the line becoming broader and shewing two components, whereas the M\(\alpha\) line for Lu(71) and heavier elements showed only one distinct component. For the elements Dy(66) to Er(66), M\(\alpha\) appeared as a broad band, whereas for the elements Sm(62) to Tb(65), several broad lines were visible. However, at Nd(60) the M\(\alpha\) line became sharper. In 1931, Hirsh investigated the M spectra of several heavy elements reporting as many as four satellites of M\(\alpha\) and three satellites of M\(\beta\). For Yb(70) only one M\(\alpha\) satellite was reported however, with three satellites of M\(\alpha\) for Lu(71) and heavier elements, increasing to four for elements Au(79) to Bi(83). In 1950, by re-examining existing information, Hirsh showed six satellites to be present in the M\(\alpha\) spectrum of the elements Pt(78) to Bi(83), Th(90) and U(92).

Munier Bearden and Shau, in 1940, found six short-wavelength satellites in the M\(\alpha\) spectrum of W(74). Values of the wavelengths and widths of the satellites were deduced.

Investigation of X-Ray Satellites.

Wisshak, in 1937, discussed the problem of satellite lines in X-ray spectra and suggested that a satisfactory theory of their origin required a detailed study of the following characteristics;

i) Exact frequencies of satellite lines.

ii) Widths of lines.

iii) Minimum excitation potentials.

iv) Intensity variation with atomic number, exciting potential and X-ray tube current.

v) Intensity of a satellite relative to its parent line.
The Present Investigation.

Previous work in this laboratory has been concerned mainly with the M emission and absorption spectra of the rare-earth group of elements. During these investigations it was noticed that the Mα line of these elements contained voltage sensitive components, and subsequently an investigation into this phenomenon was made by P.P. Phakey in 1959, in the case of Yb(70). Since the photographic work of Phakey gave results not predicted by the generally accepted theory of Coster-Kronig transitions proposed by Hirsh, the present work was initiated, using the quantitatively more reliable method of photon counters to repeat the observations on ytterbium and also to compare the results so obtained with those of a similar investigation into the structure of the Mα line of Hf(72).

The Mα line of Lu(71) was not investigated since the satellite structure had been obtained previously by Phakey. Also, following the successful preparation, in vacuo, of ytterbium metal specimens free from oxide content by Oombley in 1963, an attempt was made to observe the Mα spectrum of the element in its pure metallic state. It was shewn by Oombley that in metallic ytterbium only one atom in a hundred contains a vacancy in the 4f shell, the core structure resembling that of the heavier elements, whereas the element in the triply ionised state contains only thirteen 4f electrons. A comparison of the Mα spectra of hafnium and metallic ytterbium was therefore pertinent to the problem of satellites in this region.
CHAPTER TWO: THEORIES OF SATELLITE ORIGIN.

Wentzel - Druyvesteyn Theory.
Richtmyer Double Jump Theory.
Coster - Kronig Theory.
Origin of Low Frequency Satellites.
Other Theories.
Theories of Satellite Origin.

Whereas the emission of X-ray diagram lines may be successfully explained in terms of single electron transitions between atomic states of single ionisation, X-ray satellites are now attributed to single electron transitions between states of double or multiple ionisation. The mode of production of the multiple ionisation, forms the basis of the several theories of satellite origin.

Wentzel - Druyvesteyn Theory.

The first attempt to explain the origin of high frequency satellites was made by Wentzel in 1921, and later modified by Druyvesteyn in 1927. It was suggested that the energy necessary to remove two electrons from the atom was supplied by the impact of a single bombarding electron. The following initial and final states were assigned for the K satellites:

\[
\begin{align*}
K^*_{1} &= KL \rightarrow L^2 \\
K^*_{2} &= K^2 \rightarrow KL \\
K^*_{3} &= KL^2 \rightarrow L^3 \\
K^*_{4} &= K^2L \rightarrow KL^2
\end{align*}
\]

the \(K^*_{1,2}\) diagram lines arising from the transition,

\[
K^* = K \rightarrow L
\]

If the energy required to remove one K electron from an atom of atomic number \(Z\) is \(K^*_{2}\), then the energy required to remove the second K electron will be approximately \(K^*_{4+1}\), since the core remaining after the removal of one K electron will resemble that of the next heaviest element, the effective atomic number being increased by one. By similar reasoning, the energy required to remove two K electrons and one L electron will be approximately \(K^*_{2+1} + K^*_{4+1} + L^*2\). By using similar approximations,
and substituting in the given relationships, it can be shewn that

\[ \nu \alpha_4 - \nu \alpha_3 = \nu \alpha_6 - \nu \alpha_5 \]

\[ \nu \alpha_5 - \nu \alpha_3 = \nu \alpha_3 - \nu \alpha_1 \]

when: \( \nu \alpha_6 - \nu \alpha_4 = \nu \alpha_5 - \nu \alpha_3 = \nu \alpha_3 - \nu \alpha_1 \) or, the energy separations of alternate satellites should be equal. Wetterblad, in 1927, shewed some experimental verification of this in the spectra of elements Na(11) to Si(14).

Druyvesteyn, in 1927, compared the experimental data with the theoretical predictions for the separations of satellites of K\( \alpha_1 \), L\( \beta_2 \), L\( \gamma_1 \) and L\( \gamma_2, 3 \), finding good agreement. Wolfe, in 1933, tested Druyvesteyn's explanation of K\( \alpha \) satellites numerically for K(19), using Hartree self-consistent field theory. Assuming the satellites to arise from transitions between states of double K and L ionisation to states of double L ionisation, and using Russell-Saunders coupling throughout, good agreement with experiment was obtained. Kennard and Ramberg, in 1934, obtained good agreement with experiment in extending the work of Wolfe to include spin-orbit interactions, for the K\( \alpha \) satellites of Na(11) and other elements. It was shewn that the satellites K\( \alpha_1 \), K\( \alpha_3 \) and K\( \alpha_4 \) could be attributed to the transition Is 2p \( \rightarrow \) (2p)\(^2\), while the satellites \( \alpha_5 \), \( \alpha_6 \), \( \alpha_7 \) and \( \alpha_8 \) arose from transitions in atoms lacking two additional L electrons. Richtmyer, in 1936, calculated the integrated satellite intensity, relative to the K\( \alpha \) line, of K(19), using Born collision theory, and extended this work to consider the dependence of this ratio on atomic number, finding the satellite intensity to decrease with increasing \( Z \). Agreement with Parratt's work of 1936 was obtained but the agreement with Shaw and Parratt's work of the same year was poor.
Coster and Thyssen, in 1933, found the excitation potential of the Kσ3,4 satellites of sulphur to be 2700±25 volts, corresponding to KL ionisation, supporting the Wentzel/Druyvesteyn theoretical predictions. Parratt, in 1936, found the excitation potential of the Kσ3,4 satellites of titanium to be 5450±100 volts, 500 volts in excess of the excitation potential of the Kσ1,2 lines. The theoretical excitation potential, assuming an initial state of KL" ionisation to give rise to the satellites, was 5455 volts. Excellent agreement with theory was therefore obtained. It may be seen from the above, that satellites of K series lines have been firmly established as arising from transitions involving states of multiple ionisation as described by the Wentzel/Druyvesteyn theory.

Richtmyer Double-Jump Theory.

F.K. Richtmyer, in 1928, pointed out that if the square root of the frequency separation of satellite and parent line was plotted as a function of atomic number, a straight line graph results. It was suggested that this represented a Moseley or "semi-Moseley" diagram for an atomic transition, the energy of which was radiated together with that of the parent line, as a single quantum, yielding the satellite line. Richtmyer postulated that two distinct electron transitions occurred simultaneously in the atom, one to fill a core vacancy and one between optical levels. If the energy of the former is $E_1$ and that of the latter $E_0$, then the theory suggested that the sum of these two is radiated as a single quantum, yielding the satellite line of frequency $\nu_s$; $E_1 + E_0 = \hbar \nu_s$.

Since the parent line results from the inner transition, then $E_1 = \hbar \nu_p$, where $\nu_p$ is the frequency of the parent line. For $E_0$ to result from an optical transition, then in a region where outer-shell electrons increase uniformly with atomic number, the energy difference between the satellite and parent lines should be
proportional to $Z^2$

or: $\left(\nu_s - \nu_p\right) \cdot Z^2$

which was observed experimentally.

However Idei, in 1930, pointed out that the energy difference between the satellite and parent lines is itself proportional to atomic number, casting some doubt on Richtmyer's proposals. Ramberg, in 1934, cast further doubt on the correctness of Richtmyer's hypothesis, on calculating, by a perturbation method, the relative intensities of $K_{3,4}$ satellites compared with the $K_{1,2}$ diagram lines, assuming double jumps to occur. The calculated values were found to be far too small to account for the observed intensities. As a more general argument against the double jump hypothesis, it was pointed out that the line structure resulting from such a mechanism should consist of a symmetrical grouping of faint lines about the parent line, the stronger components being on the long-wavelength side. Although long-wavelength satellites are now known, the force of Ramberg's objection to the hypothesis is not entirely lost. It should also be mentioned that Bloch, in 1935, calculated that the observed $K$ satellite spectrum of Cu(29) could be due to the occurrence of simultaneous electron transitions, in obvious conflict with Ramberg's conclusions.

Coster - Kronig Theory.

Although $K$ series satellites may be explained satisfactorily on the basis of the Wentzel/Druyvesteyn theory, the peculiar intensity variations of $L$ and $M$ series satellites and their dependence on atomic number cannot be accounted for by the same process. If double ionization occurs on electron impact, then theoretically the intensity of resulting satellites should decrease continuously with increasing atomic number, which is observed for $K$ satellites. The intensity of
The difficulty was resolved by Coster and Kronig in 1935, when they suggested that the state of double ionisation necessary for the production of satellites resulted from a radiationless transition in singly ionised atoms, of the type first investigated by Auger. It was postulated that such a transition occurred between different sub-shells in the same atomic level, with simultaneous expulsion of an outer electron. It was shown that the energy of the $L_i \rightarrow L_{iv}$ transition for an element of atomic number $Z$ exceeded the energy required to ionise the $M_{iv}$ levels of the next heaviest element, of atomic number $Z+1$, except between $Z = 52$ and $Z = 74$. This fully explained the observed facts:

i) The absence of $L_\alpha$ and $L_\beta_2$ satellites between $Z = 52$ and $Z = 74$

ii) The variation of satellite intensity with atomic number, shewing a maximum at about $Z = 45$. $L_\alpha$ and $L_\beta_2$ satellites were therefore explained as resulting from the Coster/Kronig transition $L_i \rightarrow L_{iv}$, $M_{iv}$ this being the initial state of double ionisation necessary for satellite emission.

Richtmyer and Ramberg, in 1937, calculated the intensities and wavelengths of the $L_\alpha_1$ and $L_\beta_2$ satellites of Au(79), using the Coster/Kronig theory. The results agreed well with experimental data obtained from a two-crystal spectrometer. Evidence of $L_\alpha$ and $L_\beta$ satellite intensity maxima consistent with Coster/Kronig theory has been supplied by Hirsh (1935,36) and De Lagnen (1939). The threshold potential of L series satellites has been measured by Valadare and Mendes (1948), who reported the disappearance of the $L_\alpha_1$ satellites of gold below the $L_1$ excitation limit, and by Salgueiro and Blanc de Sousa (1951) who reported similar results for the $L_\beta_2$ satellites of gold, lead and bismuth. Coster-Kronig theory is now well supported by experimental evidence as
explaining the origin of L series satellites.

Attempts have also been made to explain the origin of M series satellites on the basis of the Ooster–Kronig effect. Hirsh (1935) showed that the radiationless transition $M_n ightarrow M_{n'}$ $N_{n'}$ is possible for $Z < 88$, and attributed the Mα satellites to this transition. He also attributed the Mβ satellites to the transition $M_{n'} ightarrow M_{n''} N_{n''}$ which is possible for $Z < 84$. Later, in 1940, Hirsh presented some evidence on Mα satellite intensities to substantiate his earlier theory of their origin. However, he later reported (1941) that an intensity maximum did not exist for Mβ satellites. This was explained in terms of the higher probability of the transition $M_{n'} ightarrow N_{n''}$ occurring. Threshold potentials of M series satellites do not appear to have been measured except by Phakey, and the experimental evidence at present is not sufficient to explain conclusively their origin.

Origin of Low-Frequency Satellites.

Two mechanisms for the production of low-frequency satellites have been proposed by Hulubei. The first theory proposed that the diagram lines Kα₁ or Kα₂ undergo partial self-absorption in the external atomic shells, the residual energy being radiated as a low-frequency satellite. However, it has been pointed out that the difference in energy between the diagram line and its low-frequency satellite is not equal to the ionisation energy of an external shell. This objection effectively rules out the validity of this process.

The second hypothesis suggests that although the long-wavelength satellites do not correspond to the forbidden transition K→L, they could in fact be high energy "satellites" of this process. If states of multiple ionisation existed similar to those necessary for the production of high-frequency satellites of the Kα line, the radiationless transition K→L would itself be modified, yielding lines of higher energy than K→L itself. Groven and Morlet,
using self-consistent field theory, have calculated the spectrum to be expected on this basis for the elements Zn(30) to As(33), and achieved fair agreement with experiment. The evidence at present, however, is not conclusive.

Theory of External Screening.

An attempt was made by Karalnik and Nryznik in 1957, to explain the occurrence of K series satellite lines by considering the external screening afforded by outer electrons. On wave-mechanical grounds there is a finite probability of an outer electron existing within the orbitals of the K electrons and the effective change in nuclear charge ΔZ, on removing an outer electron, may be calculated. The K series satellites were then assumed to be diagram lines of an element with atomic number Z + ΔZ, and some agreement with experiment for the K satellites of Fe(26) was claimed. However, double ionisation of the atom is assumed, and it would appear that this theory is perhaps an alternative presentation of the Wentzel-Druyvesteyn theory.

Theory of Excitation States.

Parratt in 1959, proposed two theories to explain the occurrence of non-diagram lines. A state of the atom in which an electron expelled from an inner shell is bound in an outer orbital instead of being completely removed from the field of the nucleus, is believed to be commonly produced in X-ray and ultra-violet absorption processes. Such bound ejected electron excitation states would result in X-ray energy levels being split into a number of sub-levels, depending upon the distributions of bound electrons. Also, in the solid state, each energy level should be accompanied by a continuum, resulting from the expelled electron entering the energy continuum, in the solid. Subsequent electron transitions between these split levels would result in the radiation of satellite lines. However, this process would
not appear to be important in excitation by electron bombardment.

The second theory examined the occurrence of abnormal valence electron configurations. It was suggested that the creation of a vacancy in an inner electron shell produces a change in the coulomb field which affects all the electrons in the atom in less than $10^{-18}$ seconds. The innermost electrons would be expected to move rapidly into new orbitals closer to the atomic nucleus, before the electron vacancy is filled. However, the outermost electrons would need more time to adjust to new orbitals and Parratt suggested approximately $10^{-16}$ seconds, the lifetime of an inner vacancy. Therefore, when the inner vacancy is filled with the emission of X-radiation, some of the valency electrons will have entered new orbitals, while others will have entered unoccupied excitation orbitals or perhaps entered an unoccupied part of the energy continuum. Since the energy of the atom depends upon the electron configuration and the final position of the ejected electron, it is again concluded that X-ray energy levels should be split and also have an accompanying continuum, resulting in the emission of satellite lines. Parratt suggested that such a process may be important in the spectrum of the transition metals.

Skolnik and Parratt applied the above theory to the K spectrum of solid manganese. The lines $\frac{K}{1,2}$ and $\frac{K}{1,3}$ were said to result from transitions in atoms where the 4s valence electrons have not adjusted themselves to the new coulomb field when the K vacancy is filled. However, the radiation on the low energy side of $\frac{K}{1,2}$ and the satellite $\frac{K}{3,1}$ were correlated with transitions in atoms where the 4s electrons have adjusted to the new conditions. Consequently, they are more strongly bound to the nucleus, and any X-ray quantum emitted on the filling of a K vacancy will be of corresponding lower energy.
Hayasi's Theory.

Hayasi in 1961, proposed a theory similar to Parratt's bound ejected electron theory to explain the occurrence of X-ray satellites. It was suggested that electrons removed from an inner shell may enter unoccupied optical levels in "quasi-stationary" states. Satellites were said to be due to simultaneous electron transitions occurring, one in which the inner vacancy is filled and one between quasi-stationary states.

It was pointed out that the excitation of an inner electron into an outer orbital is the process suggested by Kossel to explain the secondary structure near an X-ray absorption edge. Therefore, the energy difference between a satellite line and its parent should be equal to the energy difference between two absorption maxima in the secondary structure of the corresponding absorption spectrum. Hayasi claimed good agreement in these energy differences for a number of metals. However, this theory bears great resemblance to Richtmyer's double jump theory and could be criticised on the same grounds.

Kakuschade's Theory.

In 1959, Kakuschade put forward a theory to explain the occurrence of X-ray satellites in transition metals and alloys. In these materials, the 4s and 3d energy level bands overlap, and it was suggested that iso-energetic electron transitions may occur between these bands, causing the formation of a layer of electrons in the 4s band. At the absolute zero of temperature, the number of electrons entering the 4s band from the 3d band would equal the number passing the other way. However, at higher temperatures the transport rates are not equal and a redistribution of electrons between the overlapping bands takes place. This results in the formation of a layer of electrons in the
4s band above the level existing at the absolute zero of temperature, causing the Fermi level in the 3d band to be depressed by a corresponding amount. It was suggested that X-ray satellites result from the filling of an inner electron vacancy simultaneously with an electron transition from the layer of electrons with excess energy in the 4s band to the Fermi level in the 3d band. As the electron distribution in the overlapping bands will depend on temperature, then it was concluded that the intensity of X-ray satellites in these materials should also be a function of temperature. This theory, however, is similar to the double-jump theory proposed by Richtmyer, and in addition would appear to be applicable only to certain materials.

Theory of Plasmon Interaction.

It has been shown that oscillations are possible in the plasma of free electrons existing in a metal. The quantum of energy, or plasmon, associated with these oscillations, is greater than the energy of electrons situated at the top of the Fermi distribution in the material. Consequently, no electron in a metal has sufficient energy to excite a plasma oscillation into a higher energy state, and these oscillations exist in metals in their ground state only. However, they may be raised into a higher energy state by the passage of fast charged particles through the material.

It was suggested by Shmidt, in 1961, that short wavelength satellites may result from the simultaneous excitation of an atomic X-ray state and a plasma oscillation, which is possible, as the lifetimes of these phenomena are comparable. If an electron in the conduction band of a metal absorbs a plasmon and subsequently fills, say a K vacancy, a high energy satellite of the shortest wavelength diagram line in the K series, will be radiated.
In this case, the energy difference between the parent line and high energy satellite should be equal to the "characteristic energy loss" of electrons in the material under examination. Shmidt claims reasonable agreement in measurements on a number of metals.

Menshikov's Theory.

In general, high energy X-ray satellites are observed in spectra obtained by electron bombardment, whereas they are absent in fluorescent spectra. This absence may be attributed to two facts. Firstly, the small intensity of quanta capable of exciting L and M levels present in continuous X-ray spectra and secondly, the low probability of double ionisation occurring when a material is excited by high energy characteristic X-rays.

Menshikov proposed in 1962 that the production of satellites in spectra obtained by electron bombardment may be brought about as follows. After the bombarding electrons strike the X-ray target, a flux of electrons with different energies is created due to repeated energy losses in the material. It was therefore assumed that sufficient electrons would be present with the energy required to ionise L or M levels, together with those energetic enough to ionise K or L shells.

Confirmation of the theory was sought by exciting a solid chromium target with X-rays of energy sufficient to ionise the K shell together with electrons having enough energy to ionise the L or M shells. In the resulting spectrum, Menshikov observed the $K_{\beta''}$ satellite in the position normally observed in normal cathode ray excited spectra, although of smaller intensity, whereas in the fluorescent spectrum $K_{\alpha''}$ was absent.

This theory, however, suggests the production of double ionisation by multiple electron impact, and would not appear to be generally acceptable.
Summary.

To sum up, it has been fairly well established that the high frequency K series satellites are due to single electron transitions in multiply ionised atoms, as described by the theory of Wentzel and Druyvesteyn. However, although a considerable amount of evidence exists to attribute L series satellites to multiple ionisation by the Coster-Kronig effect, the origin of M series satellites is still uncertain.
CHAPTER THREE: EXPERIMENTAL APPARATUS.

Curved Crystal X-ray Spectrometry.
Choice and Preparation of Analysing Crystal.
The Two-Metre Spectrometer.

  i) The X-ray Source.
  ii) The Crystal Chamber.
  iii) The Detector Chamber.
  iv) The Proportional Counters.
  v) Spectrometer Mounting and Vacuum System.
  vi) The Vacuum Oven.

Electronic Apparatus.
Curved Crystal X-ray Spectrometry.

Previous work in this laboratory has been carried out using curved-crystal X-ray spectrometers of the reflection type, and an existing instrument was adopted for use in this investigation.

The geometry of curved-crystal spectrometers which would give focussed X-ray images, was given by Dumond and Kirkpatrick in 1930. Two main types have been described, the reflection type, proposed by Johann in 1931, and the transmission type, developed by Cauchois in 1932. In both these forms of the instrument, the analysing crystal is curved to a radius equal to twice that of the focussing circle. In the reflection type, the circle is analogous to the Rowland circle of a concave diffraction grating, and is known by this name. Figure 3.1 indicates the similarities of the two types of spectrometer.

Theoretically, it is possible to obtain exact focussing in the reflection instrument if the analysing crystal, first curved to a radius equal to the diameter of the Rowland circle, is ground out to a radius equal to that of the Rowland circle.

Since the radiation to be studied is too soft to pass through any appreciable thickness of crystal, a reflection type of instrument must be used. Also, since mica is the most suitable crystal, and will not readily grind in order to give an exact focussing instrument, the geometry of Figure 3.1(A) is used. Consider a crystal curved to a radius \( R \) in one direction, and placed on the circumference of the Rowland circle of diameter \( E \). If a point source of X-rays is placed at \( S_1 \), on the Rowland circle, then those X-rays having a wavelength \( \lambda_1 \) will be focussed at \( P_1 \), also on the Rowland circle. \( \lambda_1 \) is determined by the glancing angle \( \theta_1 \) at which the X-rays leave the crystal, and the lattice spacing of the crystal, according to Bragg's law of reflection. Similarly, X-rays arising from a point \( S_2 \), having a wavelength \( \lambda_2 \), will be focussed at \( P_2 \). Similar reasoning shows that an extended source
FIGURE 3.1a THE REFLECTION SPECTROMETER

FIGURE 3.1b THE TRANSMISSION SPECTROMETER
placed along the Rowland circle will produce a continuous spectrum of X-rays focussed and analysed by the crystal according to the Bragg law. To increase the intensity of this spectrum the extended source may be placed close to the crystal as shewn by $E_1$ and $E_2$, the focussing properties being unaltered. The spectrometer used in this investigation was designed by Russell (1958) and employs the geometry as in Figure 3.1A, with an extended X-ray source close to the crystal. A schematic representation of the instrument is given in Figure 3.2., shewing the relative positions of the components with respect to the Rowland circle. Due to the soft nature of these M radiations, the whole of the instrument must be enclosed in a vacuum system. In order to reduce the pumping time, and also for reasons of economy, the articulated system was designed, the X-ray tube chamber, only, being evacuated with an oil-diffusion pump, the remainder of the system being evacuated by a rotary pump.

Choice and Preparation of Analysing Crystal.

Since the wavelengths of the lines to be investigated are approximately eight Angströms, the crystal used as the analyser must have a lattice spacing greater than four Angströms, in order to satisfy the Bragg reflection conditions. Also, the crystal must remain undistorted when curved. Two crystals meet these requirements, mica and gypsum. However, it has been found that under the conditions existing in the vacuum spectrometer, gypsum rapidly dehydrates, making it unsuitable for use. Mica however, is perfectly stable under the conditions of the spectrometer and was chosen for the present work. On the other hand it has the disadvantage of having a slightly variable lattice spacing, depending upon the particular sample of material. Williams, however, found that the values for the lattice spacing given by Siegbahn in 1931 were reliable and these were therefore used in the present investigation.
Pieces of mica were examined for obvious flaws by reflection from their surfaces, and a specimen free from imperfections was chosen and mounted between two steel crystal holders, machined to the nominal radius required. The steel blocks are lapped together with grinding paste, until a smooth surface is obtained. They are held together by four screws, which also serve as adjusting screws for bending the crystal. The crystal was adjusted optically and its radius of curvature measured by observing reflections from its surface, used as a cylindrical concave mirror.

Figure 3.3 represents a concave cylindrical mirror of radius of curvature \( R \). A point source of light situated a distance \( U \) from the mirror, making an angle of incidence \( \varphi \), will produce an image distant \( V \) from the surface, according to the equation.

\[
\frac{1}{V} + \frac{1}{U} = \frac{2}{R \cos \varphi}
\]

Therefore, if a parallel beam of light is allowed to fall on the mirror at an angle of incidence of \( 45^\circ \), a line image will be produced a distance \( V = \frac{R \cos 45^\circ}{2} \) from the mirror, the angle of reflection also being \( 45^\circ \).
27.

A point source of light was arranged at the focus of a convex lens and the resulting parallel beam of light allowed to strike the crystal with an incident angle of 45°. The reflected image was viewed through an eyepiece, of known focal length, in a direction perpendicular to the incident light beam. The crystal block clamping-screws were adjusted until a sharp line image was observed. In general, the sharp main image was accompanied by several faint lines, due to the crystal being imperfectly bent near the edges. These faint lines were easily removed by sliding small pieces of brass sheet over the edge of the crystal surface until a sharp single image was obtained. When the best image had been obtained, the image distance \( v \) was measured, yielding the radius of curvature of the crystal. It has been found that crystals yielding good optical images require no further adjustment for use in the spectrometer.

The Two-Metre Spectrometer.

The two-metre spectrometer was designed for photographic work and is shown schematically in Figure 3.2. It consists essentially of three parts, the X-ray tube, the crystal chamber and the film or detector chamber.

The X-ray Source.

Previous work in this laboratory has indicated the necessity of using thin target techniques for observing the M spectra of the rare-earths, due to the self absorption of these radiations in conventional sloping sources as represented in Figure 3.4(A). If an atom situated below the surface of such a target is excited, the resultant radiation must penetrate a considerable thickness of rare-earth material before leaving the target. Since the \( \text{M}_\alpha,\beta \) spectra overlap the \( \text{M}_{\nu,\nu} \) absorption spectra, and very strong absorption lines exist, the resultant X-rays are subject to selective self absorption in the target material, and
FILAMENTS
ELECTRON BEAM
TARGET
\rightarrow X RAYS

FIGURE 3.4a  SLOPING TARGET

FILAMENTS
TARGET
\rightarrow X RAYS

FIGURE 3.4b  NORMAL TARGET
this modifies considerably the shape of the resulting spectrum line. Wilson and Russell adopted the technique illustrated in figure 3.4(b) to minimise this effect. The X-ray target is bombarded with electrons having trajectories perpendicular to the surface of the target and the resultant X-rays are observed in a direction normal to the target between the filaments of the X-ray tube cathode. In addition, only a small amount of rare earth material is evaporated onto the target surface, so that the X-rays traverse the smallest possible amount of absorbing material.

The construction of the X-ray tube is indicated in Figures 3.5 and 3.6. The anode consists of a hollow brass disc of 1\(\frac{1}{4}\)" diameter screwed onto a tube of external diameter 1\(\frac{3}{4}\)", which passes through the wall of the tube chamber by way of an 'O' ring seal. A water pipe passes down the centre of the anode tube ensuring efficient cooling of the target, and enable tube currents of up to 250mA to be used without overheating. The simple 'O' ring seal allows the anode to be rotated with respect to the filament-holder assembly, and also allows the cathode - anode distance to be altered from outside the chamber. It was found that the existing filament-holder assembly was not satisfactory in as much as it allowed the filament strips, when hot, to bow out towards the anode, hence tending to give local spots instead of a focussed line source. To overcome this a new filament holder was constructed as shown in Figure 3.7. A Micalex former supports two L-shaped copper focussing blocks and also a T-shaped member pivoted as shown. The oxide coated nickel filament strips are clamped between the movable and fixed members by stainless steel clamps, the filaments being kept taut by a spiral spring fixed between the pivotted arm and the Micalex former. The filaments are joined in series ensuring that both attain the same operating temperature, the resultant expansion being taken up by the spring. The whole filament assembly may be demounted from the X-ray tube chamber for filament replacement, a rubber 'O' ring being used for a vacuum seal. This assembly was
found to be quite satisfactory in use, producing good line sources approximately one millimetre wide, over wide ranges of accelerating potentials.

The X-ray chamber is evacuated to a pressure of about $10^{-5}$ torr, and the rest of the spectrometer to a pressure of approximately $5.10^{-2}$ torr. The pressure difference between the X-ray tube and the rest of the apparatus is maintained by a window of 6$\mu$ Melinex supported on a brass holder. To use the instrument with a photographic detector for aligning purposes, aluminised Melinex may be used for the window material, to shield the X-ray film from visible radiations produced in the tube. In order to prevent charged particles emitted from the cathode assembly, from being accelerated towards the window and puncturing it, copper deflector plates are fitted. One plate is attached to the cathode assembly, at the potential of the X-ray tube, and the other to the window holder, at earth potential. The resultant field, through which the X-ray beam must pass, is sufficient to deflect the charged particles, preventing them from striking the window.

The Crystal Chamber.

The design of the crystal chamber is illustrated in Figures 3.5 and 3.6. Six outlet ports are provided at angles of 60, 80, 120, 140 and 160 degrees to the direction of the incident X-ray beam. The X-ray tube chamber may also be rotated through an angle of twenty degrees relative to the crystal chamber, allowing the reflected beam to leave the crystal chamber at any angle between 50 and 170 degrees to the entrant X-ray beam. This enables a series of Bragg angles between 10 and 65 degrees to be obtained for any crystal. The assembly containing the crystal is suspended from the lid of the crystal chamber by means of a universal coupling so arranged that final alignment of crystal may be carried out from outside the chamber.
The Detector Chamber.

The X-ray beam reflected from the analysing crystal enters the detector chamber through a sliding vane valve. This valve makes it possible for the detector chamber to be isolated from the rest of the system, enabling the loading and unloading of film for test purposes to be carried out, whilst the X-ray tube is under vacuum. The chamber is constructed of Paxolin tubing, into which fits a piston arrangement carrying the detector assembly. The length of the piston may be easily adjusted for focussing purposes, with an accuracy of better than one millimetre. The twin counter assembly is arranged to traverse the spectrum in a direction perpendicular to the incident X-ray beam, and is shown in Plate 1.

A six inch diameter aluminium disc is fixed to the end of the brass piston assembly by means of a simple 'O' ring seal. The disc contains a 4" x 1" rectangular central aperture, and affords a means of orientating the counter head about a horizontal axis. An aluminium block, containing slots for the counters and film holder, is screwed to the face of the disc, incorporating an 'O' ring vacuum seal.

The gas flow proportional counters are carried on 11" x 1½" rectangular brass plates, which allow the counters to scan the spectrum in a horizontal plane, perpendicular to the direction of the incident radiation. Also mounted on the counter plates are the cathode followers associated with the counters. The counter plate assemblies may be moved across the spectrum by accurately cut lead screws, anchored at one end to the supporting aluminium block. Using these lead screws, the counters may be positioned with an accuracy of one-thousandth of an inch. It is also possible to use a film detector, by moving the counters to the limits of their travel and including a film holder in their place. This is mounted on a brass plate which may be screwed onto the vertical face of the aluminium counter block, in place of the perspex plate which is
normally used to close the aperture. The film holder is arranged so that the film is positioned in the same plane as that in which the counters move. All joints in this assembly are made vacuum tight by rubber 'O' rings, a sliding seal being incorporated in the counter plate mounting.

The Gas - Flow Proportional Counters.

Figure 3.8 shows the construction of the gas-flow counters. The bodies of the counters consist of ¼" diameter brass tubes, soldered to 1½" diameter brass rings, which are screwed onto the counter plates. The counters are closed by polythene plugs which also carry the gas-flow pipes and counter anode supports. The anodes consist of tungsten wire loops which are fixed to their supports by means of metal beads, and are so arranged as to be immediately behind the counter windows. Radiation may enter the counters through ¼" wide slots which are covered with 4μ Melinex, affixed to the counter bodies with adhesive obtained from the Minnesota Mining & Manufacturing Company. The Melinex windows are further secured by clamps made of brass shim material, these clamps affording an easy method of adjusting the window width. To prevent end effects at the anode supports, guard rings are provided, which are held at the same positive potentials as the counter anodes.

Spectrometer Mounting and Vacuum System.

The arrangement of the spectrometer is shown in Plate 2. A 6" x 4" I-section steel girder forms the frame of the spectrometer, and is supported by two tripods constructed of "Dexion" slotted angle iron. A steel tube of 2" diameter is fixed to one end of the girder by means of two U bolts, and is supported at its base by two narrow angle hardwood wedges. The lower end of the tube passes through a ring with adjusting screws, which enables the tube to be aligned vertically. The top of the steel tube carries a thrust-race which forms the bearing for the crystal chamber. By this means, the crystal
PLATE 2 GENERAL VIEW OF THE SPECTROMETER
The film tube and crystal chamber were evacuated to a pressure of approximately $5 \times 10^{-2}$ torr by using two rotary vacuum pumps, whereas a pressure of about $1 \times 10^{-5}$ torr was obtained in the X-ray tube using a molecular diffusion pump with silicone fluid. In order to minimise the backstreaming of oil vapour into the X-ray chamber, a carbon dioxide trap was used in conjunction with the diffusion pump. To attain a higher standard of trapping when investigating the ytterbium metal spectrum a liquid nitrogen vapour trap was used. A liquid nitrogen trap was also fitted above the X-ray chamber. Pirani thermocouple gauges were employed to register the pressures in the film and crystal chambers, whilst the X-ray tube pressure was measured using a Genevac type PNGI Penning gauge.

The X-ray Vacuum Oven.

To investigate the emission spectrum of pure ytterbium metal it was necessary to adapt the X-ray tube chamber of the spectrometer, to enable the metallic targets to be prepared in situ. Since ytterbium in the metallic state is readily oxidised in air, the usual procedure...
for preparing targets, i.e. in a separate evaporating apparatus, could not be used. A method similar to that previously used by Combley to prepare metallic ytterbium absorption screens, was adopted.

The system is shown schematically in Figure 3.9. The design of the anode assembly, only, has been altered, the filament holder being unchanged. A brass tube, of internal diameter sufficient to accommodate the anode disc, is brazed into the rear of the vacuum chamber eccentrically, as shown. This ensures that only one half of the anode disc is bombarded with electrons at any one time. The anode support tube is of sufficient length to allow the disc to be withdrawn into the extension tube, the whole assembly being kept rigid by a long aluminium support screwed onto the end of the main tube. An 'O' ring seal at the end of the support tube, allows the anode disc to be moved along the axis of the extension tube. Two further pieces of tubing are brazed into the main tube at angles of 45° to the main axis. One is closed by a perpex window, enabling the evaporation process to be observed. Alternatively, an ionisation vacuum gauge may be mounted in this position. The other tube is adapted to enable a 4½" long pyrex appendix to be screwed into place. The ytterbium metal is placed inside a tubular tantalum "boat" arranged to be on the axis of the evaporating tube with the aid of mica formers. A "Radyne" 3½/5 K.VA. radio frequency heater is used to heat the boat to incandescence, the heating coils being arranged outside the glass appendix. With the anode tube drawn out to its fullest extent, material may be easily evaporated onto the surface of the target disc. The anode may then be pushed readily into the main X-ray tube chamber, without breaking vacuum. By using a commercial liquid nitrogen vapour trap between the oil diffusion pump and X-ray tube chamber, in conjunction with a similar trap constructed to fit onto the top of the main chamber, pressures better than 5 x 10⁻⁶ torr may be obtained. Since ytterbium metal evaporates more readily than its oxide, quite pure metal targets may be obtained at these pressures. However, on bombarding the anode with electrons, the target is heated, and oxidation then occurs quite rapidly.
Electronic Apparatus.

The electronic counting equipment is shown in block form in Figure 3.10. The loops of the proportional counters were held at different positive potentials supplied by the E.H.T. unit (I.D.L. type 532(A) used in conjunction with a potential divider (Labgear type 4143). The spectrometer was operated in the second order and negative going pulses from the counters were fed, via cathode followers, into wide band amplifiers (I.D.L. type 652) containing discriminator circuits, by means of which, pulses resulting from first order X-rays, and noise, were eliminated. The amplified pulses were passed into the gating circuits of a Triple Gate Ratio Counter (Labgear type D4107), the output of one counter being registered on this instrument, whilst the output of the second counter was recorded by an associated Dekatron Counter (Labgear type D4104/B). Although the triple gate scaling unit contained a source of 100 pulses per second, the use of two counters made it necessary to rely on a stop-watch for timing purposes, the counting being controlled by means of the manual switch incorporated in the gating circuits.

The X-ray tube cathode was held at a negative potential supplied by a 5kV. maximum, stabilised E.H.T. unit (A.P.T. model 5705/1) used in conjunction with a stabilised filament supply unit (A.P.T. model 5706/1). Anode currents up to 250 mA. could be obtained from these supply units. The anode potential was measured with an accurate potentiometer (Pye), used in conjunction with a potential divider supplied by Cambridge Instruments Ltd.

The mains electricity supply to the E.H.T. and filament control units, and to the oil diffusion pump, was controlled by a relay system shown in Figure 3.11, which switched off the current in the event of a failure of the cooling water supply.
Figure 3.10 Block diagram of electronics
240 V MAINS INPUTS

KEY
SW. A: SAFETY SWITCH
SW. B: MICRO SWITCH OPERATED BY WATER CIRCULATION
L. A: 'WATER OFF' INDICATOR LAMP
L. B: 'MAINS ON' NEON INDICATOR
R. A: GRAVITY LOADED RELAY
R. B: MAINS OPERATED RELAY
P. A: PLUG BOARD FOR E.H.T. AND FILAMENT SUPPLY UNITS
P. B: PLUG BOARD FOR DIFFUSION PUMPS

FIGURE 3.11 DIAGRAM OF RELAY CIRCUITS
CHAPTER FOUR: EXPERIMENTAL TECHNIQUES.

Alignment of Analysing Crystal.
Calculation of Dispersion.
Preparation of Targets.
Production of Line Profiles.
Line Profiles obtained from Ytterbium Metal Targets.
Experimental Errors.
Analysis of Line Profiles.
Alignment of Analysing Crystal.

In order to align the crystal to investigate a particular spectrum line, it is first necessary to arrange the normal to the crystal surface so that it lies along the axis of the detector tube. This is accomplished with the aid of a simple optical device. The counter head is removed and replaced by an aluminium plate containing a point source of light and also a cross wire, placed equidistant from the centre line of the detector tube, the whole assembly being horizontal. If the crystal is now turned until it is perpendicular to the tube axis, the light will be reflected from its surface forming a defocussed line image which may be observed with an eyepiece. Careful alignment of this image on the crosswire produces the degree of accuracy necessary, and the vernier setting of the crystal holder may be read, using the scale attached to the detector tube.

The Bragg angle necessary to observe a particular spectrum line is calculated using the wavelength values tabulated by Cauchois and Hulubei, and the lattice spacing for mica given by Siegbahn, for second order reflection. Now, by turning the crystal holder through the complement of the Bragg angle, it may be brought into the required position. In order to arrange the X-ray tube to be in the optimum position, the filament holder is illuminated and its image viewed by reflection from the crystal. The X-ray tube may be rotated about the crystal axis until the reflected image of the filaments appears centrally in the field of view as seen along the detector tube. To focus a particular spectrum line in the plane of the counters, the length of the detector tube may be altered until the distance between the detectors and the crystal is equal to \( R \sin \theta \), where \( R \) is the radius of curvature of the crystal, and \( \theta \) the Bragg angle. This adjustment may be made to an accuracy of at least one millimetre.
Calculation of Dispersion.

Since it was not intended to make an accurate determination of wavelengths in this work, the dispersion, in the region of the particular spectrum line under investigation, was calculated.

If the Bragg relation, $2d \sin \theta = n \lambda$ is differentiated, we have

$$2d \cos \theta \, d \theta = n \, d \lambda$$

where $d$ is the lattice spacing of the analysing crystal for reflections of order $n$, and $\theta$ the reflecting angle for wavelength $\lambda$. The dispersion is given by $\frac{d\lambda}{dS}$, where $dS$ is the distance in the plane of the detectors, corresponding to a wavelength change of $d\lambda$

Hence dispersion

$$\frac{d\lambda}{dS} = \frac{d\lambda}{d\theta} \times \frac{d\theta}{dS}$$

But since the focusing distance $D = R \sin \theta$

then $dS = D \, d\theta$

or

$$\frac{d\lambda}{dS} = \frac{2d \cos \theta}{n} \times \frac{1}{R \sin \theta}$$

$$= \frac{2d \cot \theta}{nR}$$

The Bragg angle for the line under investigation was calculated, for second order reflection, using the wavelength value given by Cauchois and Hulubei, and the corresponding value of the dispersion obtained. This value was checked by photographing known K lines, in high orders of reflection, as reference lines, and good agreement with calculated values was found. At the same time the quality of the analysing crystal, judged by the appearance and clarity of the K doublets, was also displayed, and found to be satisfactory.
Preparation of Targets.

As already mentioned, the self absorption of the Mx line, which occurs in ytterbium salts, makes it necessary to prepare very thin target layers. To record the ytterbium profiles, small quantities of ytterbium fluoride, chosen due to its ease of evaporation and chemical stability were evaporated in vacuo onto the brass target disc, which had been previously cleaned and polished. These evaporations were carried out in a separate evaporation plant, in which pressures of about $10^{-5}$ torr could be obtained. Weighed quantities of the material were placed on a tantalum 'boat' which was heated to incandescence by the passage of an electric current, until the evaporation was complete. The target disc was then transferred to the spectrometer.

To prepare metallic ytterbium targets the vacuum oven was used. The target disc was cleaned and polished and screwed onto the anode support tube. A small quantity of ytterbium metal was placed inside a tube formed from tantalum sheet and placed inside the glass evaporating tube. The system was evacuated to a pressure of about $1 \times 10^{-6}$ torr, liquid nitrogen vapour traps being used. To remove adsorbed air, the target was bombarded with electrons from the X-ray tube filament, the whole surface being treated by rotation of the target disc. The disc was then withdrawn into the evaporating position and ytterbium metal evaporated onto it by heating the tantalum boat to incandescence with the radio heater. The target was then carefully and rapidly returned to the X-ray chamber, when, since ytterbium metal is more readily evaporated than its oxide, the spectrum of reasonably pure ytterbium could be investigated.

Since hafnium salts show no line absorption in the M spectrum, it was not necessary to use the thin target technique to examine the Mx line profile. As the conventional paste target was found to be unsuitable, due to unstable running conditions, the brass target disc was roughened with a vibrating tool and hafnium oxide simply pressed into the roughened surface. Sufficient of the material adhered to the disc, under the running conditions of the spectrometer, to enable the profile of the hafnium Mx line to be observed.
Production of Line Profiles.

i) Early Attempts.

At the inception of this work it was realized that some correction must be made to the experimental data to take account of the ageing of the X-ray target, and the counter assembly was designed with this in mind. Since only two counters may sensibly be used, the line profile must be determined point by point and is hence time consuming. Over a period of several hours, the continual cathode ray bombardment progressively removes the target material by evaporation, and also pump oil decomposition products may be deposited over the target surface, hence reducing the absolute intensity of the emission line under investigation. To counteract this, one counter was placed permanently in the position of maximum line intensity, and the second used to scan through the region under investigation. By taking the intensity recorded by the movable counter as a ratio of intensity recorded by the fixed counter, some correction for loss of target material was made. However, using this technique, no reproducible results were obtained.

ii) Revised Method.

In general, X-ray line spectra are superimposed on a continuous background which is limited in the short wavelength region according to the Duane-Hunt law:

\[ eV = \frac{hc}{\lambda} \]

where \( \lambda \) is the shortest wavelength possible for an exciting voltage \( V \). This radiation emanates, not only from the evaporated layer of material under investigation, but also from the material of the anode, in this case brass. No account had been taken of this radiation in the previous treatment.
This continuous radiation was examined in a region far removed from the emission line, and its intensity found as a function of time. After allowing time for equilibrium to be attained it was found that, within statistical error, the decay of this continuous radiation was linear with time. Also, in any such work, it is assumed that the variation of continuous radiation with wavelength, over the range embracing the emission line, is linear. These two observations form the basis of a revised approach, Figure 4.1. It should be stressed that this is made necessary only by the time factor involved in recording a profile.

In order to know the value of the continuous radiation intensity at any time and in any position in the spectrum, it is necessary to ascertain, for each counter, its intensity at the two extremes of the line emission at the beginning and at the end of each profile determination. Absolute values of time and wavelength for each point in the profile are not needed as an inspection of the expression for continuous intensity will reveal that only ratios are involved. Hence, after determining the intensity of the continuous radiation at the commencement of an experiment, the fixed counter is placed at a known distance from the two extremities, in the position of maximum line intensity. The second counter is now moved into various positions of known spacing, and the relative intensities noted for each position, in numbers of counts per minute, the actual sampling time depending on the line intensity. After the whole region has been so treated, the intensity of the continuous radiation at the extremities is again found. The values of wavelength in the expression are correlated with the positions of the screw drives to the counters, and provided that the experiment is carried out at a uniform rate from start to finish, the corrected value for continuous intensity at any point may be obtained. The small background intensity due to natural radiation, is accounted for directly in this treatment. Knowing the continuous intensity for each point and for both counters it is simply subtracted from the total intensity due to line and continuum.
Figure 4.1.

Treatment of Continuous Radiation.

The intensity at $\lambda$, line maximum, is composed of

(a) $B$, background intensity due to natural radiation, which is constant.

(b) Contribution due to continuous radiation.

(c) Contribution due to line emission.
If the extremities of the spectrum occur at $\lambda_o$ and $\lambda_1$, then at a time $t = 0$, the corresponding intensities due to continuous radiation are $C_o$ and $D_o$.

If it takes a time $T$ to produce a complete line profile, then at time $t = T$ the intensity of continuous radiation will be $C_T$ and $D_T$.

Then, for an intermediate time $t = t$ we have, using the stipulation of linear variation with time,

$$C_t = C_o + \frac{t}{T} (C_T - C_o)$$

similarly

$$D_t = D_o + \frac{t}{T} (D_T - D_o)$$

Now, using the second stipulation, we have the continuous radiation intensity at time $t$, wavelength $\lambda$ as:

$$C_{\lambda,t} = C_t + \frac{\lambda - \lambda}{\lambda_i - \lambda_o} (D_t - C_t)$$

Expanding,

$$C_{\lambda,t} = C_o \left(1 - \frac{t}{T}\right) \frac{\lambda - \lambda_o}{\lambda_i - \lambda_o} + C_T \frac{t}{T} \frac{\lambda - \lambda}{\lambda_i - \lambda_o} + D_o \frac{\lambda - \lambda_o}{\lambda_i - \lambda_o} \frac{(T - t)}{T} + D_T \frac{t}{T} \frac{\lambda - \lambda_o}{\lambda_i - \lambda_o}$$
Now if a ratio of moving counter intensity to fixed counter intensity is taken, the continual change in target composition may be corrected for. Using this method, good reproducibility of results was obtained, justifying its adoption for this work.

**Line Profiles obtained from Ytterbium metal targets.**

Since the ytterbium metal targets oxidise extremely rapidly in the spectrometer under the action of the bombarding electrons, the time available for obtaining useful results by the previous method is extremely limited. If the line profile is obtained by simply scanning the spectrum and recording the observed intensity, the shape as in Figure 4.2(A) is obtained, when the anode voltage is approximately 3-5 K.V. On repeating the observations; approximately one hour later, the profile as in Figure 4.2(B) results. To allow for the change in target composition, the following procedure was adopted.

In Figures 4.2(A) and (B), the line shapes to the low energy side of point A are similar in both cases, any change in the absolute intensity of the line at A being due to loss of target material. However, the increase in absolute intensity of points such as B is due to the gradual oxidation of the target material. If, therefore, the ratio of B to A is observed as a function of time, the value at zero time should approximate to that corresponding to emission from metal of the highest purity obtainable in the vacuum oven.

The approximate line shape was obtained by observing the intensity distribution across the spectrum, and point A chosen so as to be on the low energy side of the observed line peak, whereas point B was chosen to lie on the high energy side of the peak. A pure ytterbium metal target was prepared, and without altering the positions of A or B, the intensities at points A and B were observed as a function of time, measured from
**FIGURE 4.2A**  M\(\alpha\) LINE PROFILE OBTAINED FROM ALMOST PURE YTTERBIUM METAL TARGET

**FIGURE 4.2B**  M\(\alpha\) LINE PROFILE OBTAINED FROM AGED YTTERBIUM METAL TARGET
the commencement of the excitation. A third counter, of the sealed-off gas-filled type, was used to observe the variation of continuous radiation intensity at point C concurrently with these observations, in order to determine the variation of continuum intensity over this period. Counter B was now moved into position C, to correlate the intensity values obtained from each counter. The line shape on the low energy side of point A was now observed, by moving counter B through the region, and observing the ratio of intensities as recorded by B to A being unmoved. Finally, A and B were moved to the extremities of the emission line and the intensity of the continuous radiation obtained for each counter, allowing the intensity of the continuum to be calculated for each position of B, as in the previous method.

Subtracting the intensity of the continuum in each case, the ratio of B to A was obtained as a function of time, which extrapolated to zero time was taken as that obtained from pure metal. The shape on the low energy side of A was obtained as before, when a point on the curve at B, corresponding to the state at zero time, could be related to this curve. Hence for each preparation of a pure metal target, the shape of the low energy side of the profile was obtained, together with one point on the high energy side. The procedure was therefore repeated with different positions of B, to obtain a complete high energy side profile.

**Experimental Errors.**

The spectrum obtained from any spectrometer is distorted to an extent determined by the resolving power of the instrument. If the reflected intensity is \( I(\lambda) \) at infinite, or ideal, resolving power, the experimentally obtained function for the intensity, \( E(\lambda_0) \), is related to this by the folding integral:

\[
E(\lambda_0) = k \int_{-\infty}^{\infty} I(\lambda) \cdot P(\lambda - \lambda_0) d\lambda \quad (1)
\]
where \( P(\lambda - \lambda_o) \) is the spectral window function, \( \lambda_o \) being the wavelength for which the instrument is set, and \( k \) a normalization constant. However, even if the exact spectral window function was known, it would be impossible to correct the experimental information completely, as the function \( I(\lambda) \) is not uniquely defined by equation (i). True structural details obliterated by the mathematical folding process can never be recovered, as they are no longer contained in the information supplied by the spectrometer. However, if the distorting influence of the spectral window is small, a reasonable estimate of the true spectral line shape may be obtained.

The resolving power of a spectrometer is influenced by several factors, the chief of which are:

1) The diffraction pattern of the analysing crystal.
2) The Johann focussing defect.
3) The height of the focal spot in the X-ray source, and the effective height of the analysing crystal.
4) The height and width of the detector slit.

With the spectrometer used for the present investigation the effects of the first three factors mentioned should be small in the region under investigation, the spectral window being defined mainly by the dimensions of the detector slit.

The width \( \omega_L \) of a spectral line combines with the width \( \omega_S \) of the spectral window to give a total width \( \omega_t \) according to the equation:

\[
\omega_t^n = \omega_L^n + \omega_S^n
\]  

(ii)

the value of the exponent \( n \) depending upon the shape of the spectral line and the spectral window. The shape of X-ray lines, determined using wave-mechanical arguments and also according to classical theory,
may be shewn to be Lorentzian in character. If the spectral window is assumed to be rectangular in shape, the exponent in equation (ii) will take the value 2 in the folding process. Therefore, if the width of the detector slit and the width of the observed line are known, the effect of the former may be determined from equation (ii).

Statistical Errors.

The statistical error is inherent in the method of photon counting. Since differences and ratios of photon numbers are taken in order to obtain a line profile, the statistical error may assume large proportions under certain circumstances. In order to reduce the error to reasonable proportions, large numbers of photons should be counted for each determination. At high anode potentials this may be achieved with relatively short sampling times, when the error involved in determining the maximum intensity of a line is less than one percent. However, near the extremities of the line profile, the required ratio involves the difference of similar numbers of photons, when intensity of the line emission becomes comparable with that of the continuous radiation. In this case, the error involved in such points may approach twenty percent. Near the excitation limit for a particular line, the intensity available at maximum anode current is greatly reduced, making longer sampling times necessary. However, a limit to available sampling time is imposed by the useful duration of the X-ray target. Under these circumstances, the error involved in determining the position of maximum line intensity is about two percent, while the error in the line extremities rises to about thirty percent. However, since the line tails have only small intensities, the actual errors involved are small. The counting statistics at low exciting voltages made it impossible to obtain line profiles at bombarding potentials very close to the excitation limit. However, the counter window was made relatively wide in order to obtain reasonable profiles at low exciting voltages, without unduly sacrificing spectrometer resolving power.
Resolution Time of Electronic Counters.

When large photon fluxes are being counted, the resolving time of the electronic counting equipment becomes an important factor in the interpretation of data. If the resolving time is $\tau$, and the observed number of counts is $N_0$, then the true number $N_T$ may be obtained from the relationship:

$$N_T = \frac{N_0}{(1 - N_0 \tau)} \quad (iii)$$

The resolving time of each counting set was determined using a double pulse generator, the delay between the pulses being altered until they were just resolved. Using the resolving times so obtained, each observation of photon intensity was immediately corrected using the given formula, the profiles being obtained as previously indicated.

Error in Wavelength Measurements.

The only directly measured quantity in the formula used to calculate the instrumental dispersion:

$$\frac{d\lambda}{dS} = \frac{2a \cot \theta}{R}$$

is the radius of curvature of the analysing crystal, $R$. Since this may be determined to an accuracy of about one millimetre, the error arising from this is negligible. To determine the wavelengths of the satellites, the value for the $M\alpha$ line given by Cauchois and Hulubei was used as a standard, and the satellite positions calculated from the known dispersion.
Since the profiles were analysed allowing freedom in the choice of wavelength parameters, a series of wavelength values was obtained for each satellite. A mean value for each component was therefore found, together with the mean deviation, as an indication of the error involved.

**Analysis of Line Profiles.**

The experimentally obtained line profiles were analysed into their constituent Lorentzian components using the University computer (Elliott 803). In the case of the hafnium profiles, the satellite intensity never predominates over that of the parent line, and therefore the line profile obtained with the highest bombarding potential, being the most accurate available, was used in the initial analysis. Values of the parameters defining the parent line, viz: position of maximum intensity, half width and height, were chosen to reproduce, as near as possible, the experimentally obtained profile. Using these parameters, the satellite intensity was obtained by subtraction and analysed into the least number of components by means of a curve-fitting programme the parameters of the satellite lines being chosen to reproduce as closely as possible the experimental intensity values. The computed parameters, were then used to form the integrated satellite intensity, which was subtracted from the overall experimentally obtained profile, enabling the parameters of the parent line to be obtained using the computer. By successive analyses of parent line and satellite contributions, an excellent fit was obtained between the experimental profile and that formed from the computed components. The half-width values obtained for the satellite components were used in the analysis of the remaining hafnium profiles, the heights and positions of maximum intensity being computed, in addition to the values of parameters best defining the parent line.

The satellite intensity in the profiles obtained from ytterbium fluoride targets increases rapidly with exciting voltage and soon
predominates over the parent line. For this reason it was necessary to make the initial analysis using a profile obtained at a low bombarding potential, even though the statistical errors are largest at low exciting voltages. The parameters best defining the satellite components and parent line were obtained using the same method as for the hafnium profiles. The values of half-widths so obtained were used as starting values in subsequent analyses, the heights of components and positions of maximum intensity also being used as variables.

In all these analyses, good agreement was obtained between computed and experimental profiles in the regions of high line intensities. However, near the line extremities, the computed values were invariably too large, indicating that the region of X-ray emission regarded as consisting of continuous radiation, did in fact contain some contribution from the line emission.
CHAPTER FIVE: EXPERIMENTAL RESULTS.

The Mα Spectrum of Ytterbium Fluoride.
The Mα Spectrum of Ytterbium Metal.
Thickness of Ytterbium Targets.
The Mα Spectrum of Hafnium Dioxide.
Calibration of Power Supply.
Tabulation of Results.
The Mα Spectrum of Ytterbium Fluoride.

The Mα spectrum of triply ionised ytterbium was obtained using the thin target technique to minimise the self-absorption effects, as previously described. Ytterbium fluoride was chosen as the target material due to its ease of evaporation and chemical stability, there being no possibility of the formation of metallic ytterbium during the evaporating process. The optimum amount of ytterbium fluoride to be evaporated was determined by a subsidiary experiment, since it was important to have the targets as thick as possible for intensity reasons, the limit being set by the onset of self-absorption of the Mα line. It was found that if no more than two milligrams of ytterbium fluoride was evaporated onto the target disc, which was placed six centimetres from the evaporating 'boat', no appreciable self absorption took place. Using these evaporated target layers, no appreciable amount of occluded air was released on bombardment with electrons, and consequently the maximum available tube current, 200 mA could be used with confidence. The useful duration of the target under these conditions was about three hours.

Since the satellite contribution to the Mα line profile of ytterbium fluoride grows rapidly with exciting voltage, it was necessary to analyse first a profile obtained at a low exciting potential, when the parameters, defining the parent Mα line could best be determined. Figure 5.1 shows the line profile obtained at a nominal exciting voltage of 1.7 kV., together with the statistical error involved in each point. Using the maximum available anode current, a count rate of approximately 90 pulses per second was observed for the fixed monitor counter, a maximum rate of 50 pulses per second being observed for the counter used to scan the profile. The difference between the two observed count rates is explained by the different window widths of the two counters. The peak to background ratio was found to be approximately 20:1. With a sampling time of five minutes for each point, the
resultant statistical error varied from a maximum of about 20\% in the extreme short-wavelength point, to a minimum of less than 2\% in the position of maximum line intensity.

The experimental profile was analysed into four Lorentzian components, allowing complete freedom in the choice of parameters. Figure 5·2 shows the result of this analysis, and compares the experimental profile with that obtained by summing the four components obtained by the computer. Component A was found to have an intensity of 23·5\% of that of the parent line, component B 62·2\% and component C 32·7\%. The integrated satellite intensity at the nominal exciting voltage of 1·7KV. was 118·5\% of that of the parent line.

The high voltage profile which was analysed is shown in figure 5·3, and was obtained using an anode current of 50mA. An intensity of about 1400 pulses per second was observed for the monitor counter, and a maximum intensity of about 750 pulses per second was observed for the counter used to obtain the profile. The peak to background ratio was found to be approximately 15:1. The profile was obtained using a sampling time of three minutes per point and the resulting statistical error varied from a maximum of 14\% in the line extremities to less than 0·7\% in the position of maximum line intensity.

The experimental profiles obtained at the various exciting voltages up to a maximum of 3·5KV. were analysed into four or five Lorentzian components directly, using the computer. In all these analyses, the starting values of the half-widths of the components and also their wavelength positions, were taken to be those evaluated for the profile obtained at 1·7KV. To obtain the best possible agreement between the experimental and reconstructed profiles, a little freedom was allowed in the final value of the half-width and wavelength
parameters, and complete freedom was allowed in the parameter describing the maximum height of each component. The results of the analyses are shown in figures 5-4 to 5-16, in which the experimental and reconstructed curves are displayed. Figure 5-17 shows the intensity of the separate satellite components, expressed as a percentage of the parent Mα line, as a function of the exciting voltage, whilst figure 5-18 shows the integrated satellite intensity expressed in the same manner.
FIGURE 5.4
YTERBIUM (M): LNE PROFILE AT 1.8 KV.

EXPERIMENTAL POINTS
RECONSTRUCTED FROM LORENTZ COMPONENTS

INTENSITY
EXPERIMENTAL POINTS RECONSTRUCTED FROM LORENTZ COMPONENTS

FIGURE 5.5 YTERBIUM M.K.: LINE PROFILE AT 19 KV.
Figure 5.8: Ytterbium Mα line profile at 2.2 kV.
FIGURE 5:10 YTERBIIUM Mα. LINE PROFILE AT 2.4KV.
Figure 5.12 Ytterbium Mα: Line profile at 2.6 kV.
Figure 5:7 Ytterbium Mα: Intensity of Satellite Components
The Mα Line of Ytterbium Metal.

As described earlier, the ytterbium metal targets were prepared in the specially constructed vacuum oven, in order to obtain metal as free from oxide as possible. The target disc was first bombarded with electrons from the X-ray filament in order to drive off excess occluded air, and the tantalum \textit{boat} containing the ytterbium metal was similarly treated by use of the R.F. heater. The actual evaporation of the target material was carried out with a pressure of approximately $5 \times 10^{-6}$ torr in the oven, when it was found that a comparatively thick coating of ytterbium metal contained the smallest amount of oxide.

Figure 5.19(A) & (B) shows the result of simple intensity measurement across the Mα line obtained from an ytterbium metal target prepared as above, at an exciting voltage of 3.5kV. Figure 5.19(A) is the profile obtained immediately after preparation of the target and shows a predominant peak in the long-wavelength region. However, the profile in figure 5.19(B), obtained after allowing the X-ray tube to run for approximately one hour, shows a very large component on the short wavelength side of the line, which completely masks the long wavelength component of figure 5.19(A). If it is assumed that the change in line profile is due to the oxidation, or other chemical combination, of the ytterbium metal, it is obvious that the time factor involved in obtaining a line profile must be accounted for in any useful method, and hence the procedure indicated in Chapter 4 was used. Also, to keep the rate of oxidation as low as possible and at the same time to have reasonable X-ray intensities, the profile at an exciting voltage of 3.5kV and anode current of 15mA., was obtained.

Figure 5.20 shows the profile of the Mα line of ytterbium metal obtained point by point at an exciting voltage of 3.5kV., together with the error involved in each point. The low energy side of the profile is the average of the several obtained, between which there was good agreement. The high energy side of the profile was
obtained by averaging the values found for each point, after extrapolating to zero time of excitation, the error indicating the agreement obtained. A Lorentzian curve was fitted to the low energy side of the profile by use of the computer, which when subtracted from the experimental profile enabled the contribution of the high energy components to the line area to be calculated. Figure 5.21 shows the experimental and fitted Lorentzian curves, and also indicates the satellite components. It was found that at the exciting voltage of 3.5Kv., the satellite intensity was 150% of that of the M<line. Since a useful attempt to obtain the line profile at a low exciting voltage would involve the use of high anode currents, and consequently rapid oxidation rates, such a curve was not obtained.

Thickness of Ytterbium Targets.

The mass of ytterbium fluoride deposited on unit area of the anode disc was calculated assuming the material to be evaporated uniformly over a hemisphere defined by the distance between the anode and the tantalum 'boat'. It was calculated that approximately 8 micrograms of material was deposited on each square centimetre of target, experiment shewing that this was the maximum amount allowable before self-absorption was observable. The mass of ytterbium metal to be evaporated at each target preparation was calculated on the same basis. However, on covering the anode disc with Melinex foil which was weighed after an evaporation, it was found that more than 8 micrograms of metal had been deposited on each square centimetre, indicating that the assumption of uniform distribution over a hemisphere was invalid in this case. The thicker ytterbium metal targets were persevered with however, since it was found that these contained smaller amounts of oxide than the thinner targets, and yielded more consistent experimental results.
The Mα Spectrum of Hafnium Dioxide.

As explained in the previous chapter, the Mα spectrum of hafnium was obtained using targets of hafnium dioxide simply pressed into the roughened anode disc. This was necessary, as no compound of hafnium suitable for evaporation was available. These targets had the disadvantage of containing occluded air which was slowly released on being bombarded with electrons. Consequently, the safe anode current for long periods of operation was limited to a maximum of 200 mA. However, with the lowest bombarding potential used, and with the maximum permissible anode current, such targets had a useful duration of up to three hours, and were found to be quite satisfactory.

Using the method indicated in Chapter four, several profiles were obtained for the Mα line at a nominal exciting potential of 3.5 Kv. Typical values of anode current were 45 mA., giving line intensities of about two thousand pulses per second for the fixed monitor counter and a maximum of about one thousand pulses per second for the counter used to scan the spectrum. With these photon fluxes, sampling times of three minutes per point were used. Good agreement between the several profiles so obtained was found, and a typical curve was used for the analysis into components.

The curve which was analysed into its components is shown in figure 5.22, together with the statistical error involved in each point. This error varied from a maximum of 25% in the extreme high energy point, to a minimum of 0.5% in the position of maximum line intensity. The peak to background ratio for the counter used to scan the spectrum was approximately 20:1, a similar ratio being found for the monitor counter.

After successive analyses by the method described previously, the portion of the profile due to the satellite contribution was obtained, and is shown in figure 5.23, together with the three components into which
it was analysed. The intensity of component A was found to be 10.5% of that of the M\(\alpha\) line, that of component B to be 17.4% and that of component C to be 14.6%. The integrated satellite intensity at 3.5\(\text{Kv}\) was found to be 42.5% of that of the parent line. Figure 5.24 shows the experimentally obtained line profile compared with that constructed from the components obtained as above, shewing the very good agreement between them.

Several profiles of the line obtained at a bombarding potential of 2.0\(\text{Kv}\) were obtained, and the one analysed is shewn in figure 5.25, together with the error in each point, which varied from a maximum of about 30% in the line extremities to a minimum of 1.5% in the position of maximum intensity. The sampling time used was four minutes per point, and using the maximum anode current available, 200\(\text{mA}\), the observed count rate was about 200 pulses per second for the fixed monitor counter, and a maximum of about 75 pulses per second in the counter which scanned the spectrum. The peak to background ratio was found to be approximately 26:1.

The profile was analysed as explained previously, and the final attempt to obtain the integrated satellite component is shewn in figure 5.26, together with its constituent lines. Component A was found to have an intensity of 5.8% of that of the M\(\alpha\) line, component B 8.9% and component C 4.9%. The integrated satellite intensity was 19.6% of that of the parent line. The experimental profile is compared with that obtained by summing the various components, in figure 5.27.

This process of analysis was repeated for profiles obtained at various voltages between a minimum of 1.9\(\text{Kv}\) and a maximum of 3.2\(\text{Kv}\). Figure 5.28 shews the integrated satellite intensity, and also the separate satellite components, expressed as a percentage of the M\(\alpha\) line as a function of exciting voltage.
Figure 5.22: Line profile of hafnium at 35 kV.
FIGURE 5.24

HAFNIUM Mx: LINE PROFILE AT 35 KV.

EXPERIMENTAL POINTS

RECONSTRUCTED FROM LORENTZ COMPONENTS

INTENSITY
FIGURE 5-28 HAFNIUM Mα: INTENSITY OF SATELLITE COMPONENTS
Calibration of Power Supply.

The voltages mentioned in the results section refer to the maximum available output from the stabilised power supply unit. Since a constant voltage is developed across the filament current supply unit in order to stabilise the anode current, it was necessary to calibrate the actual voltage developed across the X-ray tube against the stated output from the high voltage supply. An accurate 5000:1 potential divider was connected between the X-ray tube cathode and earth, and the voltage developed under running conditions was measured by means of an accurate Pye potentiometer. The nominal and actual voltages are shewn in table 5·1. In the graphs of satellite intensity against exciting potential, the corrected anode voltages as in table 5·1 are used. The energy positions of the M edges of ytterbium in ytterbium fluoride were taken to be those measured by Oombley, and the values for the $M_{IV}$ and $M_{V}$ edges of hafnium in hafnium dioxide were also obtained from the same source. The position of the $M_{III}$ edge of hafnium was obtained from L spectrum data.

Tabulation of Results.

The results of the investigations into the satellites of the $M\alpha$ lines of ytterbium fluoride and hafnium dioxide are collected together in tables 5·2 and 5·3. Table 5·2 shews the results for the ytterbium $M\alpha$ line, giving mean wavelength values and half widths of the various components in $\lambda$-units, and also $V'_{R}$ values. Previous results obtained by Lindberg, Hirsh and Phakey are shewn for comparison. The results for hafnium are shewn in table 5·3, together with mean half-width and wavelength values for the various components. The earlier results of Lindberg and Hirsh are also included.
### TABLE 5.1

**CALIBRATION OF POWER SUPPLY UNIT.**

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<thead>
<tr>
<th>NOMINAL VOLTAGE</th>
<th>MEASURED VOLTAGE</th>
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<tr>
<td>1700</td>
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<tr>
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### TABLE 5.2

**Ma LINE OF TRIPLY IONISED YTTERBIUM**

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<tr>
<th></th>
<th>Ma(_2)</th>
<th>Ma(_1)</th>
<th>Ma(^{1})</th>
<th>Ma(^{11})</th>
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<tr>
<td>(\lambda) X.U. 8138.0</td>
<td></td>
<td>8122.0</td>
<td>8106.0</td>
<td>8092.0</td>
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<tr>
<td><strong>Hirsh</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(\lambda) X.U. 8135.9</td>
<td></td>
<td>8124.0</td>
<td></td>
<td>8091.7</td>
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<tr>
<td><strong>Phakey</strong></td>
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<td></td>
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<tr>
<td>(\lambda) X.U. 8137.8</td>
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<td>8131.0</td>
<td>8119.7</td>
<td>8103.7</td>
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**Half Width**

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<th>Ma(_b)</th>
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### TABLE 5.3

**Ma LINE OF HAFNIUM**

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**PRESENT INVESTIGATION**

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| $\nu / \nu$ | 121.12 | 121.29 | 121.39 | 121.57 |

**HALF WIDTH**

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CHAPTER SIX: DISCUSSION OF RESULTS AND CONCLUSION.

Experimental Results.
Instrumental Resolution.
The Mα Line of Ytterbium Metal.
The Mα Lines of Ytterbium in Ytterbium Fluoride, and Hafnium.
The M Spectra of the Rare Earths.
Application of Russell Theory to Present Case.
Theory of Resonance Excitation.
The Mα Satellites of Hafnium.
Conclusion.
Experimental Results.

The results of the present investigation into the structure of the $M\alpha$ line of ytterbium in ytterbium fluoride and in ytterbium metal, and the corresponding line of hafnium in hafnium dioxide have been presented in Chapter five, together with the results of previous workers. Figure 5.18 shows the growth of the integrated satellite intensity in the $M\alpha$ line from ytterbium fluoride under the influence of the exciting potential, indicating the very rapid increase with voltage. The satellite structure persists strongly below the $M_{III}$ excitation potential, where it exceeds 300% of the intensity of the parent line. The maximum integrated satellite intensity was found to be over 1100% of that of the parent line for exciting voltages approximately twice those necessary to excite the diagram line.

Figure 5.28 shows the integrated intensity of the $M\alpha$ satellites of hafnium as a function of bombarding voltage. Again, the satellites persist strongly below the $M_{III}$ excitation level, where they exceed 20% of the intensity of the parent line, and reach a maximum integrated intensity of over 40% of that of the parent line above approximately three kilo-volts bombarding potential. The shape of the $M\alpha$ line obtained from ytterbium metal targets is shown in figure 5.21, together with the Lorentzian component best approximating to the parent line. This profile was obtained at an exciting voltage of approximately 3-5 kilo-volts, and the integrated satellite intensity was found to be over 150% of that of the parent line.

From the above observations it is clear that the presence of ytterbium in its triply ionised state, as in ytterbium fluoride has a considerable effect upon the size of the satellite contribution to the $M\alpha$ line, the satellite contribution to the $M\alpha$ line obtained from metallic, or non-ionised ytterbium, resembling more closely that obtaining in the $M\alpha$ line of hafnium dioxide.
Instrumental Resolution.

Williams, on carrying out previous photographic work using the two-metre spectrometer, found the instrumental resolving power to be good, and photographs taken during the present work would appear to substantiate this. If the resolving power is determined mainly by the effective detector aperture, the wavelength broadening due to this may be calculated according to the formula given in Chapter four. On this basis the ytterbium $\text{M}_2\alpha$ line from ytterbium fluoride targets would be broadened by approximately $1\%$, whilst the hafnium $\text{M}_2\alpha$ line would be broadened by approximately $4\%$. A fairly wide detector slit was used throughout the investigation in order to extend the statistically useful results to as low a bombarding voltage as possible, and this was achieved without great loss of resolution. The experimental results, however, have been analysed into their various components without shewing the necessity of including the $\text{M}_2\alpha$ lines.

In previous photographic work, Phakey did not resolve the $\text{M}_2\alpha$ doublet in ytterbium and shewed the value of the wavelength of $\text{M}_2\alpha$ for ytterbium previously obtained by Hirsh to be erroneous, in as much as he identified the intense satellite peak as $\text{M}_1\alpha$, and the parent line as $\text{M}_2\alpha$. In addition, the present work did not resolve the $\text{M}_2\alpha$ doublet in hafnium, whereas Hirsh, in 1931, identified the $\text{M}_2\alpha$ component. This was achieved using a Siegbahn type plane crystal spectrograph employing photographic detection, and wavelength measurement using a travelling microscope. This arrangement may be criticised since it would allow oblique incidence of X-rays onto the photographic plate, which would penetrate the emulsion and perhaps produce erroneous images to the low energy side of the main lines. Since only wavelength values were given by Hirsh without relative intensity data, his identification of $\text{M}_2\alpha$ may have been mistaken.
It would appear that the most definite identification of the \( \text{M} \alpha_2 \) line in this region has been made by Munier, Bearden and Shaw, who used a two-crystal spectrometer in their work on tungsten(74), and employed Geiger/Müller detectors. They obtained the line profile at a bombarding potential of 4800 volts and found \( \text{M} \alpha_1 \) to have a width of 6.6 x.u., \( \text{M} \alpha_2 \) to have a width of 1.2 x.u. and their separation to be 9 x.u. Assuming the relative intensities of the \( \text{M} \alpha \) doublet to be those given by the sum rules, the doublet has been reconstructed from the above data, using a dispersion factor equal to that calculated for the hafnium \( \text{M} \alpha \) region in the present investigation. The resulting curve is shown in figure 6·1A, and contains two very obvious, well-resolved components. Assuming the hafnium \( \text{M} \alpha \) doublet to be similar to that of tungsten, it would be expected that the present equipment should resolve such a structure, even with the fairly wide detector aperture.

The situation regarding the \( \text{M} \alpha \) doublet appears to be confused; however, since Parratt, in 1936, found the widths and relative intensities of the \( \text{M} \alpha \) doublet of \( \text{Au}(79) \), again using a two-crystal spectrometer. The structure was resolved arbitrarily into its components, when the \( \text{M} \alpha \) line was found to have a width of 7·0 x.u., \( \text{M} \alpha_2 \) to have a width of 6·5 x.u., and the intensity ratio of \( \alpha_2 : \alpha_1 \) was found to be approximately 2·5%, whereas theory predicts the ratio to be 5%. These obviously conflicting results in this region do not lend confidence to the acceptance of either set of values, and the situation regarding the hafnium doublet is uncertain. The profile of the hafnium \( \text{M} \alpha \) line obtained during the present work at 3·5Kv is also shown in figure 6·1B, in comparison with the results of Munier, Bearden and Shaw on \( \text{W}(74) \). The Lorentzian curve fitted to this profile does not allow the possibility of the inclusion of a further low energy component, and if indeed an \( \alpha_2 \) component does exist, it was not resolved in this work.
FIGURE 6.1A
TUNGSTEN M\(\alpha\) DOUBLET
[MUNIER BEARDEN & SHAW]

FIGURE 6.1B
HAFNIUM M\(\alpha\) PROFILE

FIGURE 6.1C
TUNGSTEN M\(\alpha\) DOUBLET
To investigate the instrument resolution further, the Mα line of tungsten was recorded. Photographic evidence indicated the existence of a weak component on the low energy side of the main Mα line. However, on recording the profile with the counter technique, the a doublet was not definitely resolved, although on analysing the experimental profile into Lorentzian components, the presence of Me₂ was indicated. Figure 6.1 C shows the result of this analysis in which Me₂ was found to have an intensity of approximately 5% of that of Me₁, c₂ to have a width of 10.2 x.u. and a₁ a width of 7.7 x.u. The width of the Mα line of tungsten was measured, and, allowing for the broadening due to the counter aperture, was found to be approximately 7.9 x.u.

Sandström (1954), using a large curved crystal spectrometer with counter detectors, measured the width of this line, and after allowing for all broadening effects found a width of 7.67 x.u. This would indicate that the resolving power of the spectrometer used in the present investigation compares quite well with that of Sandström's instrument. It would appear that Sandström did not resolve the Me doublet, since no indication of the width of Me₂ is given. In addition, the width of Mβ was found to be 7.25 x.u., compared with a width of 7.85 x.u., found by Munier, Bearden and Shaw with a two-crystal spectrometer. Since it would be expected that a two-crystal instrument would show less line broadening than a curved crystal instrument, the result for the Mβ line of tungsten throws some doubt onto the accuracy of Munier, Bearden and Shaw's result.

The Mα Line of Ytterbium Metal.

The vacuum oven designed to prepare ytterbium metal targets, although allowing worthwhile results to be obtained, was not sufficiently refined to enable the spectrum of pure metal to be observed. However, it is obvious that the previous attempt, by Phakey, to prepare metallic ytterbium targets, was unsuccessful. The amount of material to be evaporated was calculated, assuming the metal to be uniformly distributed.
over a hemisphere defined by the distance between the anode and the tantalum 'boat', whereas subsequent investigation shewed this assumption to be incorrect. However, since the amount of material which was evaporated could not be accurately controlled, no sustained attempt was made to prepare thinner target layers. In addition, if thinner target layers were prepared, it was found that the subsequent rate of oxidation was much greater, and also, due to the small amount of emitting material the registered X-ray intensity was lower, leading to statistically less reliable results. Therefore it was decided that although the thicker target layers involved the possibility of self-absorption occurring, the statistically more reliable and reproducible results so obtained, justified their use. Even so, the line profile close to the high energy side of the main peak could not be obtained with any accuracy, presumably due to the indeterminate amount of oxide present, producing indefinite self-absorption effects. The resulting profile, therefore, is perhaps distorted in as much as the main line peak may have been reduced an unknown amount by self-absorption. For this reason, the integrated satellite intensity found for the Mα line of ytterbium metal can only be regarded as an upper limit to its true value. The qualitative results however, would not be affected by the above considerations.

The Mα Lines of Ytterbium in Ytterbium Fluoride, and Hafnium.

The analysis of the hafnium line profiles was made difficult by the relatively small intensity of the satellite components, any direct attempt at analysis yielding only two components, the main line and one satellite, whereas photographic evidence indicated the existence of at least three satellites. It was necessary, therefore, to analyse the profiles as indicated in chapter four, allowing no freedom in component widths. Good results were obtained, however, by this method. The analysis of the ytterbium profiles was made easier since the various components were of comparable sizes, and also, the operation of the computer had been improved since the analysis of the hafnium results.
It was found possible to allow freedom in the choice of all parameters used, allowing the best correspondence between experimental and computed values to be obtained. The curves obtained at or below an exciting voltage of 2.1 kV were satisfactorily analysed into four components, i.e., three satellites and one parent line. However, at a bombarding voltage of 2.2 kV, it was found necessary to include one more component in order to obtain the best possible correspondence between the computed and experimental profiles. It is interesting to note that Ehakey also found it necessary to include a fifth component in the analysis of his photographic work at approximately this voltage, indicating the accuracy with which his analysis was carried out. It should be emphasised that these analyses were carried out in order to obtain the best possible correspondence between experimental and reconstructed profiles, and that the best fit was obtained, which is not necessarily the correct one.

The great difference between the Mo line profiles obtained from triply ionised ytterbium and from non-ionised ytterbium is immediately apparent from the results obtained, the line profile obtained from metallic or non-ionised ytterbium resembling those obtained from hafnium dioxide. These observations would indicate that the process leading to the emission of the satellite lines in ytterbium fluoride is intimately connected with the electronic structure of the ytterbium ion.

Coble has shown conclusively, by X-ray absorption measurements made on foils of ytterbium fluoride and ytterbium metal, that whereas the neutral atom of ytterbium has an outer electronic configuration of $4f^{14}5s^2$, the triply ionised atom contains only thirteen $4f$ electrons. Also, the neutral atom of hafnium contains fourteen $4f$ electrons, together with two $6s$ and two $5d$ valence electrons, the ionisation of this atom leaving the $4f$ shell unchanged. It would appear, therefore, that the removal of an electron from the $4f$ shell leads to the enhancement of the Mo satellites.
The M Spectra of the Rare Earths.

Since the electronic structure of the Rare Earths is unique in so far as the 4f shell is concerned, a consideration of the M spectra of these elements would appear to be pertinent to the problem of the ytterbium satellites. As pointed out by Russell, the existence of Ma and Mβ lines in the spectrum of triply ionised lanthanum is difficult to explain since such an ion should contain no electrons in the 4f shell, which are necessary for the emission of these radiations. However, these lines have been observed by Kessig in 1936 and confirmed by Russell (1958), which indicated that some process must occur by which electrons may enter the 4f shell of the lanthanum ion under the conditions of X-ray excitation. In addition, the agreement noted between the wavelengths of the X-ray absorption lines and emission lines in this region indicates the possibility of some reciprocal process occurring. The Mγ absorption line in triply ionised lanthanum can be readily explained by the electron configuration change:

\[ 3d^{10} 4f^0 \longrightarrow 3d^9 4f^{1} \]

in which one electron from the full 3d sub-shell is lifted into the empty 4f shell by the incident X-radiation. However, under excitation by electron bombardment, it has previously been assumed that the removal of a 3d electron will result in complete ionisation of that shell, leaving the lanthanum ion in a state with configuration 3d^9 4f^0. It is obvious that the Ma and Mβ lines could not be produced from such an initial state. This observation indicates that some other process must take place, and such a theory was proposed by Russell.

Russell suggested that the excitation of the 3d shell by electron bombardment changes the effective nuclear charge of the ion that a re-arrangement of the electronic structure takes place, bringing an electron into the empty 4f shell. The removal of a 3d electron in the case of lanthanum(57) would increase the effective nuclear charge to 58, that of
cerium. Since triply ionised cerium contains one electron in the 4f shell the act of ionising the 3d shell of the lanthanum ion would result in the creation of a state with one 4f electron. The production of the \( M\alpha \) and \( M\beta \) lines may then be explained by the transitions:

i) Electron bombardment: \( 3d^{10}4f^0 \rightarrow 3d^{9}4f^0 + e \)

ii) Electronic rearrangement: \( 3d^{9}4f^0 + e \rightarrow 3d^{9}4f^1 \)

iii) X-ray emission: \( 3d^{9}4f^0 \rightarrow 3d^{10}4f^0 \)

It is clear that the emission process is the reciprocal of the absorption process previously described, and such a mechanism could be used to explain the presence of \( M\alpha \) and \( M\beta \) lines in lanthanum, and also the equivalence of the \( M\gamma \) absorption and emission wavelengths. This suggestion may obviously be extended to explain the observed facts in the \( M\alpha \) emission and \( M\gamma \) absorption spectra of the heavier rare-earths. For a rare-earth ion normally having \( n \) electrons in the 4f shell, the line absorption process may be described in terms of the transition:

\[ 3d^{10}4f^n \rightarrow 3d^{9}4f^{n+1} \]

According to the above theory, the result of ionising the 3d shell by electron bombardment will be to create a state represented by the configuration:

\[ 3d^{9}4f^{n+1} \]

the transition resulting in the emission of the \( M \) lines being represented by:

\[ 3d^{9}4f^{n+1} \rightarrow 3d^{10}4f^n \]

which is the reciprocal of the absorption process. Although this mechanism can be used to explain the correspondence observed between the
M absorption lines and certain emission lines in the spectra of the rare-earth elements, it cannot explain the existence of the high energy components in the M emission spectra, which have no matching absorption lines. The M\(^{\text{v}}\) emission line of the ytterbium ion shows typical structure in as much as although the parent M\(^{\alpha}\) line coincides in wavelength with the M\(^{\text{v}}\) absorption line, the high energy, voltage sensitive components, have no corresponding members in the absorption spectrum.

To account for this, it was suggested by Professor E.A. Stewardson that in the case of emission it is possible for competing processes to occur. The normally expected process of;

\[
3d^94f^n \rightarrow 3d^{10}4f^{n-1}
\]

may lead to the emission of high frequency components before the reordering of the 4f shell takes place to give the \(3d^94f^{n+1}\) state which is necessary for the emission of lines corresponding to the absorption lines. Furthermore, Russell suggested the possibility of the states concerned in the emission process being in an excited state, which may be represented by;

\[
3d^94f^{n+1} \rightarrow 3d^{10}4f^n^*
\]

the asterisk denoting that the 4f electrons are in a state other than the ground state. Such a process would presumably produce emission lines having lower energy than those produced by the normal transition;

\[
3d^94f^{n+1} \rightarrow 3d^{10}4f^n
\]

In the ytterbium ion the above process would yield the M\(^{\alpha}\) diagram line, which has not been observed in this work. The suggestion was extended to include the possibility of transitions occurring between initial and final states other than the ground states. Thus we may
have transitions from excited initial states to the unexcited final
state yielding high energy emission lines, from unexcited initial states
to excited final states yielding low energy lines and transitions between
excited initial and final states. Some of these transitions will have
equivalents in the absorptions spectrum, but the overall picture presented
by these proposals is the general overlap of emission and absorption
frequencies, the emission spectra containing members of both higher and
lower energies than the corresponding absorption lines.

Application of Russell Theory to Present Case.

It is well known that the triply ionised ytterbium atom in ytterbium
fluoride contains thirteen electrons in the 4f shell. The Mγ absorption
line may be correlated with the electron transition;

$$3d^{10}4f^{13} \rightarrow 3d^{9}4f^{14}$$

On ionising the 3d shell by electron bombardment, we would expect
on the basis of the Russell theory, the creation of a state with fourteen
4f electrons, and the subsequent emission of a line corresponding in
energy to the absorption line, according to the processes;

i) Electron bombardment: $$3d^{10}4f^{13} \rightarrow 3d^{9}4f^{13} + e$$

ii) Electron re-arrangement: $$3d^{9}4f^{13} + e \rightarrow 3d^{9}4f^{14}$$

iii) X-ray emission: $$3d^{9}4f^{14} \rightarrow 3d^{10}4f^{13}$$

The mechanism represented by the third process must obviously occur to
explain the exact correspondence between the Mγ absorption line and M α
emission line in ytterbium fluoride. Since the initial state with
fourteen 4f electrons cannot exist in an excited state, the sub-shell
being completely full, the high energy components in the M α emission line
cannot originate from such a state. Also, only one excited final level
exists, yielding the unresolved Mα component. The high energy components
could be explained in terms of the competing process represented by the transition;

\[
\text{3d}^{9}\text{4f}^{13} \rightarrow \text{3d}^{10}\text{4f}^{12}
\]

which would result in the emission of a multiplet of lines of higher energy than that of the reciprocal process shown above. However, it is difficult to explain the dependence on exciting voltage of the intensity of these components on this basis. Although the Russell process is obviously useful to explain the correspondence between emission and absorption wavelengths, it is not sufficient to explain the observed voltage dependence of the high energy components in the Mα spectrum of ytterbium fluoride.

Theory of Resonance Excitation.

The following theory was first suggested by Professor E.A. Stewardson. It has been assumed previously that the ionisation of the 3d sub-shell by electron bombardment will result in the complete removal of a 3d electron from the atom. If, however, we examine the possibility of a resonance excitation of an electron into the incomplete 4f shell, many aspects of the Mα emissions of ytterbium fluoride may be explained. It is well known that in the M absorption spectra, line structure predominates over any edge-like structure, demonstrating the very high probability of resonance excitation by incident radiation. Indeed, M edges in ytterbium fluoride were undetectable by photographic means, indicating the small relative probability of the complete removal of M electrons from the atom. Furthermore, since it is now known that ytterbium in the metallic state has a full 4f shell, the examination of the Mα line of this material should furnish some information as to the validity of the assumption of resonance excitation.
Cross sections for the complete ionisation of inner electron shells, determined by measuring the intensities of X-ray lines, typically increase to a maximum value at voltages about four times those necessary to ionise the particular shell, and then slowly decrease. For electron excitation, however, cross-sections generally increase to a maximum value for voltages only slightly in excess of the minimum excitation value, and then rapidly decrease. For the excitation of metastable states, the cross section shows an even more rapid increase and subsequent decrease near the excitation limit. Cross sections for electron excitation, as opposed to ionisation, have been measured for a few materials only, mainly gases, and little is known about similar processes in inner electron levels. Although experimental cross-section for the ionisation of the M shell appear to be lacking, it seems reasonable to expect the ionisation function to vary in a manner similar to that observed for other shells. If it is assumed that the greatest probability of a resonance excitation of a 3d electron into the 4f vacancy in the ytterbium ion occurs for incident electron energies close to the resonance value, and that the cross-section then rapidly decreases with increasing electron energy, the behaviour of the ytterbium satellites may be explained. The resonance excitation would result in the creation of an ytterbium ion with fourteen 4f electrons, in the case of ytterbium fluoride. The decay of this state would result in the emission of an X-ray line corresponding in energy to the $M_\gamma$ absorption line, according to the processes:

i) Direct excitation: $3d^{10}4f^{13} \rightarrow 3d^94f^{14}$

ii) X-ray emission: $3d^94f^{14} \rightarrow 3d^{10}4f^{13}$

However, on increasing the energy of the incident electrons, if the probability of such a resonance excitation falls away rapidly, any ionisation in the 3d shell would result in the complete expulsion of the electron from the atom. If the state so created decays before the re-ordering of the electrons postulated by Russell occurs, then the resulting X-rays will consist of a multiplet, of higher energy than the
line emanating from the above process, according to the following processes;

   i). Ionisation by electron bombardment: 3d^{10}4f^{13} \rightarrow 3d^{9}4f^{13} + e

   ii). X-ray emission: 3d^{9}4f^{13} + e \rightarrow 3d^{10}4f^{12} + e

This qualitatively explains the behaviour of the satellites of the Me line from ytterbium fluoride, in as much as the parent line may be correlated with the decay of a state containing 14 4f electrons produced by direct excitation, the satellites resulting from a competing process involving the complete ionisation of the 3d shell. The parent Me line does not completely disappear at high bombarding potentials, which is consistent with the resonance excitation theory, as, even at high bombarding potentials, the cross section does not disappear completely. Also, the possibility of the Russell process occurring must also be considered. If the reciprocal excitation process occurs in the case of ytterbium fluoride it would be expected that the Me line of ytterbium metal would not contain voltage sensitive components, the 4f shell in this case being full, excluding the possibility of such an excitation occurring. Any excitation of the 3d shell would result in complete removal of an electron from the atom, X-rays being produced by the process;

   3d^{9}4f^{14} \rightarrow 3d^{10}4f^{13}

which results in the production of the 'parent' line in the case of ytterbium fluoride. The profile obtained from ytterbium metal at 3.5 Kv, although containing some high energy structure, shews one predominant line as may be expected on the above basis.

The high energy structure may be due to impurities in the target material, or may be satellites of the type found in hafnium.

The resonance excitation theory may be qualitatively tested by comparing the Mm spectra of triply ionised ytterbium and thulium.
The high voltage or ionisation spectrum of ytterbium fluoride arises from the following processes;

i) Ionisation by electron bombardment: \( \text{3d}^{10} \text{4f}^{13} \rightarrow \text{3d}^{9} \text{4f}^{13} + e \)

ii) X-ray emission: \( \text{3d}^{9} \text{4f}^{13} \rightarrow \text{3d}^{10} \text{4f}^{12} \)

If the resonance excitation theory is valid, the low voltage, or resonance excitation spectrum of thulium, would arise from the processes;

i) Resonance excitation: \( \text{3d}^{10} \text{4f}^{12} \rightarrow \text{3d}^{9} \text{4f}^{13} \)

ii) X-ray emission: \( \text{3d}^{9} \text{4f}^{13} \rightarrow \text{3d}^{10} \text{4f}^{12} \)

Comparisons of the two emission processes shown above suggests that the emission profiles should be similar. Figure 6.2A shows the ionisation spectrum, or satellite structure, in the M α line of ytterbium fluoride at 1.7kV., and figure 6.2B shows the parent Mα profile of thulium at a voltage of 1.49kV., obtained photographically by J.E. Wilson. Although differing in quantitative details, the profiles are similar. The low energy structure in the thulium profile may be explained in terms of the competing emission process;

\( \text{3d}^{9} \text{4f}^{13} \rightarrow \text{3d}^{10} \text{4f}^{12} \)

where the twelve 4f electrons are left in a final state other than the ground state, which would lead to the emission of lines with longer wavelength compared with the previously mentioned process. This mechanism should also occur in the ytterbium ionisation spectrum but, presumably, this structure was masked by the excitation spectrum, or 'parent' line.

It has been suggested by Professor E.A. Stewardson (private communication) that a further test of the theory may be made in the case of the M α emissions of triply ionised cerium, as occurring in
FIGURE 6.2A  YTERBIUM FLUORIDE
Mα SATELLITE STRUCTURE AT 1.7kV.

FIGURE 6.2B  THULIUM Mα PARENT
LINE GROUP AT 1.49kV.
the oxide. In this ion, the 5d shell is completely full, whilst the 4f shell contains only one electron. On removing a 5d electron, therefore, a simple X-ray multiplet may be emitted according to the mechanisms:

i) Electron bombardment: \[
\text{5d}^{10}\text{4f}^1 \rightarrow \text{5d}^9\text{4f}^0 + e
\]

ii) X-ray emission: \[
\text{3d}^9\text{4f}^1 \rightarrow \text{3d}^{10}\text{4f}^0
\]

However, if resonance excitation is possible, the population of the 4f shell may be increased to two electrons, when the X-rays emitted would appear as a multiplet of lower energy than the simple multiplet produced as above. Since resonance excitation would be expected to be most probable near the excitation limit for the 3d shell, the Mα emission line would appear as a complex multiplet, with voltage sensitive components, at low bombarding potentials. However, on increasing the exciting voltage, the resonance process becomes less probable, and the emission line would be expected to simplify. This description is in complete contrast with the observed facts in the Mα spectrum of ytterbium fluoride, where the voltage sensitive components increase with increasing excitation potential, and the observation of the Mα spectrum of cerium oxide should provide further evidence to explain the origin of the voltage sensitive Mα emissions in the rare earths.

The Mα Satellites of Hafnium.

Although the satellites of the Mα line of hafnium never predominate over the parent line, as in the case of the ytterbium fluoride satellites, they obtain a maximum integrated intensity of over 40% of the parent line. This compares with a maximum integrated satellite intensity of over 75% of the parent line found by Phakey for lutecium. The satellites of hafnium Mα clearly occur when the exciting voltage is between the M_{III} and M_{IV} excitation potentials, the position being similar for lutecium. However, it is difficult to say whether they exist below the M_{IV} excitation potential, since results here were statistically unreliable.
due to the poor intensity of X-rays. It has been suggested by F.R. Hirsh (1936, 1942) that the $\text{M}_\alpha$ satellites are due to the radiationless Ooster-Kronig transition $\text{M}_{\text{III}} \rightarrow \text{M}_\gamma \text{N}_{\text{IV},\gamma}$ which is energetically possible for elements $Z < 89$, (Cooper 1944). The above results shew that this transition above cannot account for the satellites of lutecium and hafnium, indeed, no marked change in the gradient of the satellite intensity versus exciting voltage graph was observed at $\text{M}_{\text{III}}$ excitation potential, when such a radiationless transition becomes possible. However, the appearance of component $\alpha_\gamma$ in the spectrum of ytterbium fluoride could be correlated with this Ooster-Kronig transition. According to Cooper, the radiationless Ooster-Kronig transitions $\text{M}_{\text{IV}} \rightarrow \text{M}_\gamma \text{O}_{\text{IV},\gamma}$ are possible below $Z = 82$, which may explain the occurrence of the satellites below $\text{M}_{\text{III}}$ potential, although it has not been shown that below $\text{M}_{\text{IV}}$ excitation potential the satellites disappear, as would be expected on this basis.

It would not be expected that the creation of states of double ionisation by single electron impact could produce satellites of the intensity observed for the hafnium $\text{M}_\alpha$ line. Richtmyer (1936) calculated the intensity of the Ka satellites, assuming they arise from double ionisation by single electron impact, for various values of atomic number, and found that the intensity should decrease fairly rapidly with increasing $Z$. Parratt and Shaw (1936) made measurements which agreed substantially with Richtmyer's calculations, but for elements heavier than $Z = 36$, the integrated satellite intensity never exceeded 1% of that of the parent line. Even for light elements, the ratio of satellite to parent line intensity never exceeds 5%. Although theoretical results for the probability of double ionisation occurring which involves the removal of electrons from the L or M shells are lacking, such high satellite intensities as observed for hafnium $\text{M}_\alpha$ would not seem likely to be due to Wentzel-Druyvesteyn excitation.
Hirsh in 1952, measured the integrated intensity of the $M \alpha$ satellites of Pt(78), which was found to be 17% of the parent line. Since Coster-Kronig transitions are most probable when the energy of the expelled electron is small, and also since the transition $M_{\text{III}} \rightarrow M_{\nu} N_{\nu} V$ first becomes possible below $Z = 89$, and the transition $M_{\nu} \rightarrow M_{\nu} 0_{\nu}^+_{\text{III}}$ is possible below $Z = 82$, then assuming the $M \alpha$ satellites of hafnium arise from the same source as the $M \alpha$ satellites of platinum, it would be expected that the integrated satellite intensity in hafnium would be less than 17%. Phakey made suggestions to account for the small satellite intensity observed by Hirsh as compared with the intensity of the lutecium $M \alpha$ satellites, approximately 75% at twice the excitation potential, observed in his own work. Assuming these suggestions to be valid, the integrated satellite intensity in hafnium $M \alpha$ found in the present investigation, should compare reasonably with the results of Hirsh. Although the intensity observations for the hafnium satellites are not in complete accord with those of Hirsh for heavier elements, it seems likely that the $M \alpha$ satellites arise partly from the Coster-Kronig transition $M_{\nu} \rightarrow M_{\nu} 0_{\nu}^+_{\text{III}}$, although it can not be stated that the satellites definitely disappear below the $M_{\nu}$ excitation potential.

Conclusion.

It has been shown that the $M \alpha$ satellites of ytterbium fluoride and ytterbium metal differ completely in character, their large intensity in ytterbium fluoride being dependent upon the vacancy in the 4f shell in this material. The suggestion made to account for this phenomenon, the resonant excitation of an $M_{\nu}$ electron into the 4f vacancy by direct electron bombardment, may be tested by satellite observations in the $M \alpha$ spectra of the lighter rare earths. If such a process is possible, the $M \alpha$ line of lanthanum(57) should decrease in absolute intensity with increasing excitation potential and also, the $M \alpha$ line of uranium(58) should show complex structure at low exciting potentials, which simplifies on raising the bombarding potential. Although it has been shown that the
Hafnium Mα satellites cannot be entirely due to the $M_{\alpha} \rightarrow M_{\gamma^*}$ Coster-Kronig transition, some doubt remains as to their origin. However, it seems likely that they arise in part from the Coster-Kronig transition $M_{\gamma^*} \rightarrow M_{\gamma^*} O_{\alpha}$. Further work in this region to accurately determine threshold potentials and relative satellite intensities using photon counting technique would appear to be useful.
### REFERENCES

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal/Work</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger P.</td>
<td>Comptes Rendus</td>
<td>180, 165</td>
</tr>
<tr>
<td></td>
<td>Jour. de Phys.</td>
<td>6, 205</td>
</tr>
<tr>
<td>Barrere.</td>
<td>Comptes Rendus</td>
<td>233, 376</td>
</tr>
<tr>
<td>Beuthe H.</td>
<td>Zeits f. Phys.</td>
<td>50, 762</td>
</tr>
<tr>
<td>Block F.</td>
<td>Phys. Rev.</td>
<td>48, 187</td>
</tr>
<tr>
<td>Bishop E.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cauchois Y.</td>
<td>Jour. de Phys.</td>
<td>3, 320</td>
</tr>
<tr>
<td></td>
<td>Comptes Rendus</td>
<td>202, 169</td>
</tr>
<tr>
<td></td>
<td></td>
<td>205, 519</td>
</tr>
<tr>
<td>Cooper J.N.</td>
<td>Phys. Rev.</td>
<td>65, 155</td>
</tr>
<tr>
<td>Coster D.</td>
<td>Phil. Mag.</td>
<td>44, 545</td>
</tr>
<tr>
<td>Coster D. &amp; Kronig R. de L</td>
<td>Physica.</td>
<td>2, 13</td>
</tr>
<tr>
<td>Coster D. &amp; Thyssen W.J.</td>
<td>Zeits f. Phys.</td>
<td>84, 686</td>
</tr>
<tr>
<td>De Langen.</td>
<td>Physica.</td>
<td>6, 27</td>
</tr>
<tr>
<td>Druyvesteyn M.J.</td>
<td>Zeits f. Phys.</td>
<td>43, 707</td>
</tr>
<tr>
<td></td>
<td>Dissertation (Groningen)</td>
<td></td>
</tr>
<tr>
<td>Daene &amp; Hunt.</td>
<td>Phys. Rev.</td>
<td>6, 166</td>
</tr>
<tr>
<td>Damond J.W. &amp; Kirkpatrick</td>
<td>Rev. Sci. Int.</td>
<td>1, 88</td>
</tr>
<tr>
<td>Ford O.R.</td>
<td>Phys. Rev.</td>
<td>41, 577</td>
</tr>
<tr>
<td>Groven L.</td>
<td>Comptes Rendus</td>
<td>225, 572</td>
</tr>
<tr>
<td>Groven L. &amp; Legasse A.</td>
<td>Comptes Rendus</td>
<td>228, 1642</td>
</tr>
<tr>
<td>Groven L. &amp; Morlet J.</td>
<td>Bull, Royal Acad. (Belgium)</td>
<td>37, 630</td>
</tr>
</tbody>
</table>
REFERENCES.

         Phys. Rev. 50 191 1936.
         Phys. Rev. 57 662 1940.
         Phys. Rev. 59 766 1941.
         Physica. 16 377 1950.


Lindberg E. Zeits f. Phys. 50 82 1929.


Moseley H. Phil. Mag. 26 1024 1913.


         Phys. Rev. 50 1 1936.
         Phys. Rev. 50 598 1936.
         Phys. Rev. 54 99 1938.
         Rev. Mod. Phys. 31 616 1959.


<table>
<thead>
<tr>
<th>Reference</th>
<th>Journal</th>
<th>Volume</th>
<th>Page 1</th>
<th>Page 2</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Randall C.A. &amp; Parrett L.G.</td>
<td>Phys. Rev.</td>
<td>57</td>
<td>756</td>
<td></td>
<td>1940</td>
</tr>
<tr>
<td>Richtmyer F.K.</td>
<td>Phil. Mag.</td>
<td>6</td>
<td>64</td>
<td></td>
<td>1928</td>
</tr>
<tr>
<td></td>
<td>J. Frank. Inst.</td>
<td>208</td>
<td>325</td>
<td></td>
<td>1929</td>
</tr>
<tr>
<td></td>
<td>Rev. Mod. Phys.</td>
<td>9</td>
<td>391</td>
<td></td>
<td>1937</td>
</tr>
<tr>
<td>Richtmyer R.D.</td>
<td>Phys. Rev.</td>
<td>38</td>
<td>1802</td>
<td></td>
<td>1931</td>
</tr>
<tr>
<td></td>
<td>Phys. Rev.</td>
<td>49</td>
<td>1</td>
<td></td>
<td>1936</td>
</tr>
<tr>
<td>Richtmyer F.K. &amp; Kaufmann</td>
<td>Phys. Rev.</td>
<td>44</td>
<td>605</td>
<td></td>
<td>1933</td>
</tr>
<tr>
<td>Richtmyer F.K. &amp; Tamberg E.G.</td>
<td>Phys. Rev.</td>
<td>51</td>
<td>925</td>
<td></td>
<td>1937</td>
</tr>
<tr>
<td>Richtmyer F.K. &amp; Taylor L.S.</td>
<td>Phys. Rev.</td>
<td>36</td>
<td>1044</td>
<td></td>
<td>1930</td>
</tr>
<tr>
<td>Sakellarides M.P.</td>
<td>Comptes Rendus</td>
<td>236</td>
<td>1767</td>
<td></td>
<td>1953</td>
</tr>
<tr>
<td>Sandstrom A.E.</td>
<td>Arkiv Fys.</td>
<td>8</td>
<td>129</td>
<td></td>
<td>1954</td>
</tr>
<tr>
<td>Schörling P.O.</td>
<td>Arkiv. Fys.</td>
<td>27</td>
<td>143</td>
<td></td>
<td>1964</td>
</tr>
<tr>
<td>Shaw C.H. &amp; Parrett L.G.</td>
<td>Phys. Rev.</td>
<td>50</td>
<td>1006</td>
<td></td>
<td>1936</td>
</tr>
<tr>
<td>Siegbahn M.</td>
<td>Spektroskopie der Röntgenstrahlen. Berlin</td>
<td></td>
<td></td>
<td></td>
<td>1931</td>
</tr>
<tr>
<td>Siegbahn M. &amp; Stenström W.</td>
<td>Physik Zeits.</td>
<td>17</td>
<td>48     &amp; 318</td>
<td>1916</td>
<td></td>
</tr>
<tr>
<td>Stenström W.</td>
<td>Ann. d Phys.</td>
<td>57</td>
<td>347</td>
<td></td>
<td>1918</td>
</tr>
<tr>
<td>Valedores M. &amp; Mendes.</td>
<td>Comptes Rendus</td>
<td>226</td>
<td>1185</td>
<td></td>
<td>1948</td>
</tr>
<tr>
<td>Van der Tuuk.</td>
<td>Zeits f. Phys.</td>
<td>44</td>
<td>157</td>
<td></td>
<td>1927</td>
</tr>
<tr>
<td></td>
<td>Zeits f. Phys.</td>
<td>31</td>
<td>445</td>
<td></td>
<td>1925</td>
</tr>
<tr>
<td>Wetterblad</td>
<td>Zeits f. Phys.</td>
<td>42</td>
<td>611</td>
<td></td>
<td>1927</td>
</tr>
<tr>
<td>Williams K.C.</td>
<td>Thesis University of Leicester.</td>
<td></td>
<td></td>
<td></td>
<td>1959</td>
</tr>
<tr>
<td>Wissbak F.</td>
<td>Ann. d. Phys.</td>
<td>28</td>
<td>71</td>
<td></td>
<td>1937</td>
</tr>
<tr>
<td>Wolfe H.C.</td>
<td>Phys. Rev.</td>
<td>43</td>
<td>221</td>
<td></td>
<td>1933</td>
</tr>
</tbody>
</table>