

THE $M_{iv,v}$ XRAY ABSORPTION SPECTRA
OF YTTERBIUM AND SOME HEAVIER ELEMENTS

by

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A thesis submitted to Leicester University for
the degree of Ph.D. in the Faculty of Science

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Abstract.

A new curved crystal Xray spectrometer, with a spot focus Xray source and proportional counter detector, has been constructed and its design is described. The results of a preliminary investigation into the variation of the intensity received at the detector, with movement of the source, are discussed.

A study of the M_V absorption line of ytterbium has been made and the M_{IV} and M_V absorption edges of ytterbium, lutecium and hafnium together with the M_{III} edge of ytterbium are reported for the first time. The discrepancy between the observed positions of the M_{IV} and M_V edges and those calculated from data on the L spectra of these elements is discussed.

A comparison has been made between the absorption of ytterbium in the pure metal and in compound, and the absence of the M_V absorption line for the metal clearly indicated. The M_{IV} and M_V edges of the metal have been found to occur at energies some 14 ev lower than those of ytterbium fluoride (or oxide) and the cause of this shift is indicated. To facilitate the preparation of pure metal foils an evaporation chamber attached to the spectrometer tank has been designed and constructed. By this means the foils could be prepared and transferred into the Xray beam without exposure to air.

The measurement of the M_{IV} and M_V edges of tantalum (oxide) is described and a suggestion made to account for the difference between their previously reported positions.

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CHAPTER ONE: INTRODUCTION.

Xray Absorption.

The Absorption Coefficients.

Xray Absorption Spectra.

Previous Measurements of M Absorption Spectra.

The Present Investigation.

Xray Absorption.

The Absorption Coefficient.

The absorption of Xrays follows the same logarithmic law as all electromagnetic radiation, thus if I_0 is the incident intensity, μ_1 the linear absorption coefficient and d the thickness of absorber traversed then the transmitted intensity is given by

$$I = I_0 e^{-\mu_1 d}$$

Here μ_1 is a function of the atomic number of the absorbing atoms and the energy of the incident photons. It is also a function of the density of the absorber and in order to remove this dependence on physical state it is usual to consider the mass absorption coefficient which is given by the following expression

$$I = I_0 e^{-\mu m}$$

where m is the mass per unit area of the absorber. From these two expressions it can be seen that the mass absorption coefficient is equal to the linear absorption coefficient divided by the density of the substance. These absorption coefficients are really the sum of two coefficients, thus

$$\mu = \tau + \sigma$$

where τ refers to absorption through photo effect and σ to scattering by electrons. However as Sandström³⁶ has pointed out, in comparison with τ , σ is very small in the region of soft Xrays and for heavy atoms and so, for the purposes of the present investigation it may be considered that the mass absorption coefficient is a measure of the photo effect alone.

A measure of the amount of energy absorbed by individual atoms is given by the atomic absorption coefficient which is related to the mass absorption coefficient in the following manner:

$$\mu_a = \mu \frac{A}{N}$$

where A is the atomic weight of the material and N is Avogadro's number.

Xray Absorption Spectra.

The interaction between a beam of photons and a particular atomic system is characteristic of that system. It is selective in the sense that photons of a certain energy may be absorbed much more readily than those with an energy which differs only by a small amount. The mechanism of this absorption of energy is a change in the electronic structure of the atom. An electron is removed from its state in the normal configuration to a state of higher energy; a state which is empty or does not exist in the normal atom. The energy of Xray photons is such that these transitions originate from states well within the electronic structure of the atom. The binding energy of electrons in these states is so large that it is the initial levels which predominate over the character of the absorption spectrum, whereas variations in the energy of the final state have only a secondary influence. Thus a plot of the absorption coefficient of a substance over a wide range of energy will show a series of discontinuities at energies just sufficient to remove an electron from the various inner levels. Such an absorption curve is shown schematically in

Diagram 1.1. The "edges" are labelled in the same manner as the initial level of the ejected electron and this indicates how early detection of these discontinuities in absorption, together with data on emission lines, formed the basis for assignment of electronic levels in atoms¹.

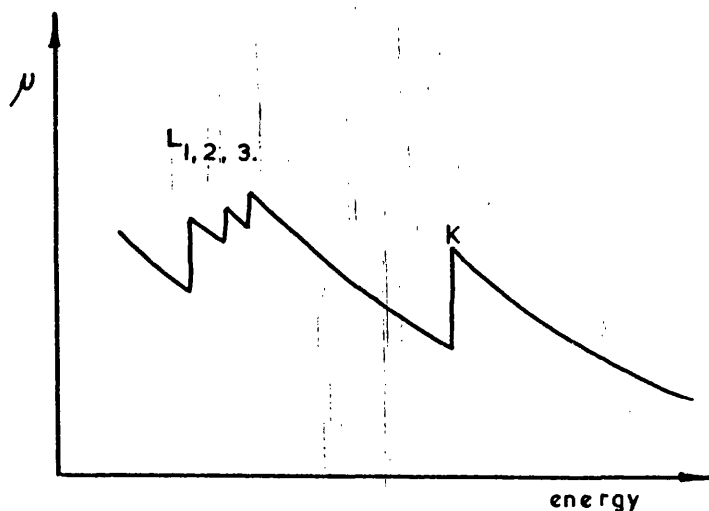


DIAGRAM 1.1 XRAY ABSORPTION EDGES.

There will be many possible end levels for a transition of an electron from an inner level and these possible transitions will follow the usual pattern of such atomic phenomena, a pattern which is conveniently described by the various quantum number selection rules. However, as has already been mentioned, differences in the energy of these various final levels exert only a secondary influence on the absorption spectrum and this influence takes the form of a structure on each of the absorption edges. From the selection rules it can be seen that if the initial state is characterised by the azimuthal quantum number L then the structure

on the absorption edge will depend principally upon the distribution of available states with an $(L+1)$ symmetry. Thus the K edge structure will depend on the available p type states, the L_{III} edge structure will depend upon the available d type states and so on. There will also be a dependence upon the $(L-1)$ states but from a consideration of X-ray emission lines it seems that these transitions are less probable and so dependence upon $(L+1)$ states will predominate^{2,3}. Thus in an assembly of non interacting identical atoms an absorption edge will commence with a converging series of maxima corresponding to transitions of an inner electron into the series of empty outer orbitals with the relevant azimuthal quantum number. A monatomic gas approximates to the condition of non interacting atoms and Parratt⁴ has shown that for the argon K edge just this type of structure is observed (Diagram 1.2.)

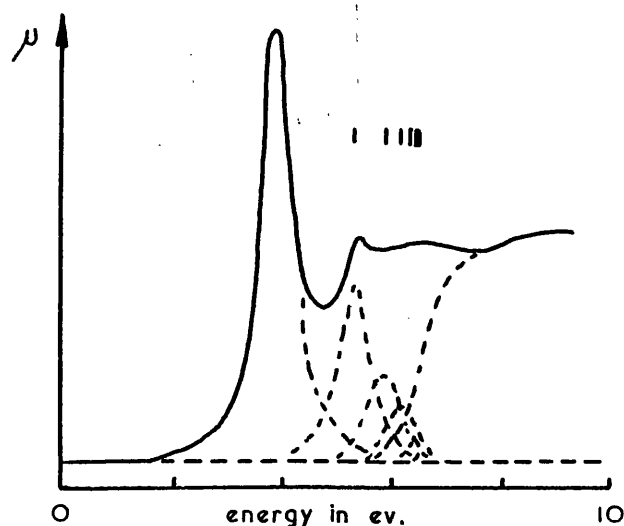


DIAGRAM 1.2. K ABSORPTION EDGE FOR ARGON
(AFTER PARRATT)

Since an inner electron has been removed the effective charge of the nucleus is increased by approximately one and so the final bound state of the electron will be similar to an optical level of an atom of the next element up in the Periodic Table, that is potassium in the particular case mentioned here. So far only the case of an atom free from the influence of other atoms has been considered, a case having limited applicability which does not include within its scope most of the observed absorption phenomena. Studies are usually made on substances in the solid state in which there is an array of mutually interacting atoms. The optical levels will still be created when an electron is removed from inside the atom but they will now be perturbed by the field of neighbouring atoms. The perturbation of the most tightly bound levels will only be slight and that only really effected by immediately surrounding atoms. In this case the structure of the edge may be treated on a "molecular" basis. For example Hanson and Beeman⁵ have shown that the K absorption structures of the manganese ion in solution and in many solid manganese salts do not differ in any essential fashion, indicating that the cause of this structure is extremely local. Levels further outside the atom will be much more disturbed by the lattice, becoming levels of the crystal lattice rather than the levels of a particular atom. Electrons which were bound in the outermost discrete levels of the free atom will now move "quasi freely" throughout the crystal in the periodic potential field of all the lattice ions. They are only

quasi free since they are still restricted to an energy range or band, the width of which depends upon the exchange probability of the electrons between individual atomic systems. Any electron ejected from an inner level of an atom in the lattice will have an energy in one of these bands, which are separated by forbidden energy regions. The two types of structure arising from the localised optical levels on the one hand and energy bands of the crystal on the other are termed Kossel⁶ and Kronig⁷ structure respectively after their first proponents. The energy bands in the crystal lattice will have a symmetry associated with them, derived from their equivalent atomic level, that is there will be s, p, d bands etcetera; however these individual bands may overlap or other bands of a hybrid type may be formed in which there is a mixture of symmetries such as a (d+f) band. Thus the structure at higher energies from the main absorption edge will be complex but will give information about the distribution of unoccupied energy bands within the lattice, just as emission spectra will provide information about the levels which are filled. Two points must be remembered however; in the first instance the shape of an absorption edge or an emission line does not give a direct picture of the density of states since it is modified by the transition probabilities between these states and the inner atomic states. Jones and Mott⁸ write for the intensity of absorption or emission

$$I(E) = N(E)T(E)$$

where $N(E)$ is the density of states and $T(E)$ the transition

probability. A subscript should be placed on $N(E)$ since it is really the density of a particular type of states (s, p or d etc.) which is involved. The second important point is that the density of states occurring in the absorption process is that for the particular case when there is a vacancy in an inner level and that occurring in the emission process is for the case when there is a vacancy in the valence or conduction band, if the emission line, which is nearest in energy to that of the absorption edge, is considered. It is interesting to note in this context that a study of absorption lines and associated emission lines should indicate quite clearly the difference between metals and insulators. In the first case there is no gap between occupied and unoccupied states and so the emission profile should come close to the absorption edge whereas in the second case there is a gap. This is illustrated schematically in Diagram 1.3. The inner atomic level is marked X and in the metal the Fermi surface refers to the boundary between occupied and unoccupied states of the one band. The ordinate in these diagrams which represents the energy of the jumping electron is not drawn to scale. As has been pointed out by Parratt³ such "one electron jump" diagrams are not a strictly accurate representation of X-ray absorption and emission processes since rearrangement of other electron states also occurs. The absorption or emission of X-rays results rather in a change in the electronic system as a whole, albeit the major part of this change involves just one electron.

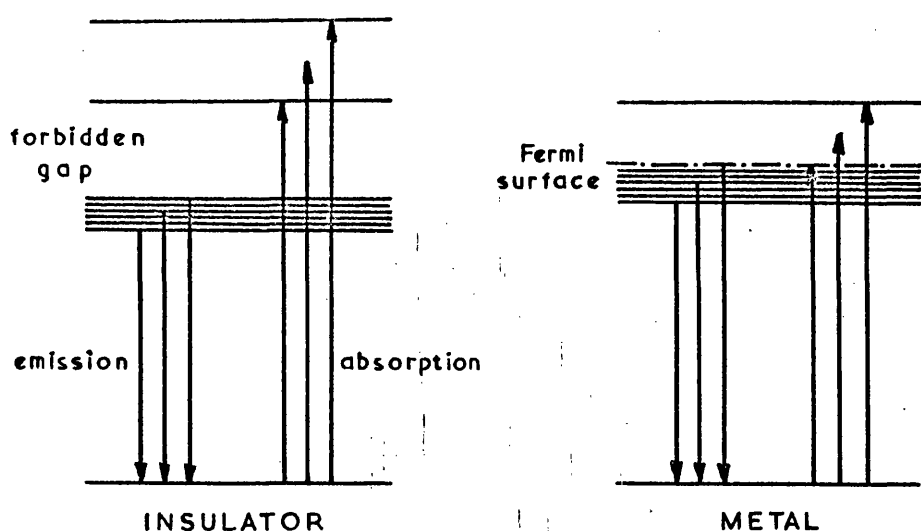


DIAGRAM 1.3. SCHEMATIC REPRESENTATION OF EMISSION AND ABSORPTION FOR INSULATORS AND METALS.

As an overall description of absorption edges Kiestra⁹ has summarised his experience as follows:

- "(a) In a region close to the edge the behaviour of the absorption coefficient is mainly a property of the atom in question.
- (b) In the following region the fine structure is determined by the immediate surroundings of the atom.
- (c) In the region of highest energy, the fine structure depends essentially on the whole crystal lattice".

The extent of these regions will depend very much upon the substance studied. Throughout, the physical process is the same; the distinction arises in the factors which must be considered and the consequent technique which must be employed in order to

obtain a viable mathematical description.

So far in the discussion no mention has been made of the possibility of X-ray absorption lines other than those associated with the absorption edges of rare gases. For such lines to exist there must be a high density of available states in a narrow region of energy. This situation will arise when the influence of the atom predominates over the influence of the crystal lattice, a situation which would be expected to occur for a transition series of elements, that is a series in which an inner electron level is partially empty. But for the three series which involve the filling of d levels there is still some exchange with neighbouring atoms as these levels are not really buried within the electronic structure of the atom. Thus although the density of states is considerable the resulting absorption line will be fairly broad and not clearly resolved from the edge. These lines will appear on edges due to transitions from p levels (eg. L_{ii} L_{iii} M_{ii} M_{iii}) and in fact have been observed by many experimenters. For the lanthanide series of elements, and also for the actinide series, the phenomena of absorption lines is much more clearly demonstrated since the vacant level involved here is well buried within the electronic structure of the atom and so the absorption lines should be sharp and well removed from the edges. The vacant inner levels are f type and so absorption lines are associated with the M_{IV} and M_V spectra. For the rare earth series such lines have been observed by many experimenters since 1931, when

Lindberg¹⁰ discovered them for ytterbium and erbium, but these will be dealt with more fully below.

Previous Measurements of M Absorption Spectra.

Most of the early measurements of M absorption edges were made with a single plane crystal spectrometer of a type originally designed by Seigbahn¹¹. Detection of the Xrays was made photographically and measurements of the wavelength position of the edges made by including reference lines on the plate which was then examined with a travelling microscope. Later microphotometer curves were made from the original photograph. In more recent times curved crystal spectrometers of the Johann¹² type have been employed but in all the work on the M absorption spectra of the rare earths and elements above in the Periodic Table the technique of photographic detection has been employed.

The absorption screens used in these investigations were prepared in different ways. At first soluble salts were employed and the screens prepared by dipping filter papers in concentrated solutions of them. Other foils were prepared by grinding the metal or compound into a fine powder and then mixing it with a lacquer or some other solution of organic substance which formed a skin once the solvent had evaporated. Examples of substances used in such a preparation are collodion in ether and celluloid in amyl acetate. Some metal foils have been prepared by rubbing the metal on a piece of paper, others by evaporation or cathodic sputtering in vacuum. Sometimes metal foils of the right thickness

were obtained by treating comparatively thick foils with aqua regia.

The first examination of M absorption edges was made in 1919 by Stenström¹³, who determined the wavelength positions of the M_V , M_{IV} and M_{III} limits for uranium and thorium, used in the form of soluble nitrates. Coster¹⁴ measured the M_{II} and M_I edges for these two elements and also the M_V , M_{IV} and M_{III} edges for bismuth in 1921. This author noticed that there was a discrepancy between his observations for the wavelengths of the M_V and M_{IV} edges of bismuth and the values obtained from calculations based on the L emission and absorption results. These calculations can be summarised by the equations

$$M_{IV} = L_{II} - L\beta_1$$

$$\text{or } M_{IV} = L_{III} - L\alpha_2$$

$$\text{and } M_V = L_{III} - L\alpha_1$$

However it was assumed that the discrepancy was experimental in origin. In 1923 Ross¹⁵ reported the five M edges for thorium again using the soluble nitrate. The next element to be studied was tungsten by Zumstein¹⁶ in 1925. Powdered tungsten trioxide mixed with collodion formed the screen and the anomalous wavelengths of the M_V and M_{IV} were noted. Two years later with the same equipment Rogers¹⁷ measured the M series absorption spectrum for osmium, iridium and platinum. All the edges, with the exception M_I for iridium and the M_{II} for platinum were detected using OsO_4 , $IrCl_3$ and $PtCl_4$ dissolved in a mixture of collodion and ether to

form the absorption screens. Two types of absorption were reported: "white line" absorption and limits separating two regions of unequal darkening on the photographic plate. Rogers also reported a similar discrepancy for the M_V and M_{IV} wavelengths as that noted by previous workers and suggested that it may be due to errors in the L data which would lead to large errors in the calculated M values, and also in some part to the fact that compounds and not pure metals were used. Continuing the work at Iowa, Johnson¹⁸ investigated the M absorption for metallic platinum and gold. All the edges with the exception of the gold M_{II} were detected and the anomaly for the M_V and M_{IV} was once more apparent. No "white lines" were observed for platinum as they had been by Rogers. In 1929 Lindberg¹⁰ commenced a survey of the M_V , M_{IV} and M_{III} absorption edges for the group of heavier elements from tungsten to uranium. Of these elements platinum, gold, thallium, lead, bismuth and tungsten were studied in the metallic state; uranium, thorium, lead and tungsten in the form of oxides; and mercury in the form of its chloride and sulphide. The discrepancies obtained for the edges were tabulated and an explanation of these differences, following that of Siegbahn¹⁹, was suggested. According to Siegbahn the normal selection rules should hold for the absorption process and so the end levels for the L edges will differ from those for the M_V and M_{IV} edges. A fuller discussion of this discrepancy is reserved for a later chapter. Lindberg detected slight differences for the

edges in pure metal and compound. These were of the order of one or two electron volts, the largest being about 4e.v. for uranium in the metal and oxide. In 1931 Whitmer²⁰ extended the elements studied to tantalum, reporting the M_V , M_{IV} and M_{III} edges, and Krafft²¹ examined bismuth, lead, thallium and gold and reported secondary structure associated with the main edge which was taken to be due to simple ionisation of the atom. The subsidiary edges were found to be mainly on the low energy side of the principal edge and it was suggested that they may be associated with transitions into the empty O level. All four elements were studied in the metallic state and also in the compounds $BiCl_3$, $Pb(NO_3)_2$, $Tl(NO_3)$ and $AuCl_3$. Phelps²² made a careful study of metallic bismuth in 1934 and verified large discrepancies for the M_V and M_{IV} edges whereas the other three edges were found to agree with calculated values. Photographic work on the M_V and M_{IV} edges of protactinium was carried out in 1936 by Dolejšek and Kunzl³⁰; these authors reported that there was no discrepancy between their measurements and values calculated from L spectra. In 1939 Polazek²³ carried out measurements on gold, thallium, lead, bismuth, thorium and uranium. The M_V edge was measured for all six elements and the M_{IV} for uranium and thorium. Pure metal foils were used except for uranium and thorium when oxides mixed in a zapon skin were prepared. A structure on the edges was reported and in all cases the energy of the edges was found to be anomalously high. Also in that year McGrath²⁴ first reported the

M_{ii} and M_i edges of lead and also measured the differences between the M_V and M_{iV} edges for gold in the pure metal and in a gold-copper alloy, reporting a shift to higher energies of 2.5 e.v. for the M_V and 6.8 e.v. for the M_{iV} . The former was substantiated with more observations than the latter, and taking the change in the lattice constant into consideration McGrath suggested that the shift for the M_V was probably about 4 e.v. Since 1939 few investigations into the M absorption edges of the heavier elements have been carried out. In 1952 measurements were made by Doughty and McGrath²⁵ on the M_V and M_{iV} edges of tantalum for which they obtained values markedly different from those of Whitmer. An investigation was carried out in 1957 by Mande²⁶ on the M_V , M_{iV} and M_{iii} edges of metallic gold. The M_V edge of plutonium was reported by Bobin and Despres³⁸ in 1961 and more accurate measurements were carried out on this metal in 1963 by Cauchois, Bonnelle and de Bersuder³¹ who reported all five M edges together with line absorptions accompanying the M_V and M_{iV} edges. The results of the work mentioned above are summarised in Table 1. (Page 97)

As has been previously mentioned, line absorption in the rare earth series of elements was first detected by Lindberg in 1939. In 1945 Rule²⁷ observed such a phenomenon for samarium and in this department Zandy²⁸ observed the lines associated with the M_V and M_{iV} spectra of praseodymium, neodymium, samarium and europium and since that time an extensive survey of this absorption phenomenon

has been carried out by this department²⁹.

The Present Investigation.

The purpose of this investigation was two-fold. In the first instance the role of the vacancies in the 4f shell in the line absorption of the rare earths was to be clearly established by studying the M_V absorption line for ytterbium in the pure metal and in a chemical compound. Since its outer electron structure in the metallic state³⁷ is $4f^{14}6s^2$ there should be no line, whereas in compound it is normally trivalent having one gap in the 4f shell giving rise to a single absorption line. The second part of the work was to be an attempt to close the gap, in the study of heavier elements, between those which exhibit the predominantly line type of absorption and those which exhibit the edge structure. This was to be done by a careful examination of ytterbium, lutecium and hafnium for any edge absorption and finally a study of tantalum to afford a comparison between this and previous work.

CHAPTER TWO: EXPERIMENTAL TECHNIQUE.

Xray Spectroscopy with a Curved Crystal Spectrometer.

Experimental Equipment.

Electrical Apparatus

The Vacuum System

The Spectrometer

The Xray Source

The Crystal

The Detector.

Preparation of the Absorption Screens.

Setting up and Calibration of the Spectrometer

Measurement of Transmission of the Absorption Screens.

Discussion of Errors.

Xray Spectroscopy with a Curved Crystal Spectrometer.

As has already been indicated the first Xray spectroscopy to be carried out in this laboratory was performed by Zandy²⁸. In that investigation a curved crystal spectrometer of the Johann¹² type was used and the Xradiation was detected by means of a photographic film. This type of spectrometer, in which the Xrays are reflected from the surface of a curved crystal, is more suitable for work with soft radiation than the transmission type of Cauchois³², and consequently has found much use in this laboratory. The principle of the spectrometer is illustrated schematically in Diagram 2.1. By analogy with the grating spectrometer used in the optical region the focussing circle is termed the Rowland circle. The crystal is bent so that it forms part of the surface of a cylinder of radius R . The Rowland circle is then a circle of diameter R which passes through the midpoint of the crystal and its centre of curvature. The focussing properties of this arrangement are indicated in the diagram and are such that a point source of Xrays situated at S_1 will give a focussed line at S'_1 of wavelength λ_1 , given by the Bragg relation:

$$n\lambda = 2d \sin \theta$$

in which n is the order, d the lattice spacing and θ the angle between the reflected beam and the tangent to the reflecting lattice plane. Similarly a source at S_2 will give a focussed line at S'_2 of a different wavelength λ_2 . The focussed line is

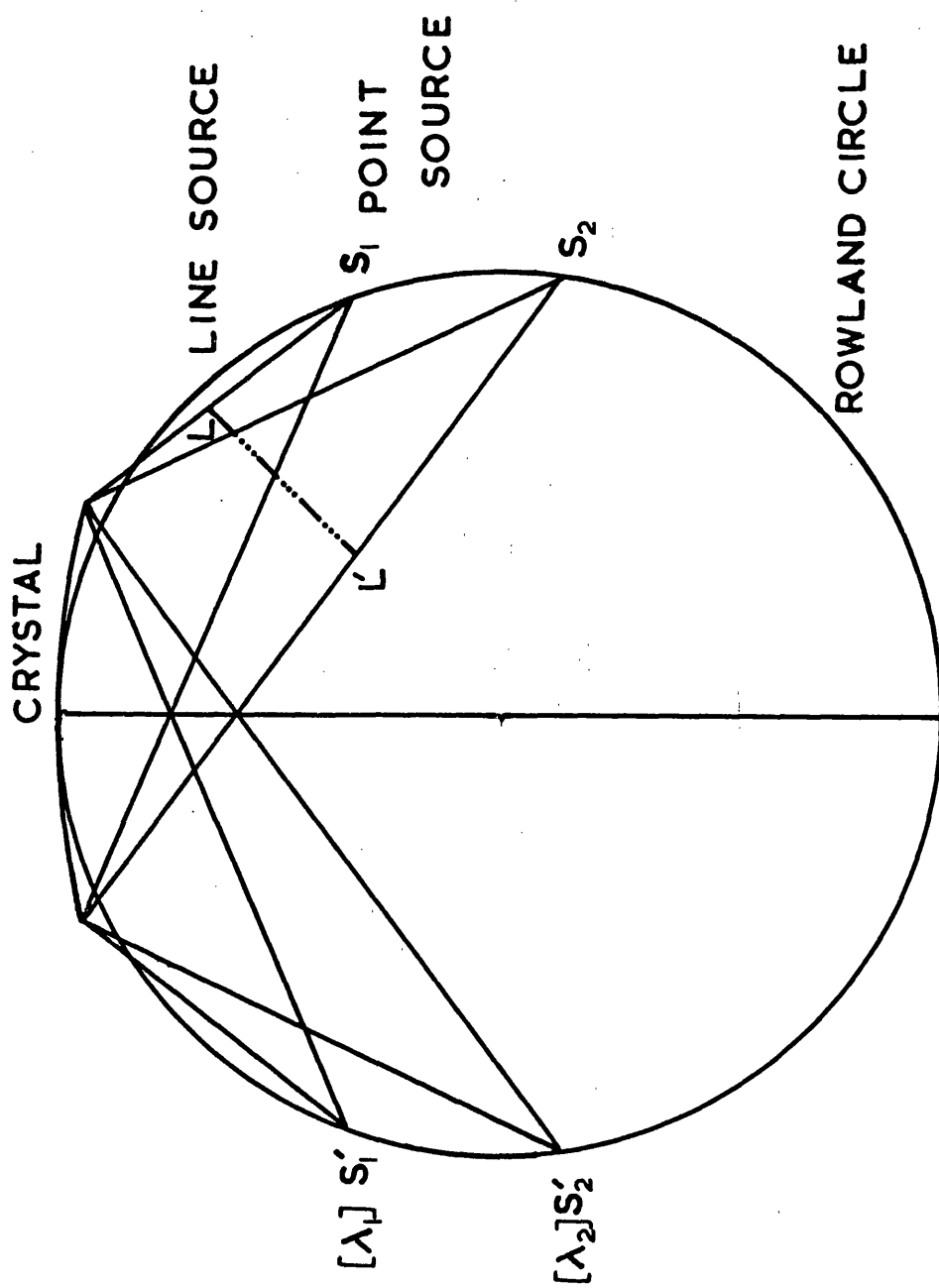


DIAGRAM 2.1. BENT CRYSTAL SPECTROMETER.

perpendicular to the plane of the diagram and arises because the crystal is only curved in one direction. Theoretically it is only possible to achieve perfect focussing with an extended crystal in which the reflecting lattice planes are curved to a radius twice that of the Rowland circle and the front surface of which has been ground out to a radius equal to that of the Rowland circle. However the simple curved crystal was used in these investigations.

In photographic work a region of wavelengths is examined with one exposure and so a continuous source from S_1 to S_2 , for example, is required. This may be achieved by placing a line source inside the Rowland circle as indicated in the diagram. In this case no parts of the spectrometer need to be moved during exposure. The absorption screen is placed between the source and the crystal and a picture of the absorption of the material over a fairly wide wavelength region is obtained. If a Geiger or proportional counter is employed as detector, however, the absorption coefficient within a very small wavelength region, defined by the slit in front of the counter window, is measured. To obtain an absorption profile over a wider range the detector must be moved in measured steps. If a line source stationary with respect to the crystal is used then the wavelength region which can be investigated is limited by the length L L' . If a moveable line or point source is used then the region is limited by the lattice spacing of the analysing crystal. In this case the maximum wavelength observable is equal to twice the spacing of the

reflecting lattice planes, although the physical dimensions of the various components of the system usually limit the range to a value less than this. Since with a proportional counter an accurate measurement of the incident and transmitted intensity can be made, this technique is to be preferred to that employing photographic detection. It is difficult to correct the photographic observation for variations of intensity along the line source and absolute intensity measurements by film calibration would show an error of about 4%. From this it can be seen that values of relative absorption coefficients obtained in such a manner would be in error by about 10% and be susceptible to fluctuations in target emission. The errors involved in converting relative values of the absorption coefficient, by weighing the absorption screen, would be the same for both techniques. Examination of the photographic film by microphotometer will broaden any structure in the same way as does the slit in front of a counter window. If the film is placed round the Rowland circle broadening will arise from the oblique incidence of the Xrays. Other film positions are tangential to the Rowland circle or perpendicular to the Xray beam and in both these cases broadening will occur due to slight defocussing. Borisov and Nemoshkalenko⁴⁰ have pointed out that the three main geometric conditions giving rise to line broadening are inaccuracy of focussing of the rays at the point of observation; vertical divergence of the beam; and oblique incidence of the beam on the

photographic film. For the case of counter detection this latter is replaced by the effect of the detector slit. If the spectrometer is set at a Bragg angle θ then the wavelength broadenings due to these three effects are given by the following three equations:

$$\begin{aligned} \text{(i)} \quad \Delta \lambda_1 &= \frac{x^2 d}{16nR^2} \cot \theta \cos \theta \\ \text{(ii)} \quad \Delta \lambda_2 &= \frac{h^2 d}{16nR^2} \cot \theta \cos \theta \\ \text{(iii)} \quad \Delta \lambda_3 &= \frac{qd}{nR} \cot \theta \end{aligned}$$

where R is the radius of the Rowland circle, x and h the width and height of the crystal, q the width of the detector slit, d the lattice spacing, and n the order. The first two expressions are basically those given in the paper referred to above and the third is derived from straightforward geometric considerations. These effects together with others including diffraction and diffuse thermal scattering by the crystal go to make up the overall spectral response or "spectral window" of the spectrometer. The absorption profile obtained is then the fold of the true profile with the "spectral window" or apparatus function. The influence of the "spectral window" on the choice of thickness of the absorption screen is discussed later in the chapter. For the present it is sufficient to note that interpretation of the observed absorption structure in terms of the widths and distribution of electron states must be made with caution.

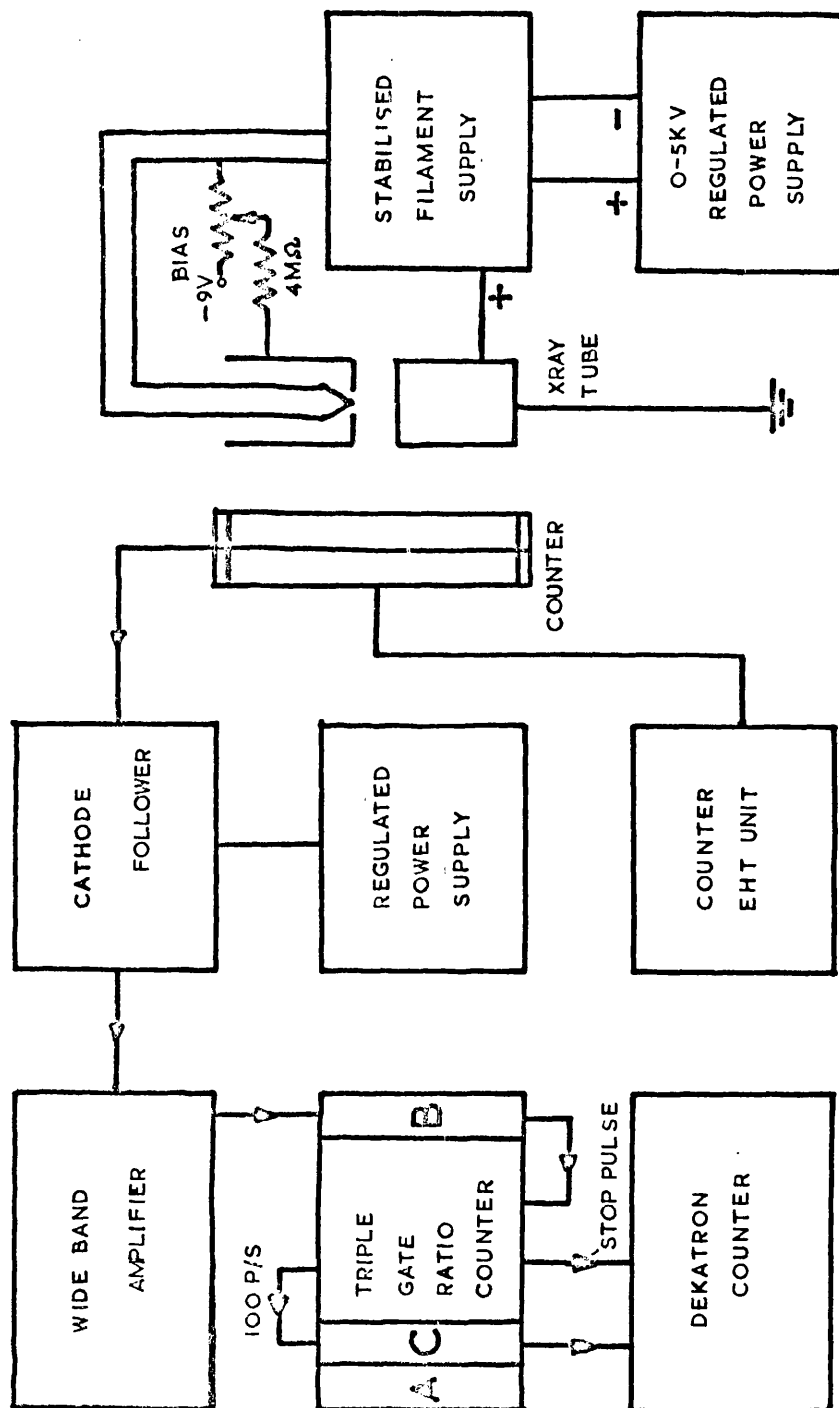
For the present investigation a spectrometer was designed

using a point source situated on the Rowland circle. The position of the source was fixed with respect to the base of the spectrometer and the positions of the crystal and detector were controlled by a system of gears such that the angular movement of the detector was always twice that of the crystal. The reasons for this choice of design are discussed in the detailed description of the instrument given below. The absorption of soft Xradiation by air is such that spectroscopy in this region must be carried out under vacuum and for this purpose the spectrometer was enclosed in a large cylindrical steel tank which was evacuated by an oil diffusion pump and a rotary backing pump.

Experimental Equipment.

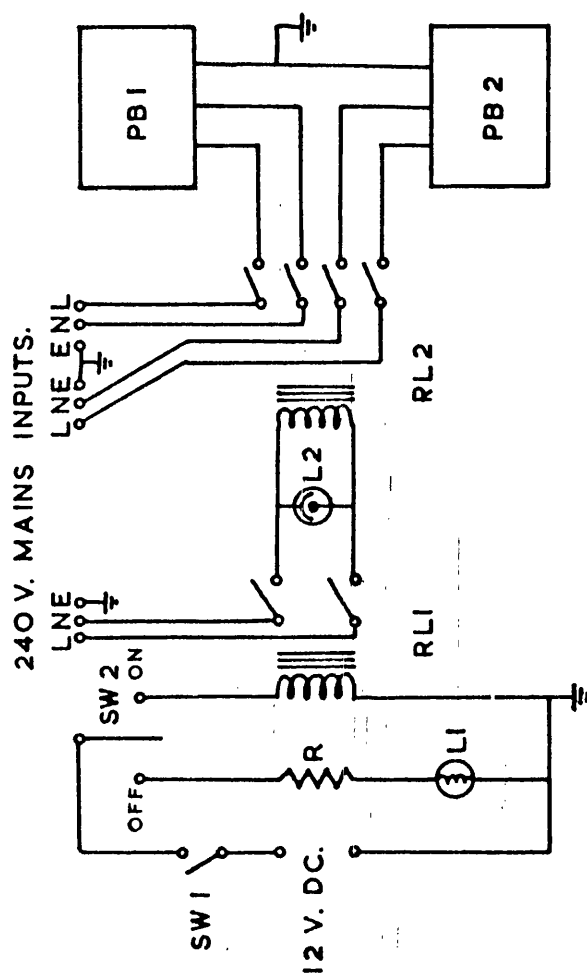
Electrical Apparatus:

The general arrangement of the electronic equipment associated with the spectrometer is illustrated in block form in Diagram 2.2. The spectrometer was operated in the second order and pulses from the proportional counter were fed via a cathode follower into a wide band amplifier (I.D.L. Type 652) containing a discriminator circuit by means of which pulses, resulting from the lower energy first order Xrays, were eliminated. The amplified pulses passed into a Triple Gate Ratio Counter (Labgear. Type D4107) which incorporated a source of 100 pulses per second which was connected to a Dekatron Counter (Labgear. Type D4104/B) and used for timing purposes. The case of the proportional counter was held at a



24.

DIAGRAM 2.2. BLOCK DIAGRAM OF ELECTRONICS.



KEY.

- SW.1: SAFETY SWITCH.
 SW.2: MICRO SWITCH OPERATED BY WATER CIRCULATION.
 L2: "WATER OFF" 6V. INDICATOR LAMP. R1: 6V. POTENTIAL DROPPER.
 RL2: "MAINS ON" NEON INDICATOR.
 RL2: GRAVITY LOADED RELAY. RL2: MAINS OPERATED RELAY.
 PB.1: PLUG BOARD FOR EHT AND FILAMENT SUPPLY UNITS.
 PB.2: PLUG BOARD FOR DIFFUSION PUMPS.

DIAGRAM 2.3. RELAY CIRCUITS.

negative voltage of 1.4 kv obtained from the E.H.T. unit (I.D.L. Type 532/A). The Xray source was driven by a 0 to 5 kv stabilised E.H.T. unit (A.P.T. Model 5705/1) operated in conjunction with a stabilised filament supply unit (A.P.T. Model 5706/1), the filament of the Xray tube being held negative and the anode earthed. The mains supply to E.H.T. and filament units and to the oil diffusion pumps was controlled by a relay system which tripped off if the cooling water circulation failed. The arrangement of this protection circuit is shown in Diagram 2.3. The pressure in the vacuum system was measured by means of a Penning gauge (Genevac Type P.N.G.1).

The Vacuum System.

The spectrometer was mounted in a cylindrical steel tank. This tank was made up of a base plate $1\frac{1}{8}$ inches thick and 25 inches in diameter; a cylindrical wall $\frac{3}{4}$ of an inch thick, 8 inches high and $23\frac{3}{4}$ inches internal diameter; and a lid $\frac{3}{4}$ of an inch thick and 26 inches in diameter. Vacuum tight seals between the three components were effected by two large rubber rings set in retaining grooves. All connections to the tank were sealed in a similar fashion with rubber "O" rings. The system was evacuated by an oil diffusion pump and a rotary backing pump to a pressure better than 10^{-4} mm of mercury. A water cooled baffle valve was mounted between the diffusion pump and base plate so that the system could be let down to air without waiting for the diffusion pump to cool.

The Spectrometer.

The spectrometer consisted essentially of three parallel sided brass arms pivoted on a central steel column. These arms carried the detector, crystal and Xray source on a Rowland circle of 40.6 cms diameter. The first two arms were attached to gear wheels and were supported on three flat brass pads so that the bearing on the central column was not subject to strain. The arm carrying the Xray source was bolted to the base plate of the spectrometer and consisted of a circular plate with the arm protruding from one side. The circular portion formed the run for two of the crystal arm support pads, the third resting on the spectrometer base plate. The gears on the counter and crystal arms were driven by a system of smaller gear wheels coupled to a spindle which passed through the base of the vacuum tank. The base plate of the spectrometer was located on the bottom of the vacuum tank by three brass stubs. Both the counter and the Xray source were fixed on rotating mountings and were pointed towards the crystal by steel tapes which were driven by pulleys. The scale was marked off in half degrees and was bolted to the counter arm. The fiduciary line was fixed to the anode arm and well illuminated thus enabling the scale to be clearly visible through the perspex window in the lid of the tank. With this arrangement of the scale and fiduciary line a change of one degree in scale reading was equivalent to a change in the Bragg angle of 15 minutes. A plan view of the spectrometer is shown in Diagram 2.4., and the

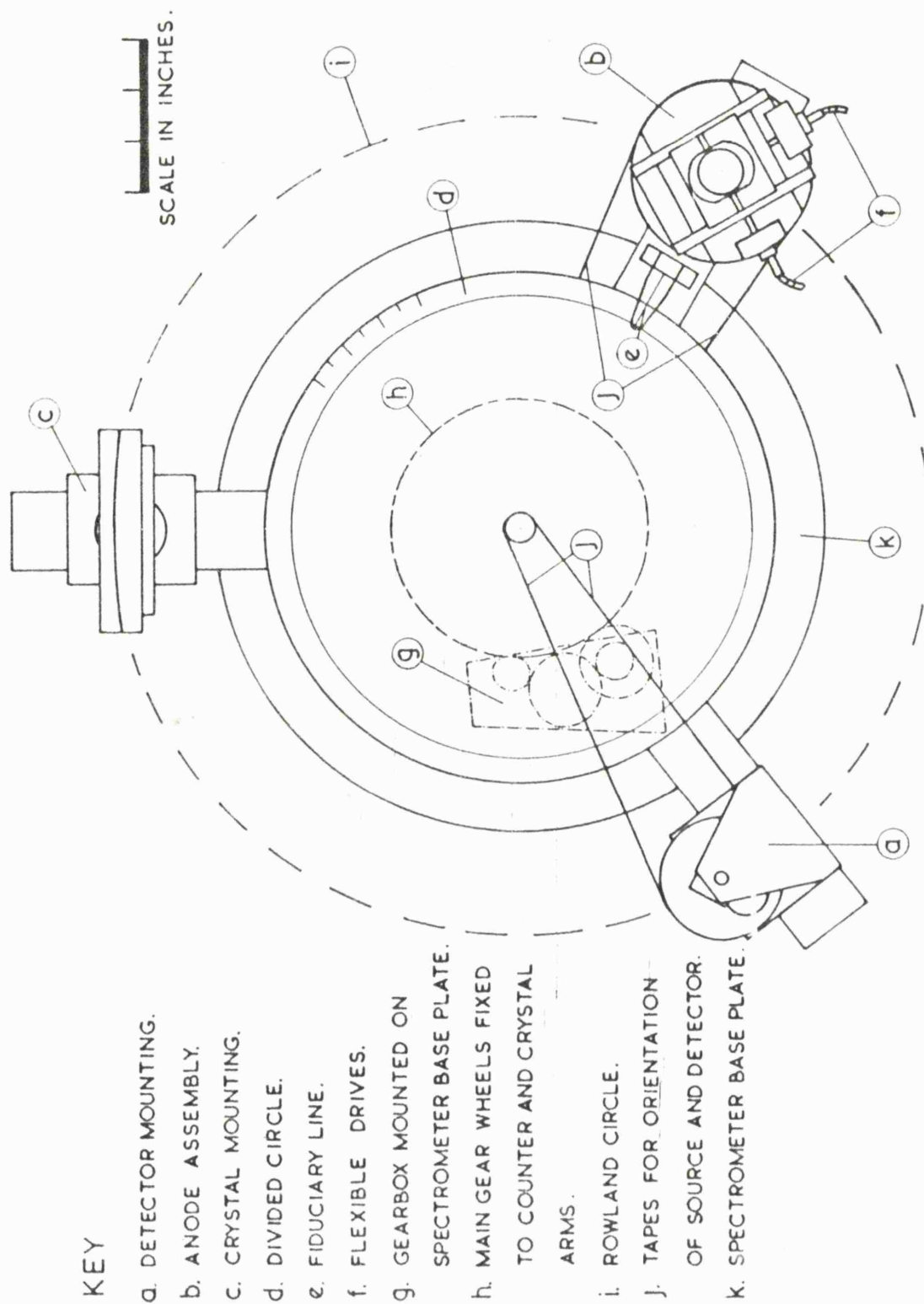


DIAGRAM 2.4. THE XRAY SPECTROMETER. PLAN.

KEY

- | | | | |
|----|---------------------------------------|----|---|
| a. | PULLEY FOR COUNTER ORIENTATION. | j. | BASE OF VACUUM TANK. |
| b. | DIVIDED CIRCLE. | k. | ANODE ARM INCORPORATING RUN FOR COUNTER ARM SUPPORT PADS. |
| c. | COUNTER ARM. | l. | CENTRAL COLUMN. |
| d. | MAIN GEAR WHEEL FOR COUNTER MOVEMENT. | m. | SILVER STEEL COUPLING. |
| e. | RUN FOR COUNTER ARM SUPPORT PADS. | n. | ECCENTRIC COLLAR FOR MAIN DRIVE. |
| f. | MAIN GEAR WHEEL FOR CRYSTAL MOVEMENT. | o. | MAIN DRIVE. |
| g. | PULLEY FOR SOURCE ORIENTATION. | p. | LOCATING STUB. |
| h. | CRYSTAL ARM. | q. | GEARBOX. |
| i. | SPECTROMETER BASE PLATE. | | |

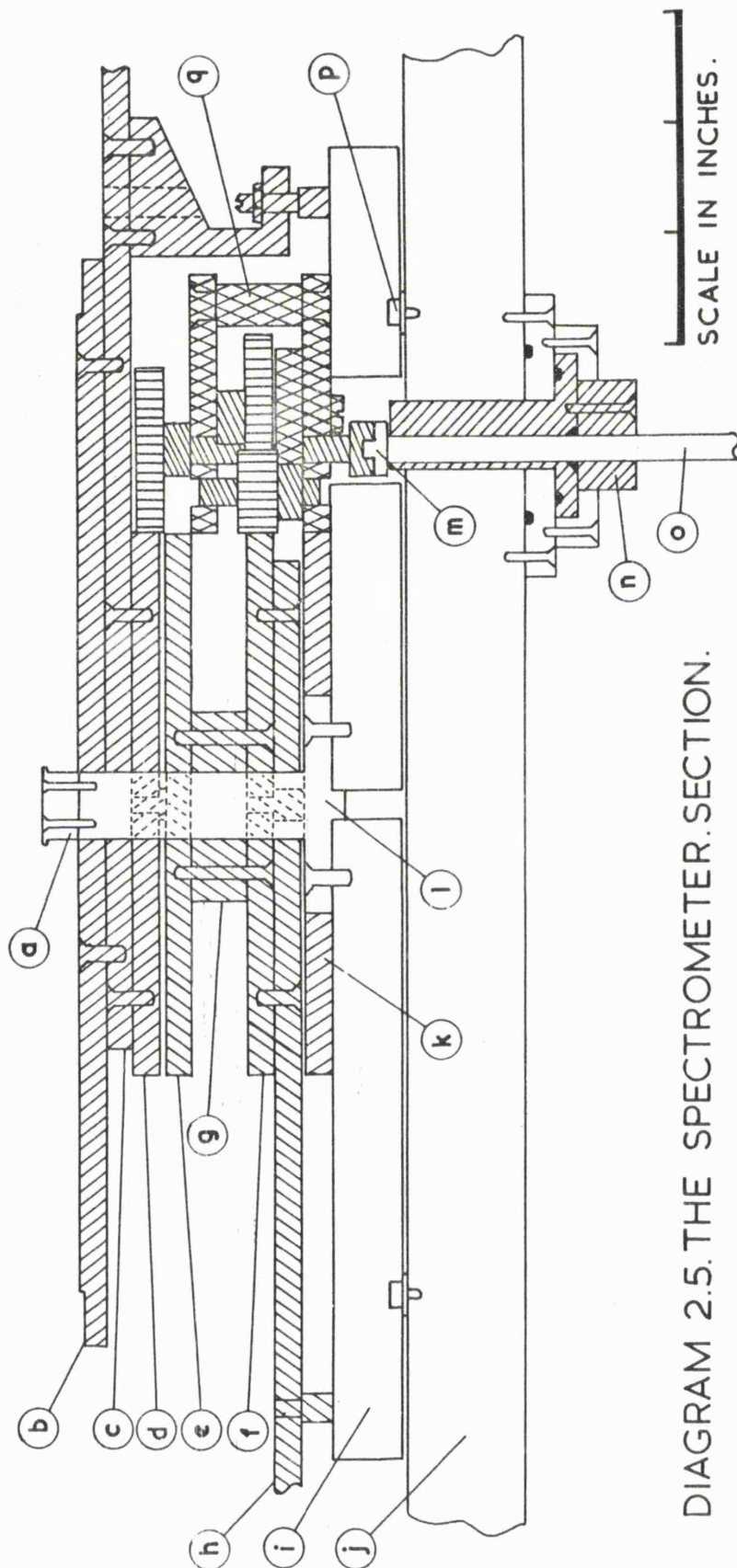


DIAGRAM 2.5. THE SPECTROMETER SECTION.

arrangement of the system on the central column is illustrated by the partial section in Diagram 2.5. A system of gears outside the vacuum tank was arranged so that four revolutions of the drive handle changed the scale reading by one degree. This system could be moved out of mesh so that the spectrometer could be quickly adjusted to another wavelength region by direct drive.

The Xray Source.

The source of Xrays was a sloping anode point focus tube, giving an increased intensity at the detector over that of a line source for a given tube current and voltage. A brief study was made of the variation of intensity received at the detector when the spot source of Xrays was moved towards the crystal. The intensity was found to fall off, following fairly closely a curve calculated from simple geometric considerations, in which the source was reduced to one dimension. For a Bragg angle of 45 degrees and the condition of the counter slit width being equal to the spot width the theoretical intensity was found to be governed by the following equation

$$I_x = I_R \frac{R^2}{\left(\frac{R}{\sqrt{2}} - x\right) (R\sqrt{2} - x)} (1 - 0.17x)$$

where I_R is the intensity with the spot on the Rowland circle, R the diameter of the Rowland circle and x the distance moved in from the circle. The term 0.17 is determined by the diameter of the circle, the width of the crystal and the width of the counter

slit and spot which was put equal to 0.8 mm in this case. This expression is only applicable over a range fairly close to the circle, a range extending for about 3 cms in this particular instance, after which the intensity decreases less rapidly. A graph of the decrease in intensity is given in Figure 2.1. and it can be seen from this that the range of movement is somewhat limited, indicating that the agreement between theory and experiment cannot be taken to have been rigorously demonstrated.

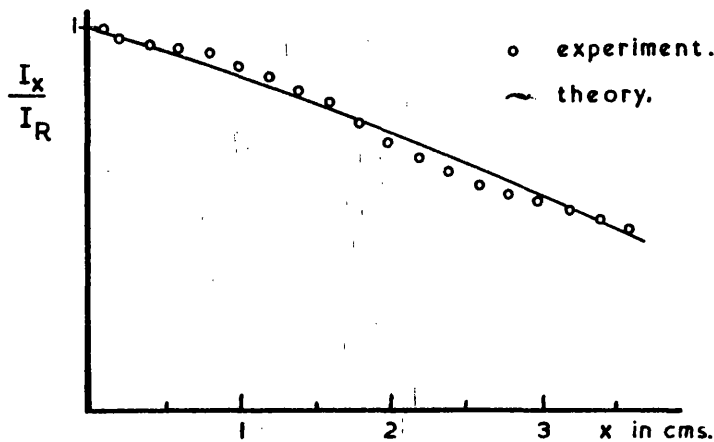


FIGURE 2.1. INTENSITY VARIATION WITH SPOT MOVEMENT.

However it is clear that, for a source of given total power, higher intensity is obtained if it is in the form of a point focus situated on the Rowland circle. More detailed calculations have been carried out by Wienmann³³ from which it can be seen that for an extended source of given power per unit length greater intensity is obtained if it is moved near to the crystal. These two cases are illustrated by the graphs shown in Figure 2.2. From these curves it can be seen that for a line X-ray source the intensity received at the detector is increased by a factor of

approximately two if the source is placed immediately in front of the crystal instead of on the Rowland circle.

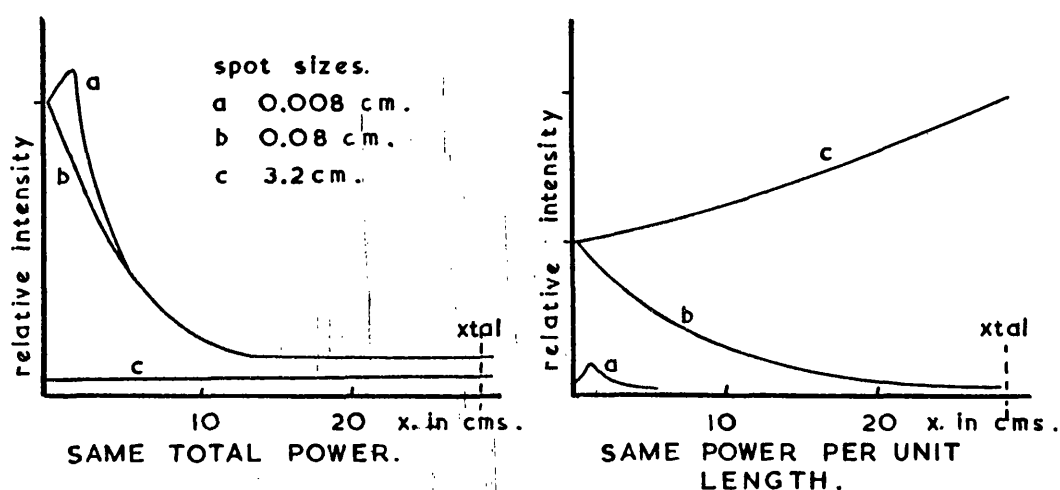


FIGURE 2.2. INTENSITY VARIATION WITH SPOT SIZE AND POSITION.

However, as has been pointed out by Goldsztaub³⁴ and Oosterkamp³⁵, the loading capacity (energy absorbed per unit area) of a particular target material is increased as the area bombarded by electrons is diminished. They have shown that if the radius of the spot is reduced to dimensions much smaller than the thickness of the anode then the loading capacity is inversely proportional to the radius. Thus a spot of 15 microns diameter can be loaded 30 to 40 times as high as a spot of about $\frac{1}{2}$ mm³⁹. It follows from this argument that for a detector which is set at a particular wavelength, greater intensity is registered with a fine focus X-ray source placed on the Rowland circle than with a fine source set near to the analysing crystal. Ideal conditions will obtain if the width of the source spot is equal to that of

the detector window.

The Xray source used was a modification of that described by Ehrenberg and Spear³⁹, and is shown in Diagram 2.6. The hairpin shaped tungsten wire filament was situated in a $\frac{1}{16}$ of an inch hole in the bottom of a copper tube to which a negative bias was applied. This acted as a grid in suppressing emission from the sides of the filament. The flat bottom surface of this grid was placed 7 thousandths of an inch from the anode which consisted of a slab of platinum silver soldered into a water cooled brass cylinder. The complete Xray source was mounted on a rotating aluminium cylinder driven by a steel tape which passed round a pulley mounted on the central column of the spectrometer and attached to the crystal arm. The ratio of the diameter of the pulley to that of the aluminium cylinder was so arranged that once the Xray source was pointed at the crystal it remained so pointed for any setting of the spectrometer. Incorporated in the source mounting were two perpendicular slides moved by screw threads attached to flexible drives. This arrangement enabled the source to be moved in the direction of the Xray beam or transverse to it. Thus once the axis of rotation of the anode assembly had been set in its position on the Rowland circle then under running conditions the source could be moved transversely until maximum intensity was registered by the detector. The method of setting up, which will be discussed later in the chapter, proved quite satisfactory in that over the range of

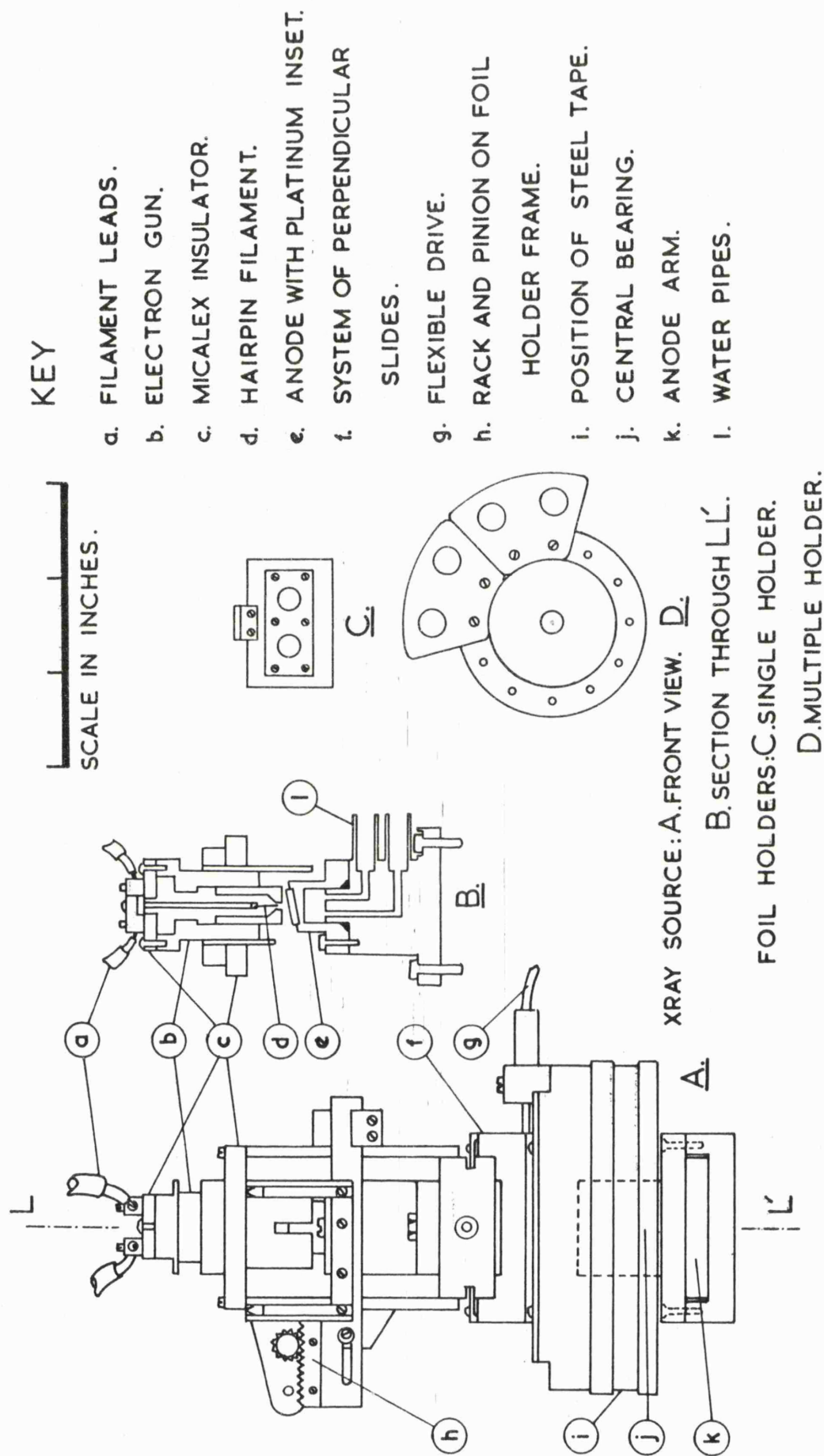


DIAGRAM 2.6. THE XRAY SOURCE AND FOIL HOLDERS.

operation of the spectrometer the spot, once adjusted, wandered only by a negligible amount from this position. The movement towards the crystal was incorporated to facilitate the preliminary investigation mentioned above. No attempt was made to produce a really fine focus Xray source but the present design was easy to construct and use and consistently produced a spot of about 0.8 mm diameter. A plot of the intensity variation across the spot situated on the Rowland circle and moved 3.6 cms towards the crystal is shown in Figure 2.3. The foil holders were also mounted on the anode assembly and the movement of foils in and out of the Xray beam was effected by a third flexible drive.

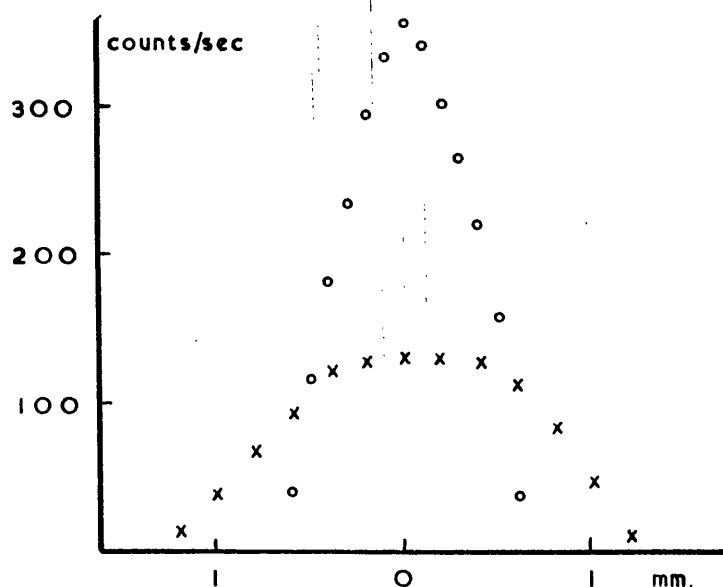


FIGURE 2.3. INTENSITY OF XRAY SOURCE.

Parratt et al⁴⁴ have shown that the best positions for the absorption foil are directly in front of the Xray source or in front of the detector and that with respect to the value of transmission obtained there is no appreciable difference between

these two positions. Because of the number of leads and flexible drives required for the anode system it was decided that this component should be fixed relative to the spectrometer base and so it was also chosen for the mounting of the foils. Those foils prepared in the main evaporation plant were mounted on the windmill foil holder shown in Diagram 2.6. This foil holder could carry six pairs of foils, which were held in the Xray beam by means of a spring loaded ball bearing and twelve locating sockets. When the evaporation plant connected to the spectrometer tank was used only a single coated foil was prepared and this, together with a piece of uncoated plastic, was mounted in the single holder which is also shown in Diagram 2.6. This holder clipped into a frame mounted on the anode assembly and moved to the two required positions by means of a rack and pinion.

The Crystal.

A crystal block and mica crystal already used in this department was fitted to this spectrometer. The crystal was clamped between two steel blocks which had been lapped together to a curvature of radius 40.6 cms. The two blocks were held together by four screws which allowed some adjustment of the bending of the crystal. The mounting of the crystal block onto the spectrometer is illustrated in Diagram 2.7. The mounting was constructed so that the block was perpendicular to the crystal arm, however the adjustment screws indicated in the diagram ensured a certain degree of rotational freedom about three perpendicular axes, one vertical

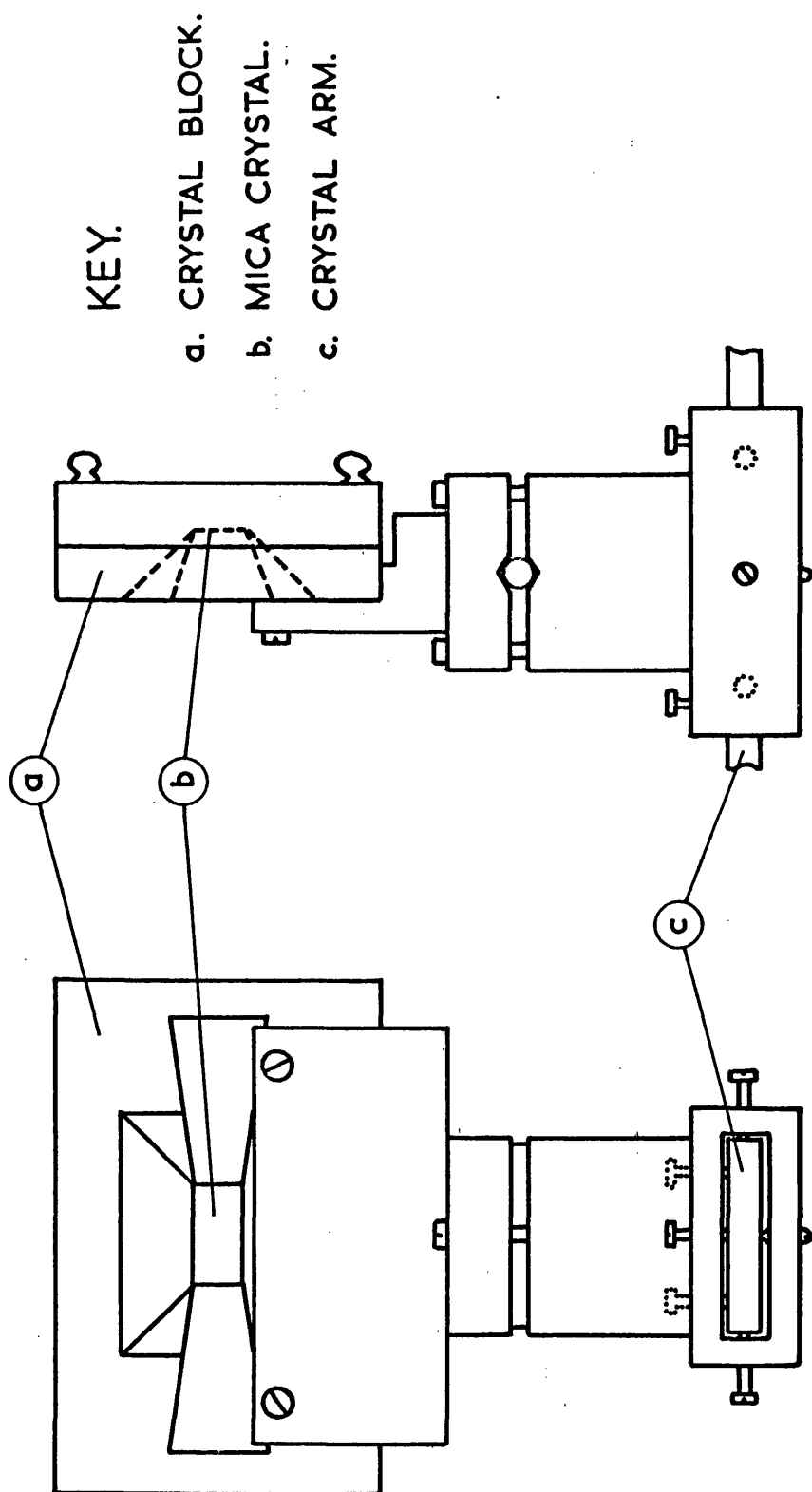


DIAGRAM 2.7. CRYSTAL MOUNTING.

and two horizontal, so that any small constructional error could be corrected for. The wavelength range to be investigated was between 5 and 9 kxu and for this range mica, with its lattice spacing of 9927.58 xu is an extremely suitable crystal. It is readily cleaved into thin sheets which may be bent without distortion, and it is stable under vacuum. Mica has, however, the disadvantage of having a lattice spacing which varies slightly from specimen to specimen, but the particular specimen used in this spectrometer has been found most reliable by many workers in this laboratory. The crystal arm was attached to a five inch diameter gear wheel the drive for which was taken from a gear box bolted to the spectrometer base plate. The operation of this gear box can be seen from Diagrams 2.4 and 2.5.

The Detector.

A sealed proportional counter was employed as detector. It was manufactured by 20th Century Electronics and was filled with a neon-methane mixture. The window material was beryllium one thousandth of an inch thick, and the window size was 9 by 1 mms. The counter and its mounting are shown in Diagram 2.8. Some preliminary work was done with an aluminium windowed counter but it soon became apparent that the situation of the aluminium K absorption edge (7935.1 xu) within the wavelength range to be investigated was a considerable inconvenience. To make measurements on the high energy side of this edge extremely low count rates had to be contended with. The beryllium windowed counter was operated

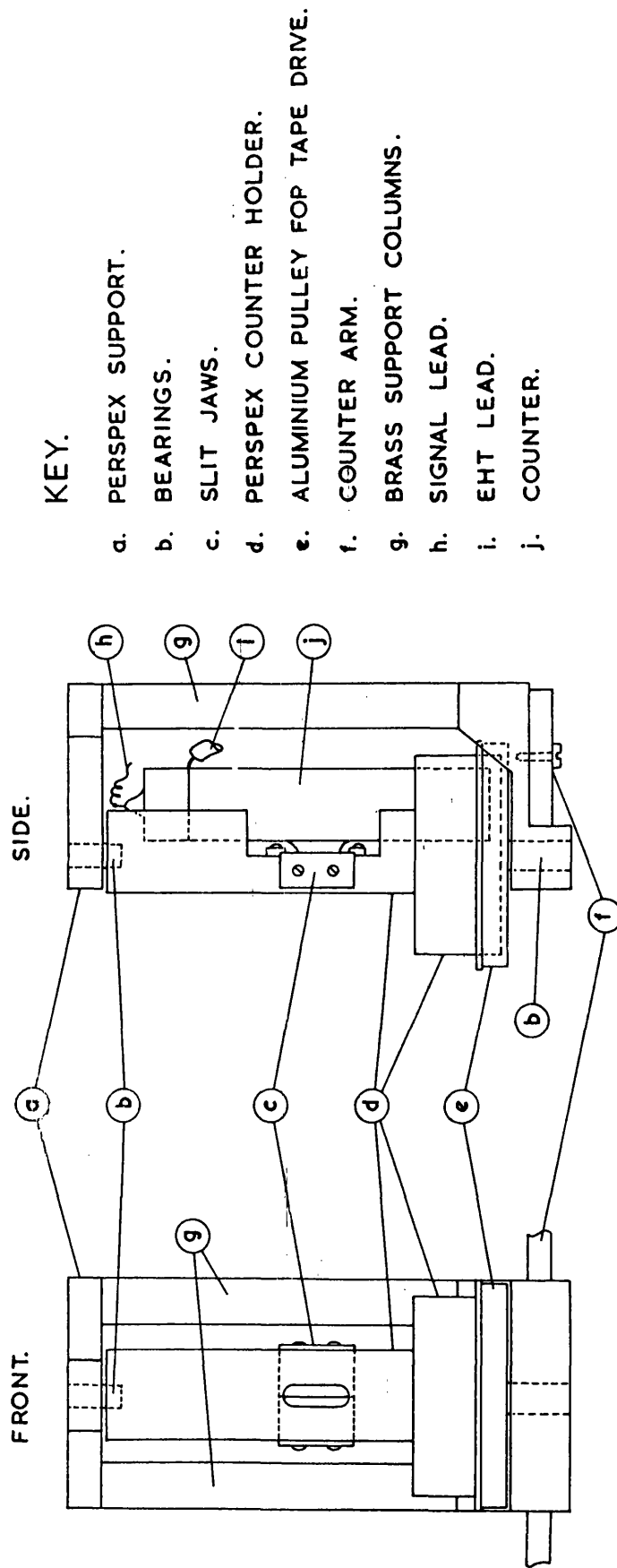


DIAGRAM 2.8. COUNTER MOUNTING.

at 1.4 kv and the pulses were fed via a cathode follower to the amplifier and display units. The slit in front of the counter window was situated on the axis of rotation of the mounting and was set to a width of 15 microns, which is equivalent to about 0.4 μ in the middle of the wavelength range investigated. The detector mounting was orientated by means of a steel tape passing round a pulley fixed to the central column of the spectrometer. The counter arm was attached to a five inch diameter gear wheel driven in a similar manner to the crystal arm. A ten inch diameter divided circle was bolted on top of the counter arm and this was read with reference to a fiducial line fitted to the anode arm.

Preparation of the Absorption Screens.

Absorption screens of all the substances, except hafnium oxide, were prepared by evaporation onto a melinex substrate 0.25 thousandths of an inch thick. The hafnium oxide screen was prepared by mixing this substance, in a finely powdered form, with a solution of collodion in ether. The mixture was spread onto a glass plate and allowed to partially dry off. A selected piece was then stretched and mounted in the foil holder. Such a screen could only be used to provide information concerning the wavelength position of absorption structure and not for absolute measurements of absorption coefficient. The evaporated screens were used for such absolute measurements, an uncoated piece of plastic being cut from the sheet adjacent to the coated portion and used in conjunction with this coated piece to obtain a measure of the transmission of

the evaporated layer. The evaporation was carried out in an evacuated chamber described previously by both Russell and Williams²⁹. A photograph of the base plate of this chamber is given at the end of the chapter. The substance to be evaporated was loaded into a tantalum boat above which a sheet of melinex was placed. The melinex was masked by a brass plate in which four holes, a $\frac{1}{4}$ of an inch in diameter, were cut. The plastic was held about 6 cms from the tantalum boat and so arranged that the centre of the line of holes was directly over the centre of the boat. A preliminary weighing of four screens prepared in this fashion showed that those due to the two innermost holes were almost equal in weight as were those due to the two outermost holes, but the former were slightly heavier than the latter. Thus, when selecting two foils for an absorption run, either of these sets could be used. A selected foil was mounted, together with a plain piece of melinex, on one of the sections of the windmill foil holder. This method of preparation was found to be satisfactory for all substances except lutecium oxide and ytterbium metal. In the first case the high temperature required to produce appreciable evaporation also caused some evaporation of the tantalum boat. This was clearly shown by the absorption curve obtained. In the second case the ytterbium metal foils were found to contain an appreciable amount of oxide. This may have been due to the gradual heating of the metal arms which supported the tantalum boat. Such a heating would give rise to continual

outgassing which would be difficult to eliminate. Further oxidation may have occurred in the transport of the prepared foil through air from the evaporation chamber to the spectrometer tank. However, the degree of oxidation was considerable and, as it was later observed that the metal readily formed a thin protective layer of oxide which prevented further oxidation, it is doubtful whether this latter was the sole cause. The manner in which the amount of oxidation was assessed will be discussed in the section dealing with the ytterbium results in the next chapter.

To overcome the difficulty encountered in the preparation of pure ytterbium metal by the method outlined above a new evaporation plant, connected to the spectrometer tank, was designed and constructed. This system enabled the whole process of evaporation and subsequent transfer into the spectrometer tank to be carried out under vacuum. The evaporation chamber, which could be isolated from the spectrometer tank by means of a sliding vane valve, was evacuated by an oil diffusion pump backed by a mechanical pump. A liquid air cooling trap for the diffusion pump was constructed with a conical system of fins mounted on the bottom of the coolant container and directly over the pump orifice. By this device the backstreaming of oil vapour was considerably restricted. Mechanical baffles of this type have been described by Morse⁴⁵, who found them extremely effective, and in the case discussed here no evidence of oil was found in the system throughout its usage. The diffusion pump and trap were bolted to

a lug at the edge of the lid of the spectrometer tank and a brass bellows joint provided some flexibility in the connection between this unit and the evaporation chamber. The ultimate pressure achieved by this pumping system was less than 5.10^{-6} mms of mercury. The evaporation chamber is shown in Diagram 2.9. The thick aluminium plate between the sliding vane valve and the lid of the spectrometer tank also contained a perspex window through which the scale was read and the foil position checked. The ytterbium metal was placed in a small tube made from tantalum sheet. This tube was mounted on thin pieces of mica inside a horizontal glass tube which acted as a shield for the larger vacuum tube of the chamber. The tantalum oven was heated by a radio frequency induction coil fed from a Radyne R.f. unit. A flat copper ring was placed round the outer glass tube to shield the metal parts of the chamber from the field. Thus only the oven was heated and by careful placing of the coil, and control of the power output of the R.f. generator this could be successfully degassed prior to evaporation. The foil holder was hooked onto a long steel rod passing through the top of the chamber and after evaporation this was lowered and the foil inspected through the vertical glass tube. If the foil was satisfactory the sliding vane valve was opened and the holder lowered into the previously evacuated spectrometer tank until it clipped into the frame on the anode assembly. It did so with the coated foil in the position of the X-ray beam, and by moving the frame so that the blank foil

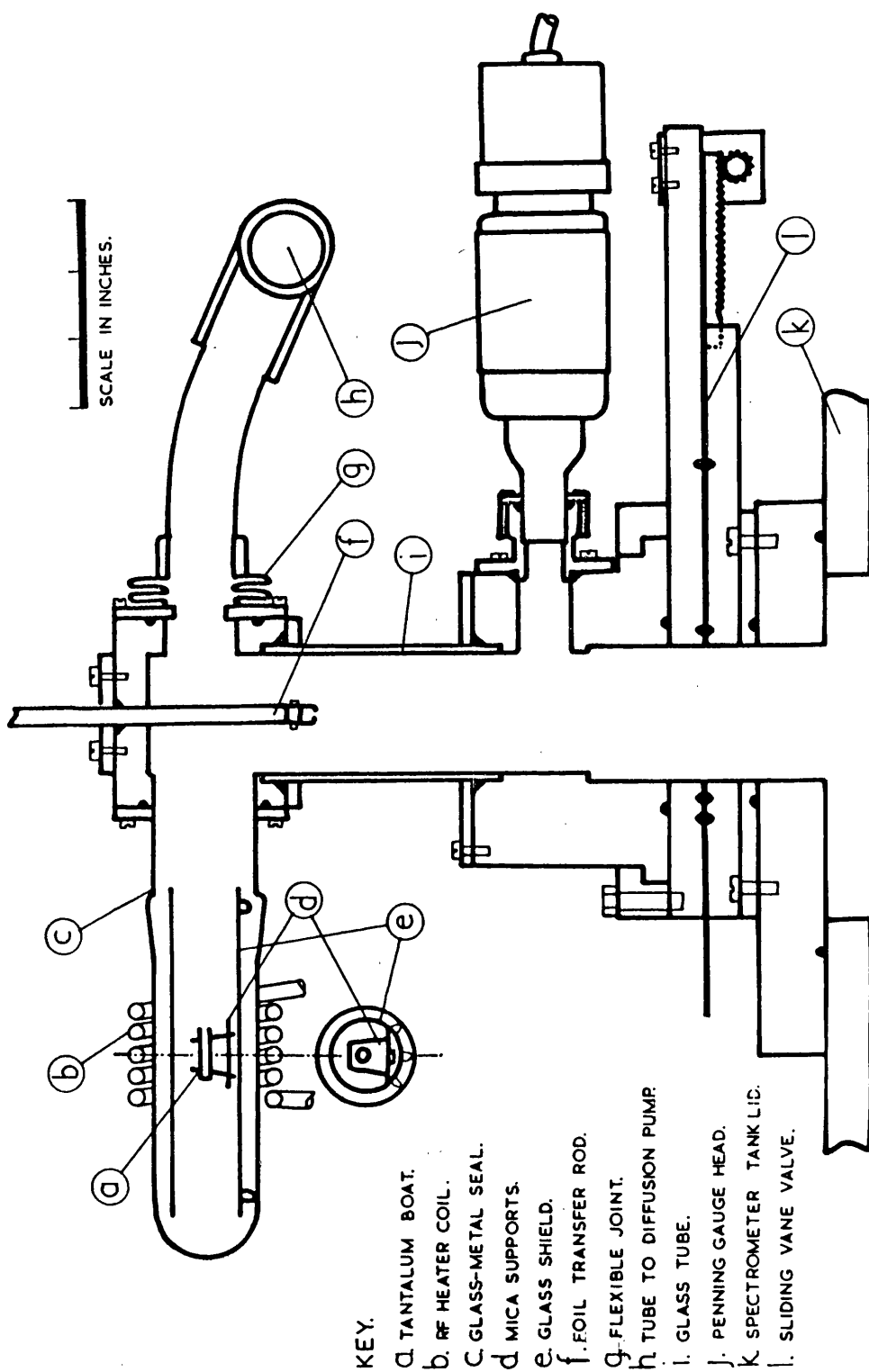


DIAGRAM 2.9 EVAPORATION CHAMBER.

was in this position the holder was unhooked from the carrying rod which could then be lifted back into the evaporation chamber.

All evaporated foils were weighed on a micro balance. The foils were cut out with a circular punch and the weight of the uncoated plastic subtracted from the weight of the coated. In choosing an optimum thickness of absorption screens for the recording of absorption structure two main factors must be taken into consideration. These are the effects of thickness on the error of a single absorption measurement and on the resolution of the structure. The first factor has been considered by Rose and Shapiro⁴¹ for the condition of constant background radiation, and by Nordfors⁴² for the case when the background is affected by the absorber. This latter is a more accurate assessment of the conditions arising in X-ray spectroscopy, but in the present investigation no correction was made for the absorption of background radiation by the foil. The second factor has been investigated by Parratt et al.⁴³. From consideration of counting statistics alone it has been deduced⁴¹ that about 10% minimum transmission is optimum when the background is low and this gives the expression

$$m = \frac{2.3}{\mu}$$

for the optimum mass per unit area. Thus for an absorption coefficient of 2500 cm²/gm the optimum thickness would be approximately 1 mgm/cm². However Parratt⁴³ has shown that the thicker the absorption foil the more the absorption structure is

"washed out" by the action of the spectral window of the instrument, and so to obtain a reliable profile of the absorption structure the foil should be as thin as possible. Thus a compromise must be made between the reduction of statistical error on the one hand and faithful reproduction of the absorption structure on the other. In the present investigation, which involved an attempt to measure structures that had proved undetectable photographically, the foils were made of the order of 0.2 mgm/cm^2 which is somewhat thinner than that dictated by statistical considerations alone.

Setting up and Calibration of the Spectrometer.

The detector, source and crystal were set on the circle described by a radius of 20.3 cms about the central axis of the spectrometer. The position of the crystal was then adjusted to be tangential to this circle by observing the reflected image of a pin set on the Rowland circle diametrically opposite to the centre of the crystal. The crystal was rotated until this reflected image was brought into coincidence with the object pin. The source and detector mountings were then pointed at the crystal and the steel tapes fitted. With the electron gun removed from the source a lamp was placed behind the detector slit and the reflected image of the slit observed with a microscope. The position of the axis of the anode assembly was then brought into coincidence with this reflected image. This process was carried out for the two extreme positions of the spectrometer, the axis

being moved tangentially to the Rowland circle when the crystal was furthest from the source and radially when the two were close together. When no further adjustment was necessary other settings were checked and found to be in good alignment. The gear box was designed to be in mesh with the main gear wheels but its position could be moved to correct for any slight constructional errors. The main drive through the base of the vacuum tank was held in an eccentric collar, rotation of which gave the degree of freedom necessary to ensure well aligned coupling with the gear box. On completion of this setting up the spectrometer was put into operation and various forms of the Xray source tested until finally the design described above was adopted.

Initial calibration of the spectrometer was carried out with the $K\alpha_1$ line of calcium. This line was recorded in the third and fifth orders which appeared at either ends of the region of the scale which was to be used in absorption measurements. After the absorption measurements had been made the observation of this line in the fifth order was repeated and no change in position detected. Theoretically only one calibration line is required for this spectrometer since the relationship between scale reading and Bragg angle is given by

$$\theta = \frac{X - S}{4}$$

and so, once the value of X has been established by obtaining the scale reading S for a known line, other wavelengths may be obtained directly. However in this it is assumed that the system

moves perfectly, always maintaining the same angle between the crystal and detector as between the crystal and source, that the scale is perfectly inscribed and that the counter slit coincides exactly with the axis of rotation of its mounting. To check the initial value of X obtained with the calcium $K\alpha_1$ line other emission lines were examined. These lines, together with the order in which they were detected, are shown in Figure 2.4. A good reference line should be well defined in shape, easy to resolve from neighbouring lines, unaffected by chemical effects, and easy to produce. Such lines are scarce, especially in the longer wavelength regions, and so shorter wavelength lines observed in higher orders have to be used. Even so, of the available lines only the molybdenum $L\alpha_1$ and $L\beta_1$ can be said to fulfil the requirements set out above. The calcium compound used was sulphate but as there have been no measurements of the $K\alpha_1$ line in this compound the values published for the oxide were used. The wavelengths of the calibration lines together with references are listed below.

Wavelengths of calibration lines.

Calcium (oxide)	$K\alpha_1$	$3351.85 \pm 0.1 \text{ xu}$	Haglund ⁴⁷
Silicon (oxide)	$K\alpha_1$	$7108.5 \pm 0.3 \text{ xu}$	Flemberg ⁴⁸
Molybdenum	$L\alpha_1$	$5395.35 \pm 0.2 \text{ xu}$	Haglund ⁴⁷
	$L\beta_1$	$5166.35 \pm 0.2 \text{ xu}$	Haglund ⁴⁷
Platinum	$M\alpha_1$	$6034 \pm 1 \text{ xu}$	Lindberg ¹⁰

49.

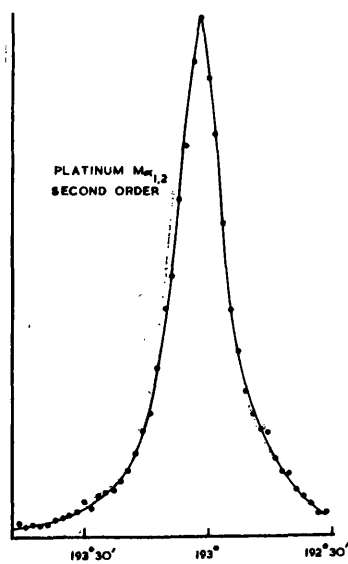
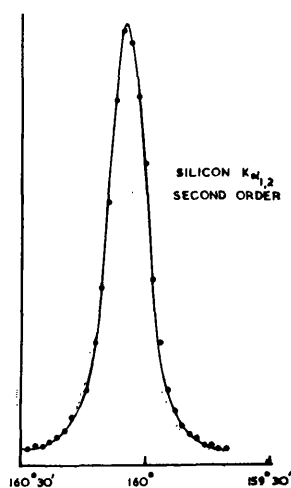
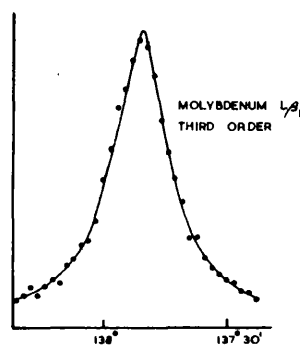
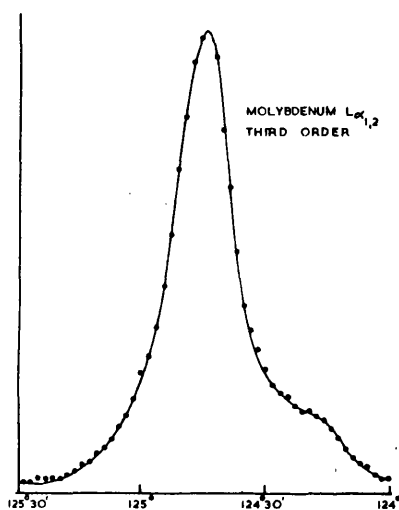
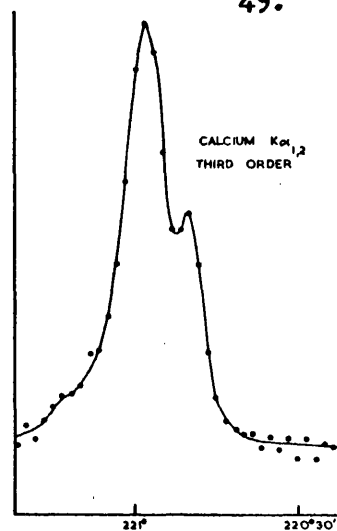
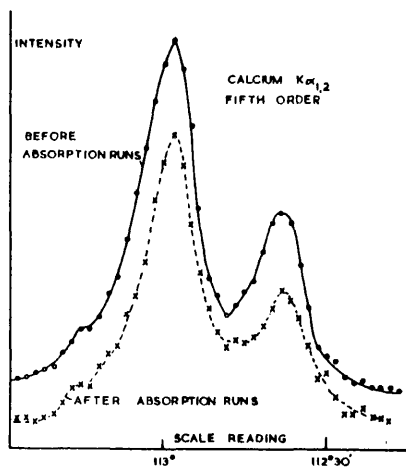


FIGURE 2.4. PROFILES OF CALIBRATION LINES.

The graph of the calcium $K\alpha$ lines in the fifth order shows the α_1 and α_2 well resolved and the value of 3.10 xu here obtained for their separation agrees well with the 3.11 xu obtained by Haglund. The full width at half maximum of the α_1 line obtained in the first observation was 1.85 xu and in the second 1.62 xu. The discrepancy may be explained in that in the first instance the coating on the anode was considerably thicker than in the second. The broadening due to the geometrical effects was calculated in the manner outlined on Page 22 and found to be 0.65 xu. Parratt⁴⁹ has given the width of this line, corrected for the overlap of the α_2 line, as 0.92 xu and as no such correction was carried out in this calculation it can be seen that in the present spectrometer, other broadening effects are minimal.

The value of the scale point X obtained for each of the calibration lines is plotted against the scale position of the line in Figure 2.5.

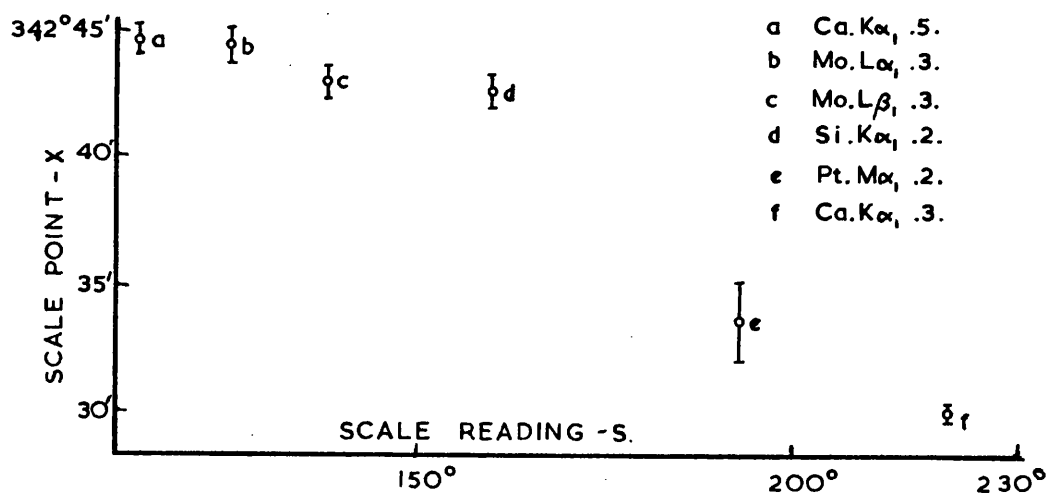


FIGURE 2.5. CALIBRATION.

The vertical lines shown in this diagram represent the errors quoted by the authors of the wavelength values used. For the scale region 110° to 160° the wandering of the "zero" is very slight and the use of any one of the four lines in this region for calibration would give wavelengths for the other three in good agreement with those quoted above. It was in this region that most of the absorption measurements were made. At larger scale readings the "zero" shifts appreciably and when calculating wavelengths in these regions this shift was allowed for.

The Measurement of Transmission of the Absorption Screens.

The transmission of the foils was obtained for a series of points through the range in which the M absorption spectra was expected to appear. This range was estimated from L emission and absorption data. The results are the averages for three such runs through the region. To overcome any gradual drift in the intensity the foils were examined for each point in a blank - coated - coated - blank sequence. The time for 1000 counts was taken for each reading and the values of incident or transmitted intensity for each wavelength setting were the result of twelve such readings. Thus the standard error in each value of the transmission was about 2%. The transmission measurements were corrected for background which was counted for 10^5 seconds at the beginning and end of each series of measurements.

Discussion of Errors.

The errors affecting these measurements may be divided into two groups; those affecting the absorption coefficient, and those affecting the wavelength values of the absorption structure, although an uncertainty in the former will obviously produce an uncertainty in the latter.

The standard error in the measured transmission will give an error in the absorption coefficient which is dependent upon the mass thickness m of the foil, being given by

$$\Delta \mu_1 = \frac{0.02}{m}$$

The method of weighing the evaporated layers gave rise to a standard error in the mass thickness of 0.017 mgm/cm^2 and this leads to a further error in the absorption coefficient given by the expression

$$\Delta \mu_2 = \frac{0.017}{m}$$

Inaccuracy in the wavelengths arises from two sources, namely the error in the reading of the scale and the error in the value of the scale "zero". The scale could be read to 0.44 minutes throughout but the error in the scale "zero" will depend very much upon the region in which the spectrometer is being operated. In the region 110° to 160° the total error will be of the order of $\pm 0.5 \text{ xu}$ but at larger angles it will be increased. The calculated errors associated with the wavelength values and the mass thicknesses of the foils are given in the next chapter.

PHOTOGRAPHS.

Plate 1. The Main Evaporation Plant.

The foil holder and mask are shown in position above the tantalum boat.

Plate 2. The Spectrometer.

The components shown are, from left to right, the counter holder, the crystal mounting and the anode assembly.

Plate 3. General View of Apparatus.

The radio frequency generator is shown to the left with the coil in position on the evaporation chamber. The Penning Gauge Meter is shown on top of the spectrometer tank and the Xray source bias control box is to the extreme right of the picture.

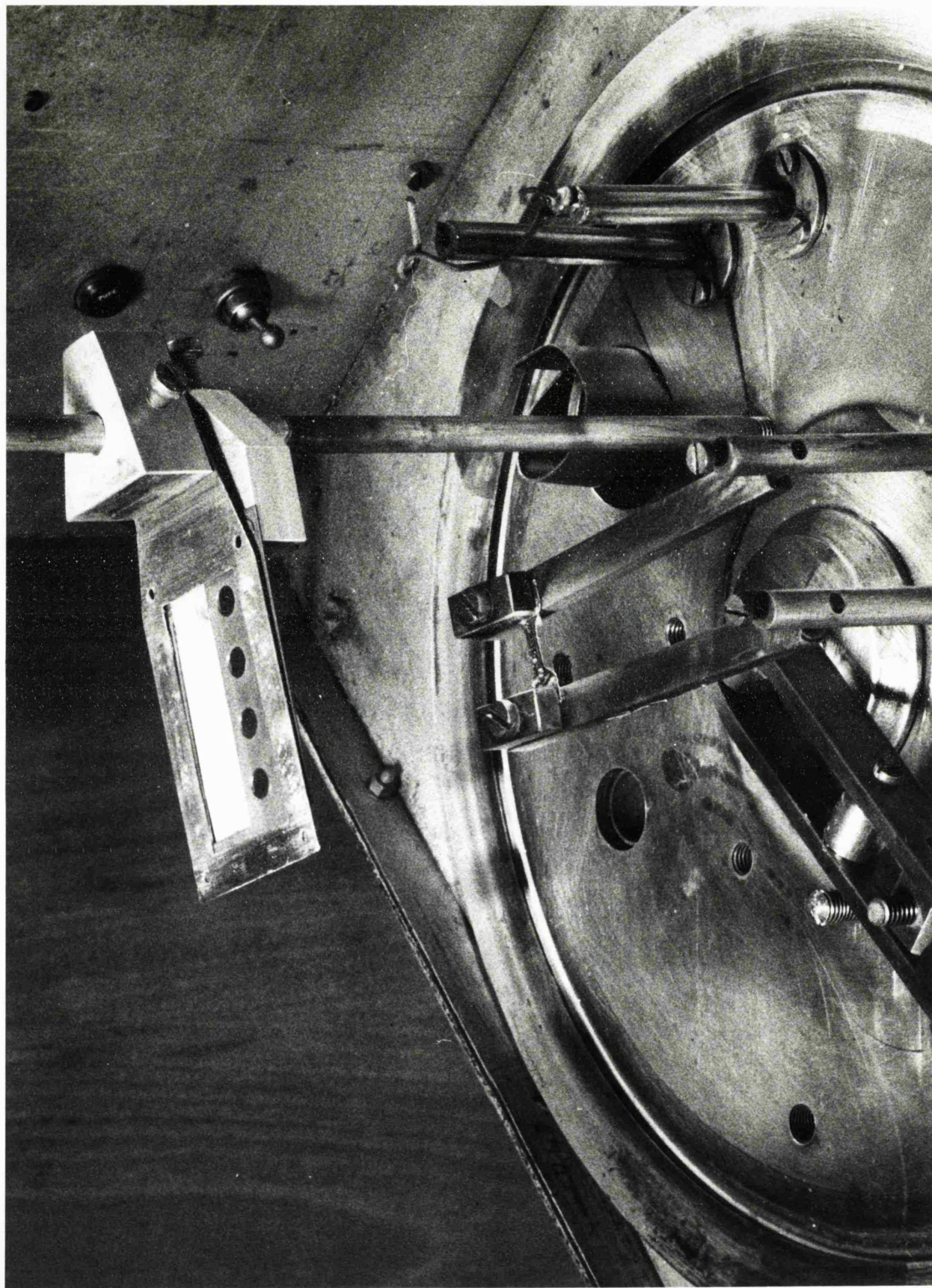


PLATE I. MAIN EVAPORATION PLANT.

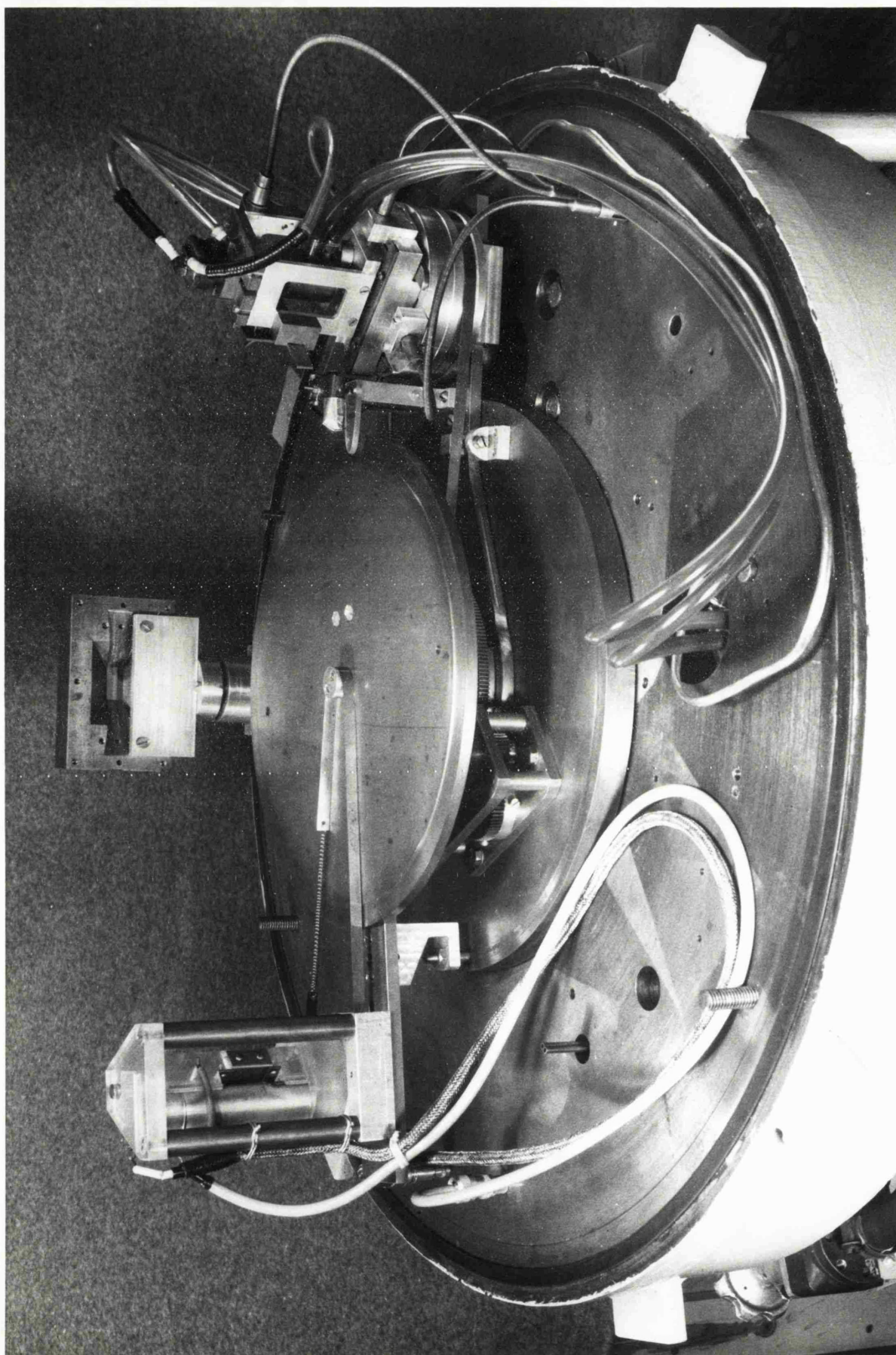


PLATE 2. THE SPECTROMETER.

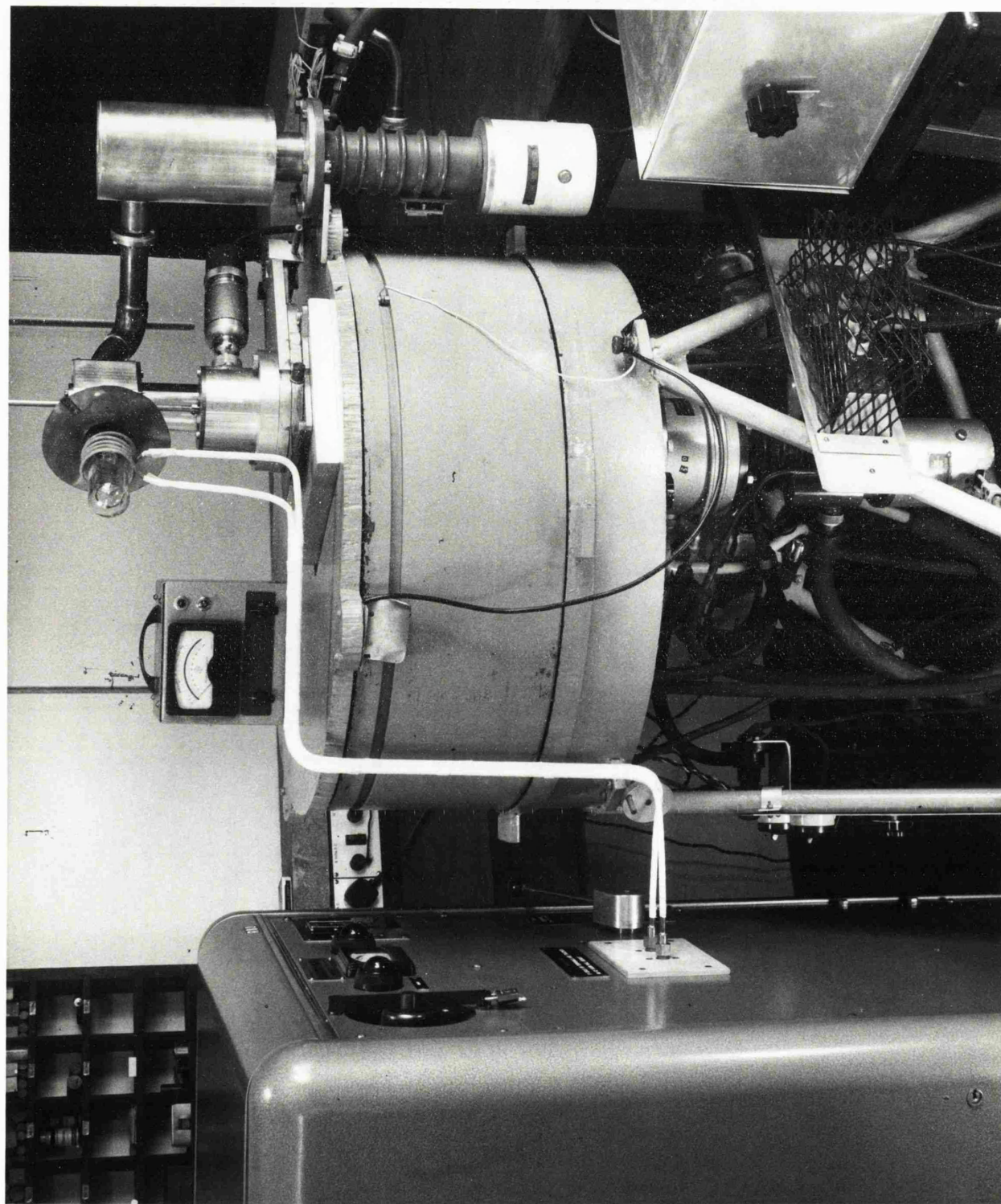


PLATE 3. GENERAL VIEW OF APPARATUS.

CHAPTER THREE: EXPERIMENTAL RESULTS.

Introduction.

Absorption Measurements on Ytterbium.

The M_V Line.

The M_{IV} and M_V Edges.

The M_{III} Edge.

The M_{IV} and M_V Edges of some Heavier Elements.

Lutecium.

Hafnium.

Tantalum.

Foil Thicknesses.

Wavelength and Energy Values.

Introduction.

As was pointed out in the first chapter the scope of this work extended to an investigation of the M_V line absorption of ytterbium in the metallic state and in compound, and a search for the M_{IV} and M_V absorption edges of ytterbium, lutecium and hafnium, together with a measurement of these edges for tantalum to provide a comparison with previous work. These investigations, the results of which are shown below, were extended to include a measurement of the M_{III} edge of ytterbium. All substances used in the preparation of the absorption foils were obtained from Johnson, Mathey and Co. and had a stated purity of 99.9%. Measurements were made on the oxides of all four elements, the fluorides of ytterbium and lutecium, and pure metallic ytterbium.

The absorption coefficients of the compounds were first calculated and these were then corrected for absorption by the oxygen (or fluorine). The absorption coefficient of these latter was obtained from an expression of the type

$$\mu = C\lambda^n.$$

To obtain the values of the constant C and the exponent n the absorption coefficients for short wavelengths from the tables compiled by Allen and published by Compton and Allison⁴⁶ were used. A plot of the equations used for the absorption of oxygen and fluorine, together with the experimental points is given in Figure 3.1. The region of wavelengths investigated was well above the K edges of these two elements and in such a region expressions

of this type have been found to be valid by many experimenters⁴⁶.

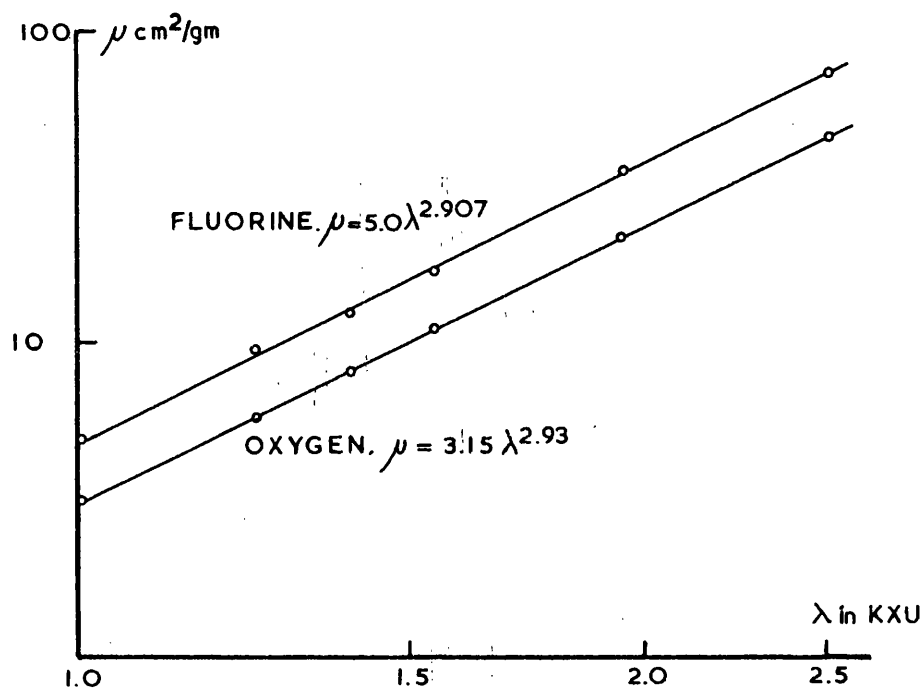


FIGURE 3.1 ABSORPTION OF OXYGEN AND FLUORINE.

The corrected absorption coefficient of the metal was then obtained from the equation

$$\mu_A = \frac{a+b}{a} \mu_{AB} - \frac{b}{a} \mu_B$$

where μ_{AB} is the measured coefficient, μ_B the coefficient extrapolated in the manner described above, and a and b the respective masses of A and B present in the compound. The corrected values obtained in this manner contain an additional source of error in the uncertainty of μ_B , but since b is much smaller than a for the compounds studied and since μ_B is usually smaller than μ_{AB} a relatively large percentage error in μ_B will

only increase the error in μ_A by a small amount. An extreme example is the absorption coefficient in the centre of the M_V absorption line of ytterbium in ytterbium fluoride; here a change of 30% in the absorption coefficient of fluorine only alters the corrected value for ytterbium by 1%. In other regions the value will alter by up to 10%. However it is not anticipated that the absorption coefficients obtained by this process of extrapolation are in error by such a large amount. The University computer (Elliott 803) was programmed to calculate the absorption coefficients of the compounds from the experimental data and then with a second programme the corrected values, together with the energy and wavelength position of each point, were obtained.

Absorption Measurements on Ytterbium.

The M_V Line.

The single line absorption of ytterbium arises from an electronic transition between the M_V shell and the gap in the 4f shell and as has been indicated in the first chapter, such a gap only occurs if the ytterbium atom is in a triply ionised state.

The study of ytterbium was commenced with a measurement of the M_V absorption line for ytterbium fluoride and a plot of the absorption coefficients of this compound is given in Figure 3.2. As can be seen from the figure the absorption line is sharp and extremely pronounced, the absorption coefficient at maximum being

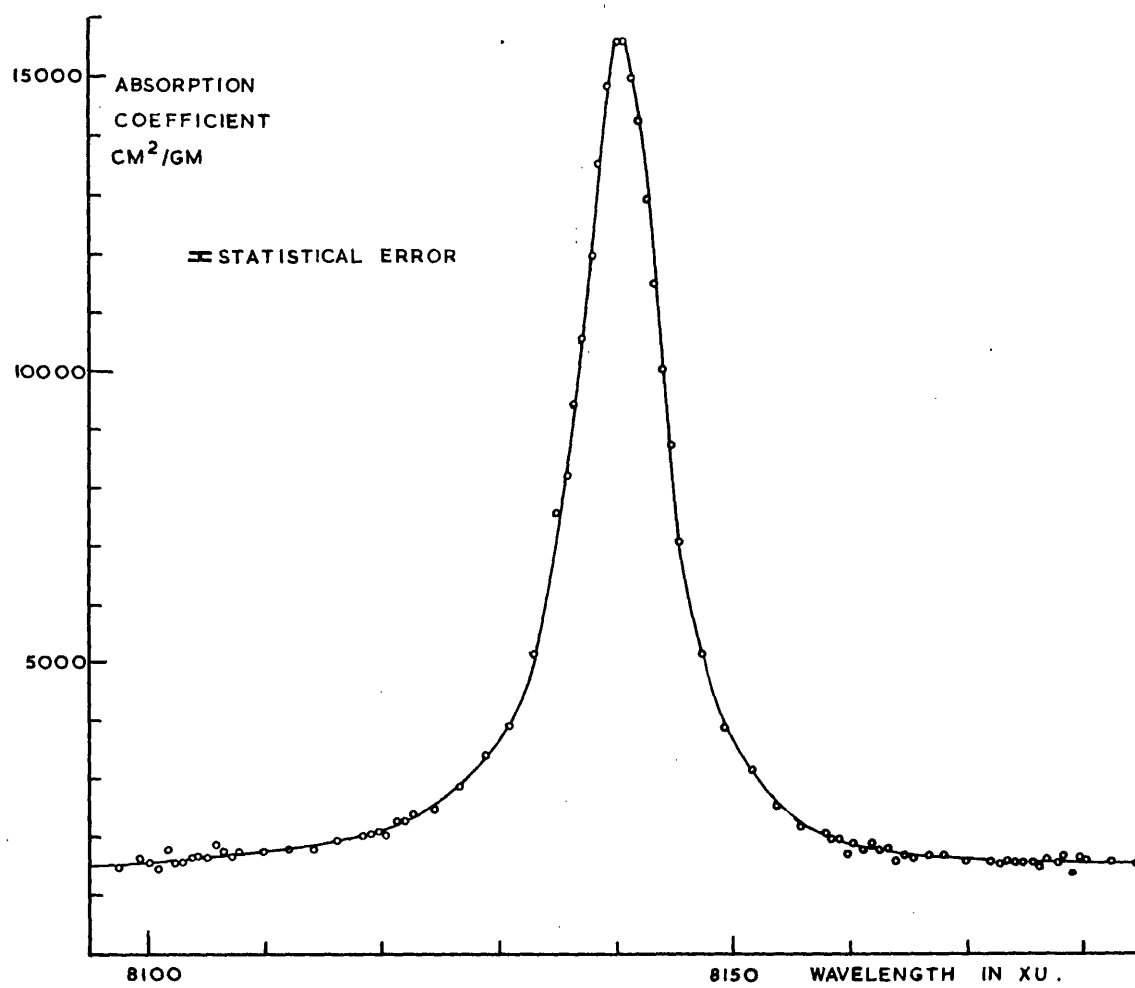


FIGURE 3.2 M LINE OF YTTERBIUM FLUORIDE.

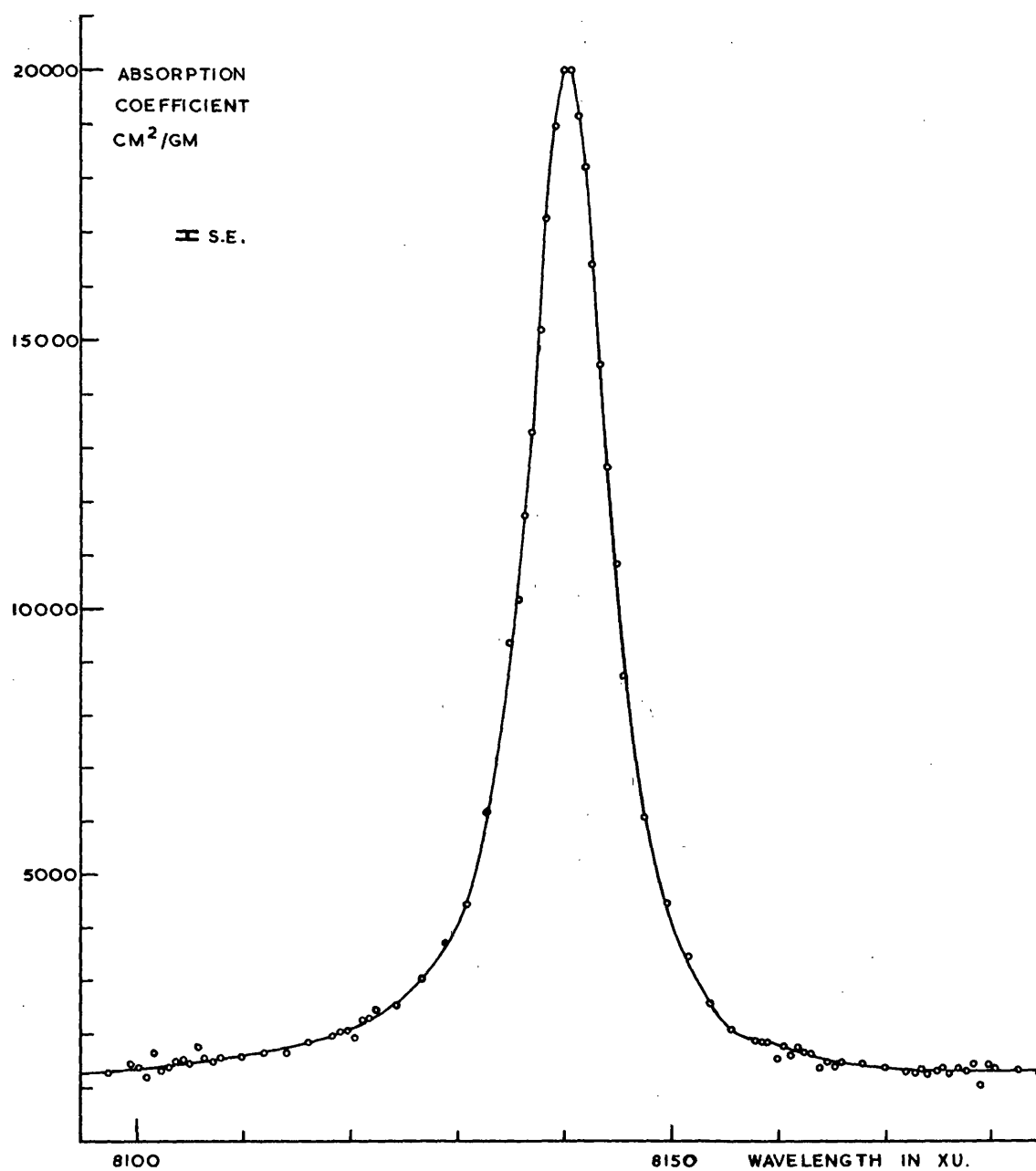


FIGURE 3.3 M LINE OF YTTERBIUM IN YTTERBIUM FLUORIDE.

a factor ten larger than that on either side of the line. This change in absorption coefficient had been measured previously in this laboratory by both Williams and Phahey²⁹ using photographic detection. They obtained values of 27,500 and 18,000 cm^2/gm respectively from measurements on ytterbium oxide layers. The foils used by Williams were prepared from metal foils oxidised in an oxygen discharge, and it was suggested that some loss of the ytterbium in this process may account for the somewhat high value obtained. The value given by Phahey is much nearer that obtained in the present investigation. The discrepancy is probably explained by the inaccuracies of the photographic technique, in addition to the errors involved in the determination of the mass thickness of the foils both in that investigation and in this. The absorption coefficients obtained for ytterbium fluoride were corrected in the way described above and the corrected curve is shown in Figure 3.3. This curve represents the variation of absorption coefficient with wavelength for the ytterbium ion in ytterbium fluoride, and it can be seen that the effect of the correction is to increase the magnitude of the absorption line.

The next stage in this investigation was the preparation of pure ytterbium metal foils. According to the magnetic data of Lock⁵⁰ the atoms in metallic ytterbium have a complete 4f shell, thus the line absorption should not appear. The first metal foils were prepared in the main evaporation plant but examination of

these foils showed an absorption line which although reduced in magnitude was still appreciable. With the introduction of the new evaporation chamber however the quality of the foils was improved until, after some refinement of the technique, a foil was produced for which only a very slight trace of line absorption appeared. The reduction of the M_V line revealed a small hump in the absorption profile to the high energy side. The metal foil was re-examined after standing in air for two and seven days; in the first instance a slight increase in the M_V line absorption was detected but thereafter no change occurred. This observation seems to indicate that the surface of the metal became coated with a protective film of oxide which then prevented further oxidation. The absorption curves obtained for the pure and slightly oxidised metal are shown in Figure 3.4, together with a curve for the purest metal foil prepared in the main evaporation plant. The metal foil was then oxidised by placing a small drop of hydrogen peroxide on it. This method of oxidation was tested on foils which had shown appreciable line absorption and it was noted that they rapidly became transparent, whereas with the pure metal foil the process was much slower proceeding gradually inwards from the edge of the layer, indicating that this foil with its coating of oxide was extremely stable and resistant to further oxidation. The absorption of the oxidised foil was then examined and the M_V line found to be strongly in evidence. The corrected curves for the oxidised metal and the

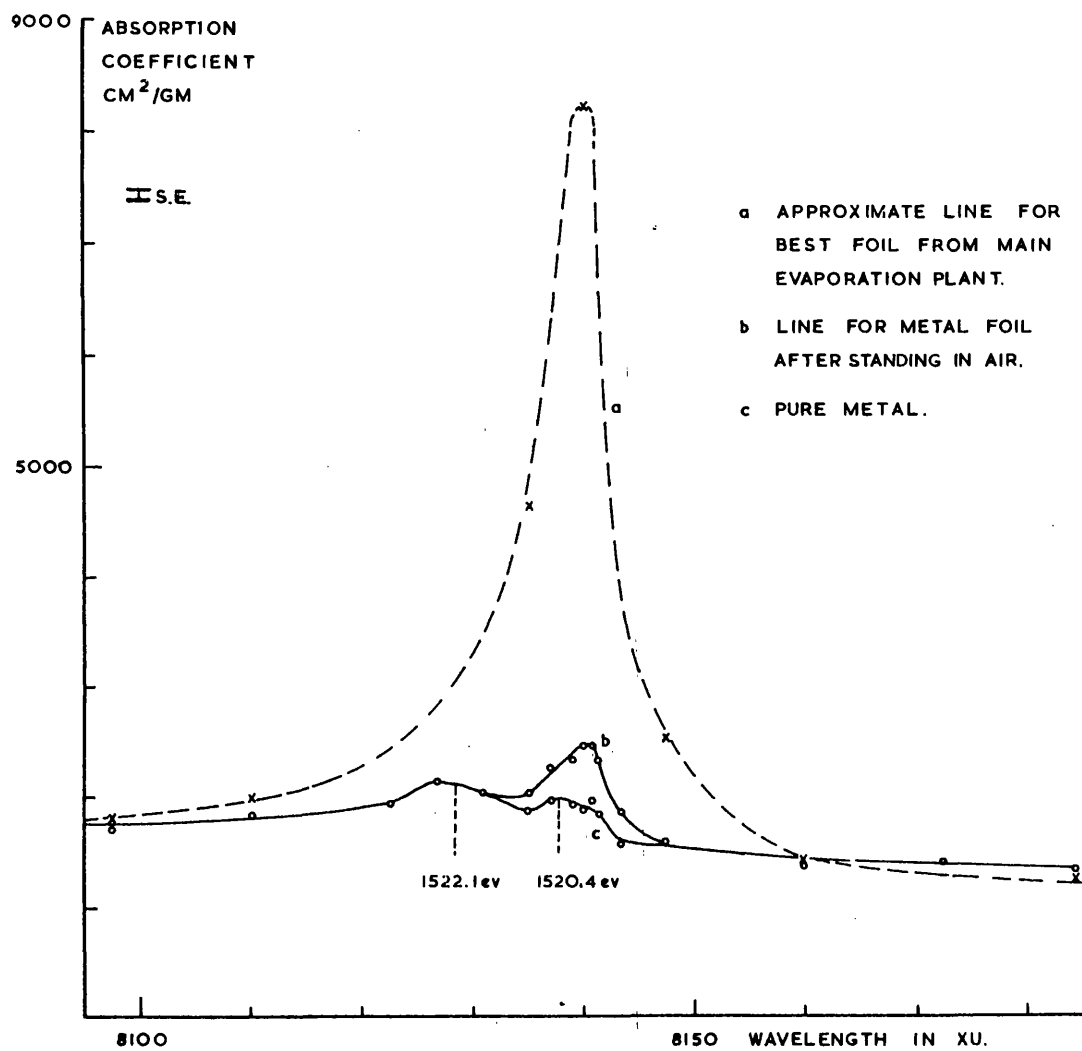
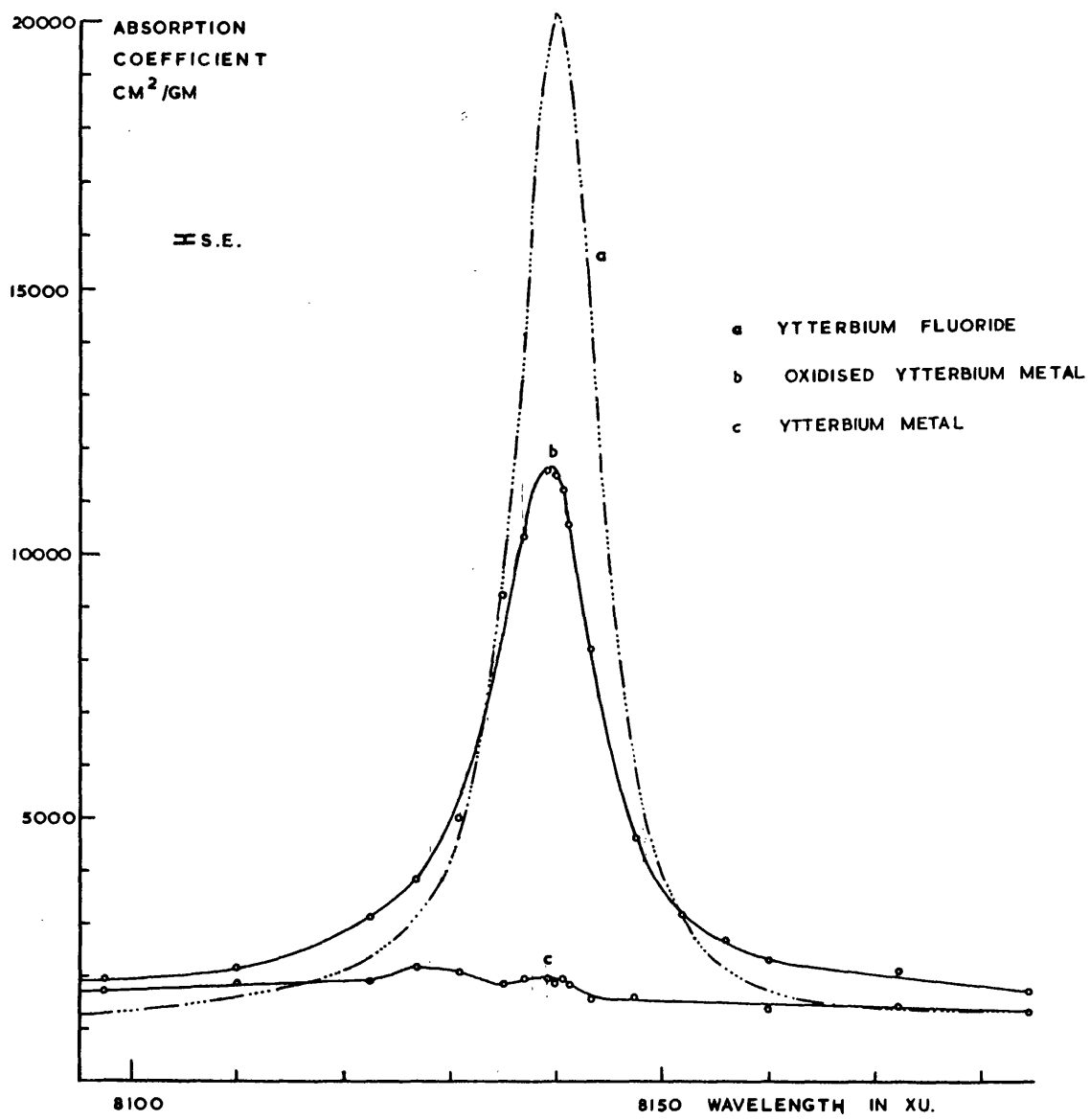


FIGURE 3.4 M_V LINE FOR PURE AND PARTIALLY OXIDISED Yb METAL.

FIGURE 3.5 M_v LINE. A COMPARISON.

fluoride foils are together compared with that of the pure metal in Figure 3.5.

The M_{IV} and M_V Edges.

Hitherto no M absorption edges had been reported for ytterbium. In this investigation the M_{IV} and M_V edges were first registered for the ytterbium fluoride foil. The variation of the absorption coefficient of this substance, with photon energy, is shown in Figure 3.6. The expected position of these edges was calculated from L emission and absorption data but it was found that the observed edges occurred at energies some 20 ev higher. A discrepancy of this type was found for all four of the elements studied. The ytterbium edges were found to be diffuse and represented a change in absorption coefficient much smaller than that of the M_V line. These two factors probably explain the failure of previous attempts to register them photographically which had been made in this laboratory. The absorption profile, corrected for the absorption of the fluorine, is shown in Figure 3.7.

The study of the pure metal foil in this region again showed the edge structures but at energies lower by about 10 ev. However on oxidation of the foil they were found to shift back to a position approximately the same as that found for the fluoride. The absorption coefficients obtained for the oxidised foil were corrected for the absorption of the oxygen and the resulting curve is shown in Figure 3.8, together with that for the pure

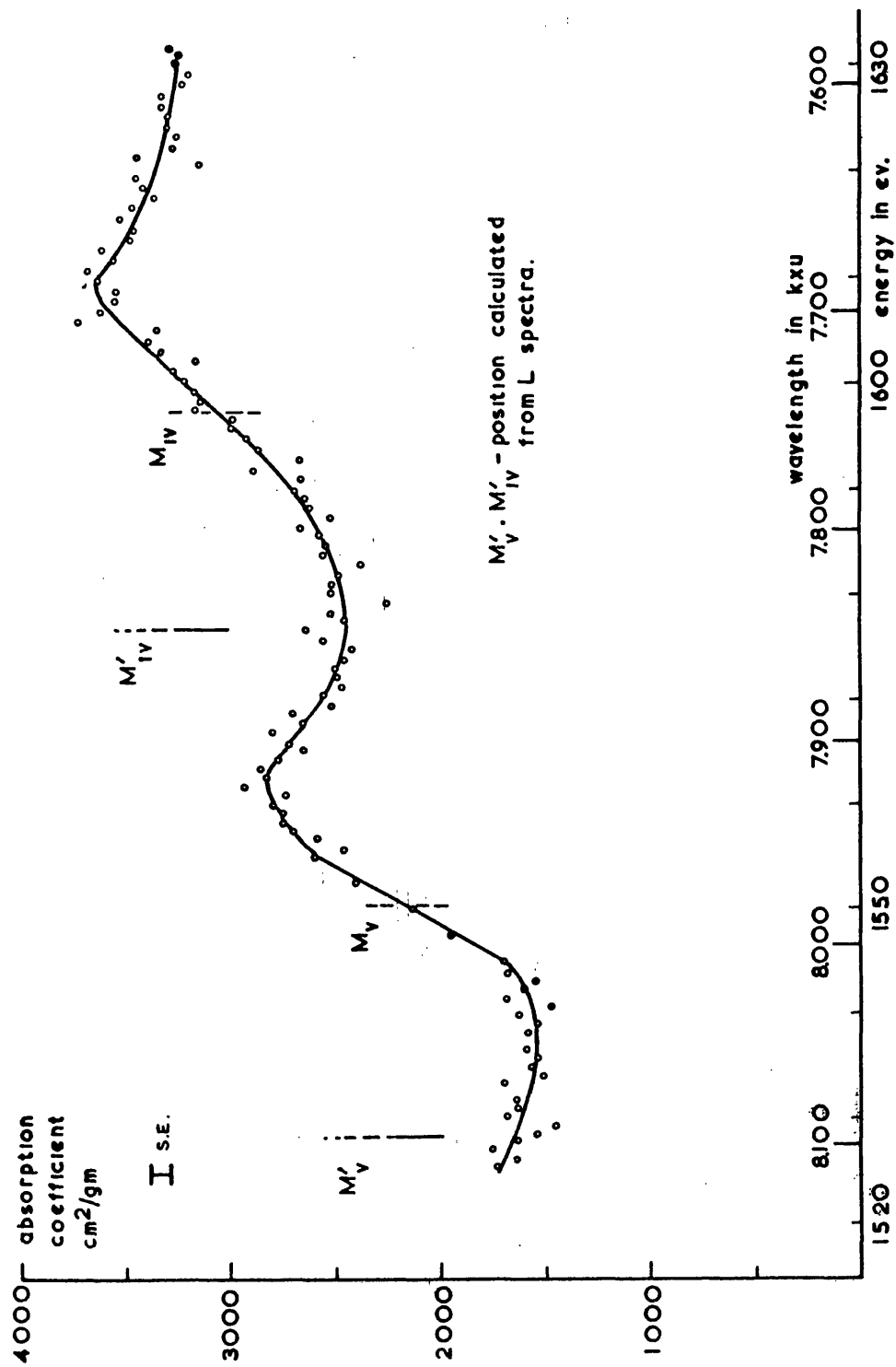
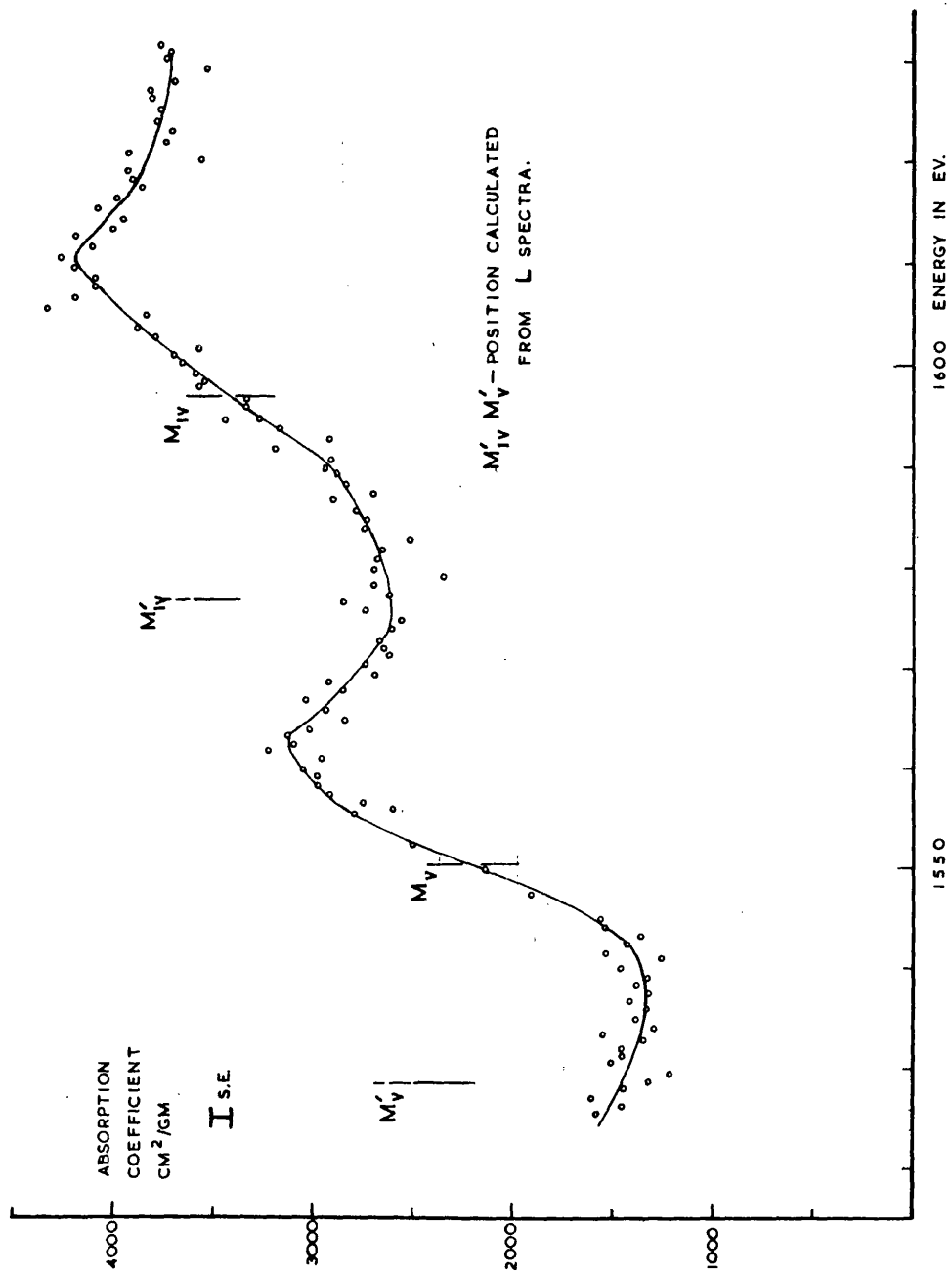


FIGURE 3.6. M_{IV} AND M_V EDGES OF YTTERBIUM FLUORIDE.

FIGURE 3.7 M_{IV} M_V EDGES OF YTTERBIUM IN YTTERBIUM FLUORIDE.

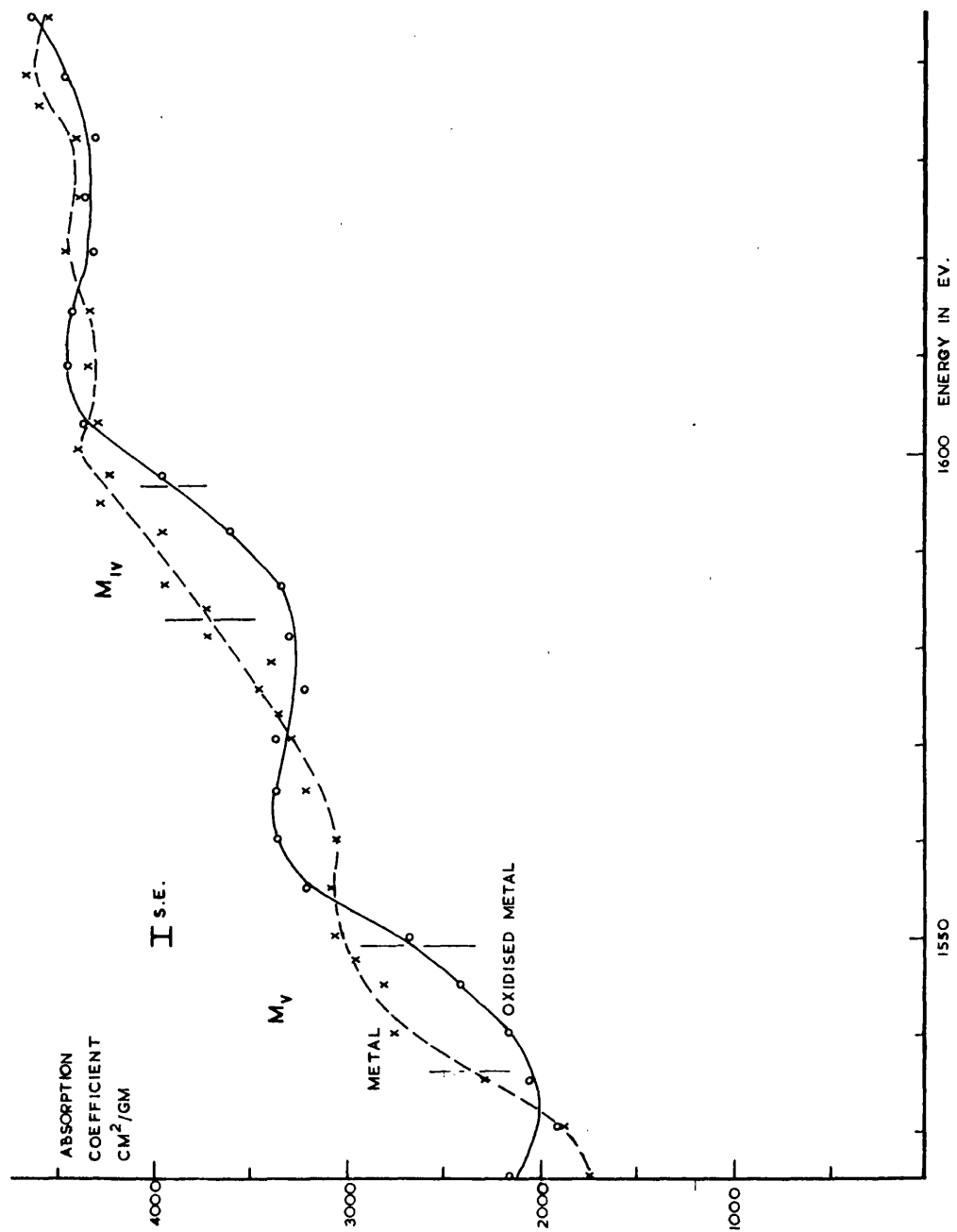


FIGURE 3.8 M_{IV} M_V EDGES OF YTTERBIUM IN PURE METAL AND IN OXIDISED METAL.

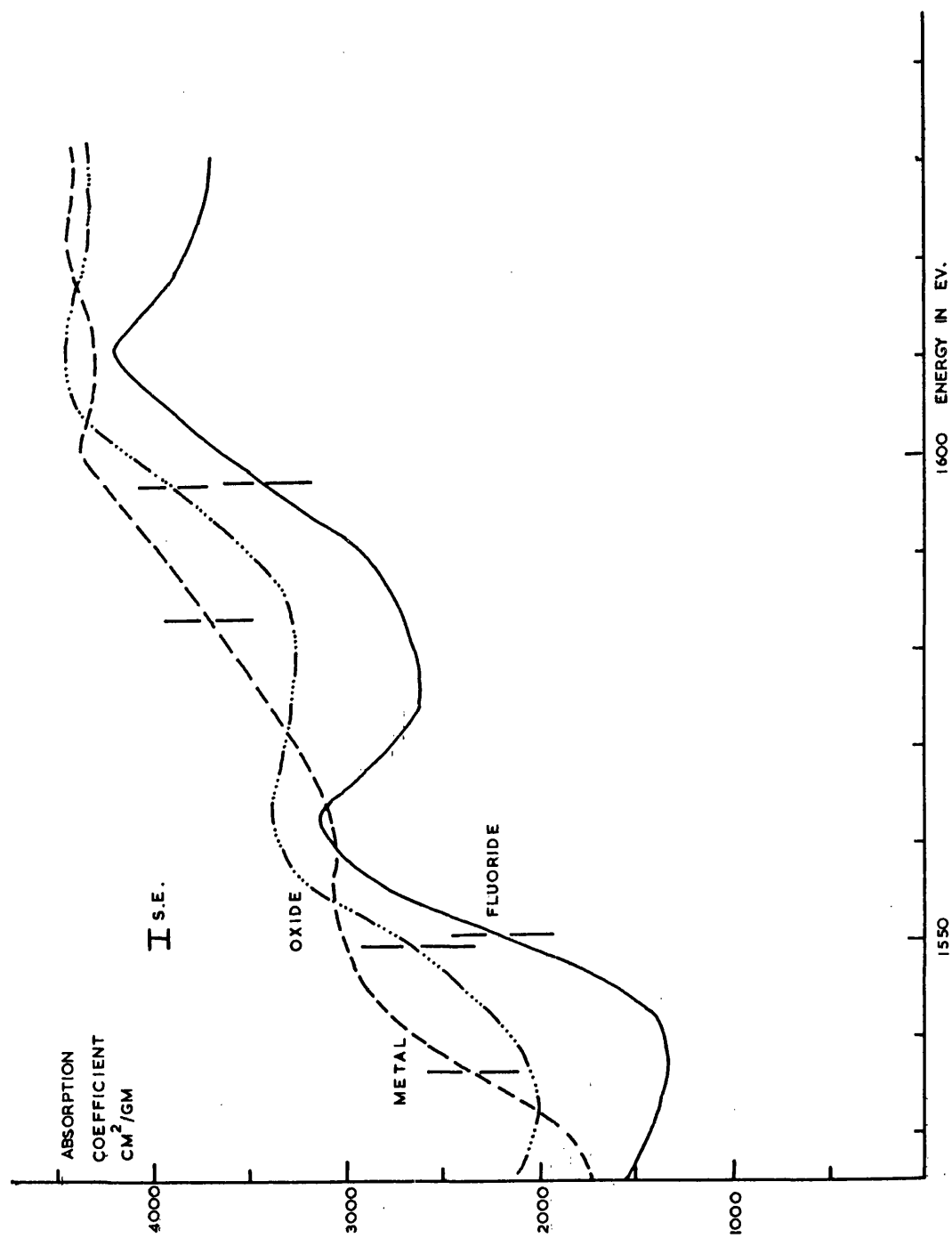


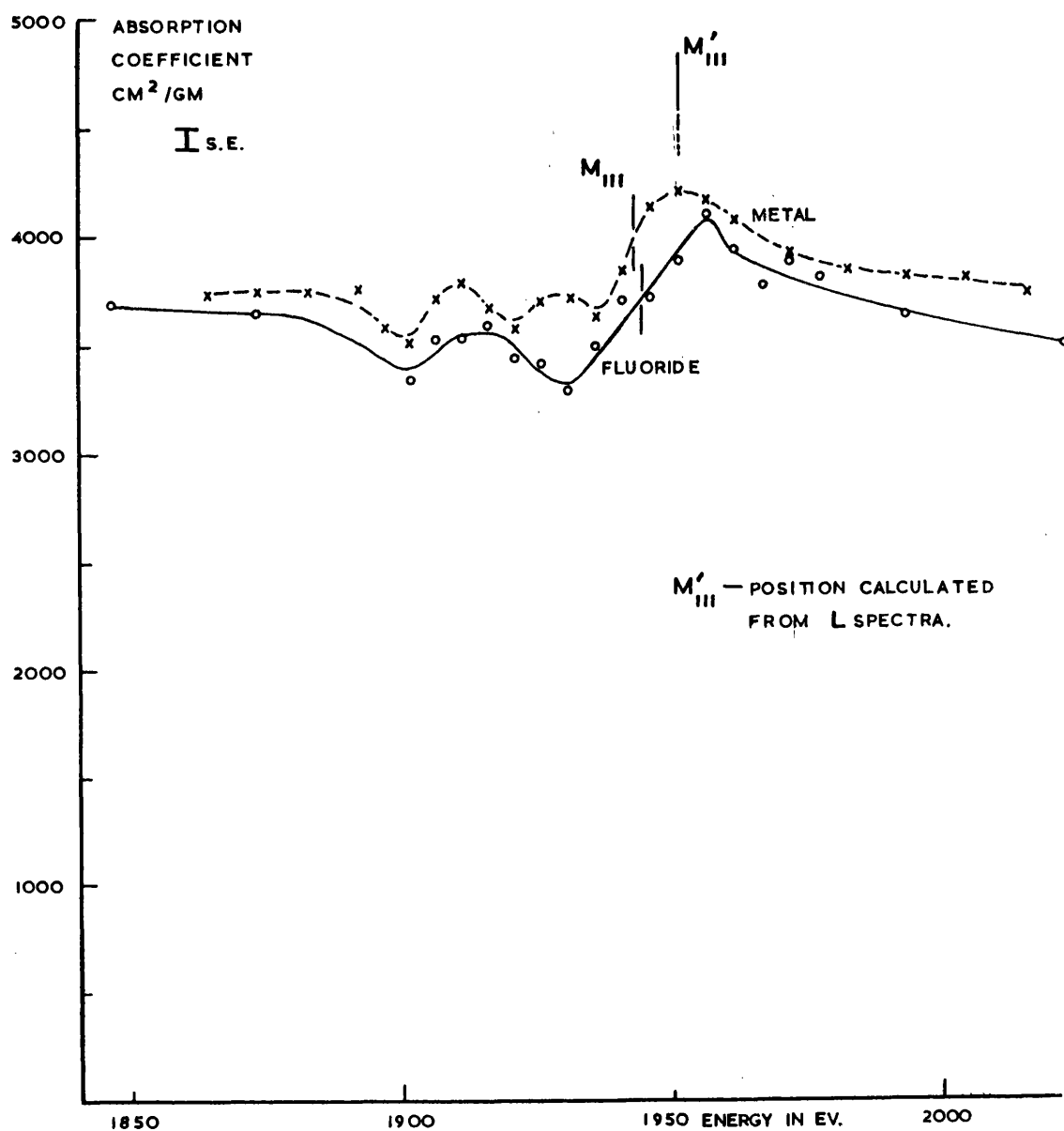
FIGURE 3.9 M_{IV} EDGES OF YTTERBIUM. A METAL-FLUORIDE-OXIDE COMPARISON.

metal. In this figure the change in position of the edges can be clearly seen. That the positions of the edges for ytterbium in the fluoride and in the oxide are almost coincident is shown in Figure 3.9. This figure consists of a comparison between absorption profiles of the ytterbium ion in the metal, the fluoride and the oxide in the region of the M_{IV} and M_V edges.

The M_{III} Edge.

The investigation of ytterbium was completed with an attempt to register the M_{III} edge. The absorption of the ytterbium fluoride foil was investigated in the region of the calculated position of this edge. The edge was found to represent only a small change in absorption coefficient and its wavelength position was found to agree very closely with the calculated value. This edge was also detected using the metal foil and although a slight shift in the wavelength position was observed it was not of the same magnitude as that observed for the M_{IV} and M_V edges. The M_{III} edges observed for these two substances are compared in Figure 3.10. The absorption coefficients for the fluoride foil have been corrected for fluorine absorption.

The relative magnitudes and positions of the absorption structures mentioned above can be seen from Figure 3.11 in which the M_V line and the M_{III} , M_{IV} and M_V edges of ytterbium in ytterbium fluoride are plotted on the same energy scale.

FIGURE 3.10 M_{III} EDGE OF YTTERBIUM.

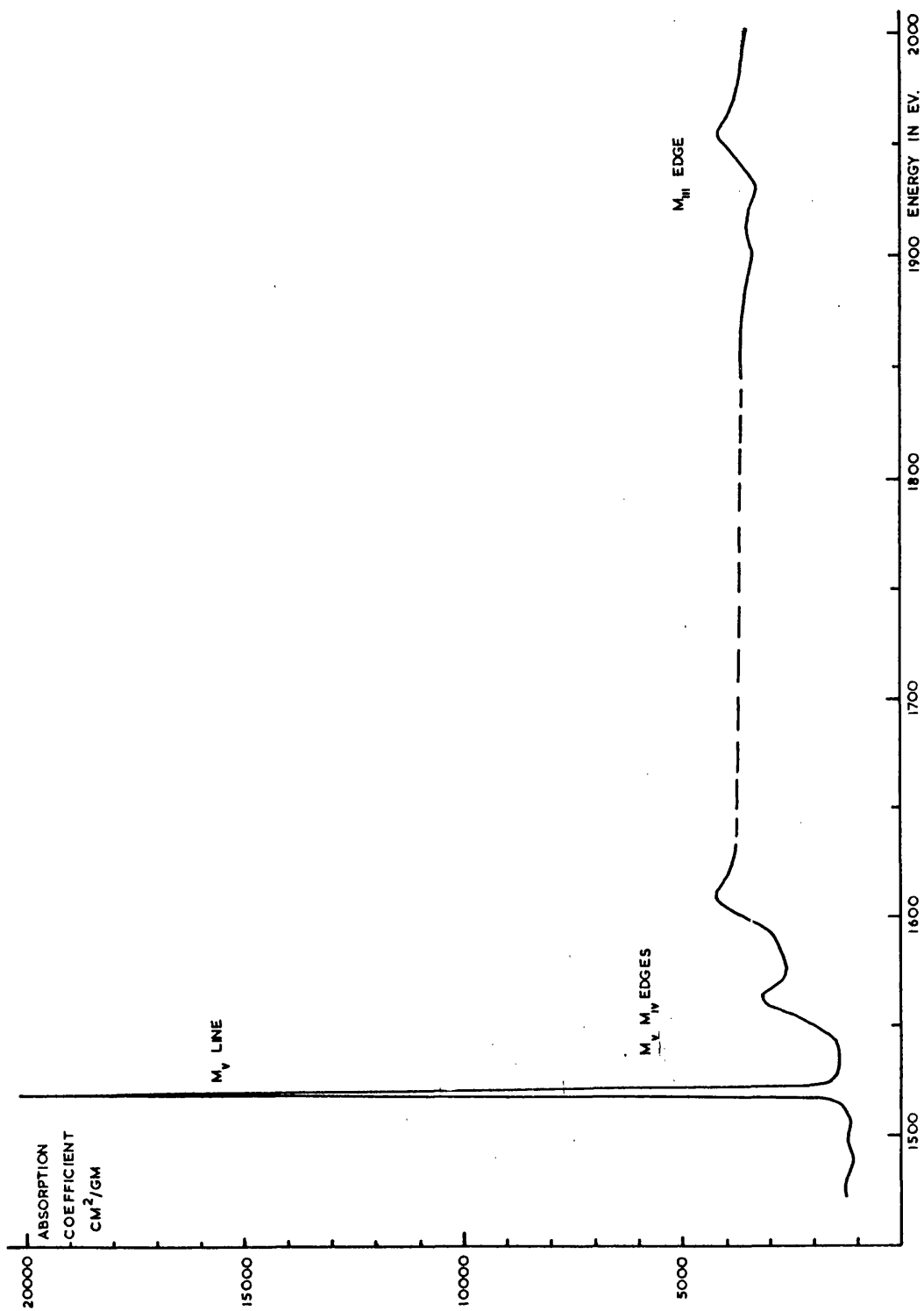


FIGURE 3.11 A COMPARISON OF THE LINE AND EDGE ABSORPTION OF YTTERBIUM FLUORIDE.

The M_{IV} and M_V Edges of some Heavier Elements.

Lutecium.

The first detection of the M_{IV} and M_V absorption edges of lutecium was made using an evaporated lutecium oxide absorption screen. However an examination of the variation of absorption on the high energy side of the edges showed a further "step" in the structure. Because of the high temperature required in the preparation of the foil it was suspected that some of the tantalum boat material had also evaporated, and this was confirmed when the absorption measurements on tantalum oxide revealed that the third step on the lutecium curve coincided with the M_V edge of tantalum. The absorption curve resulting from measurements on this tantalum contaminated lutecium foil is shown in Figure 3.12. The M_V edge observed for tantalum has been included to show the coincidence discussed above. Langmuir and Malter⁵¹ have given an equation for the rate of evaporation of tantalum which, for the conditions of the preparation of the lutecium oxide foil, indicates that the melinex substrate would also be coated with about 0.02 mgm/cm^2 of tantalum. This would mean that the lutecium and tantalum were in a ratio of approximately six to one. From the absorption curve it seems that the proportion of tantalum was nearly twice this. The absorption curve of lutecium oxide, by virtue of the contamination, does not give any information regarding the absolute values of absorption coefficient and so

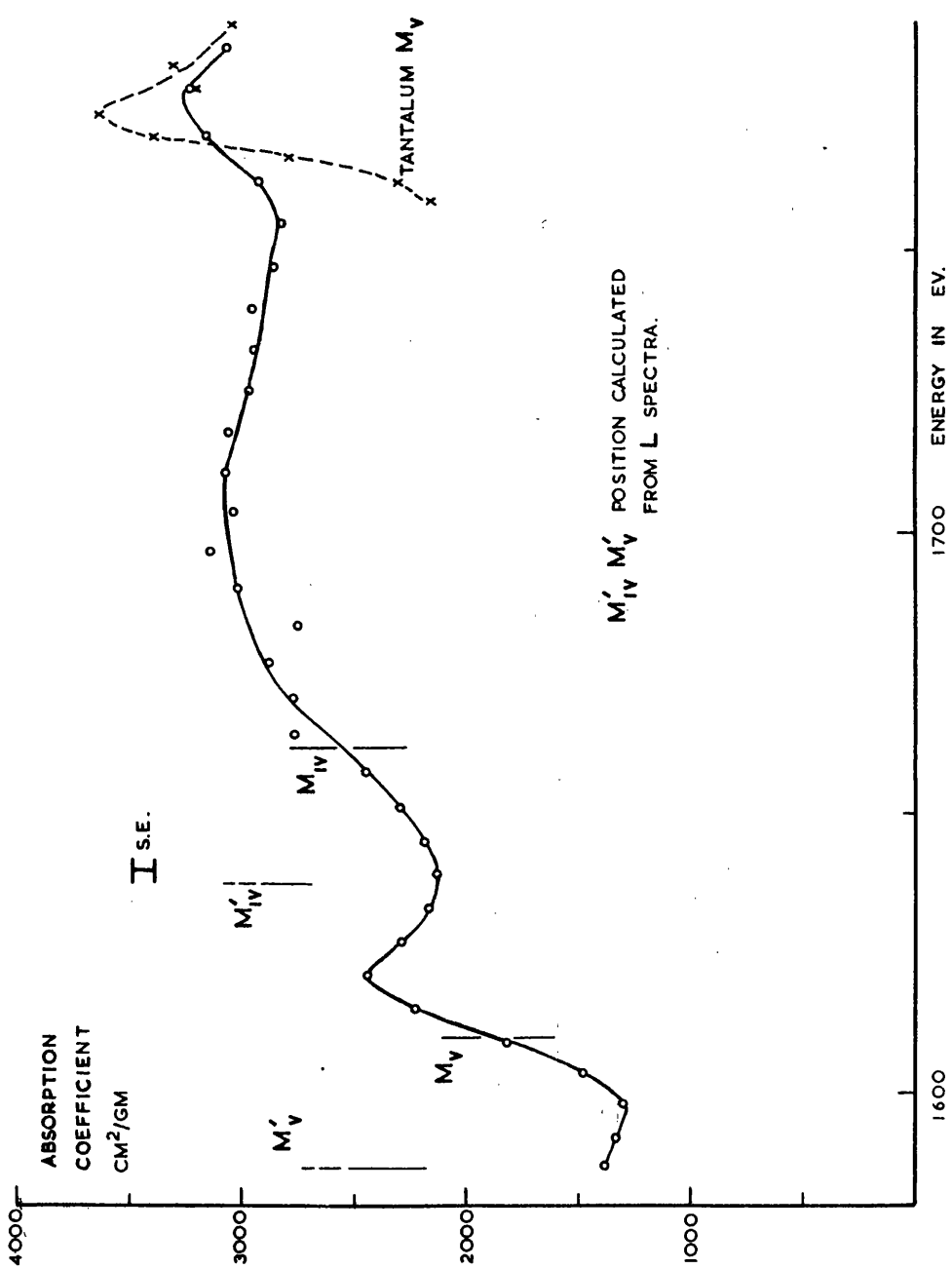
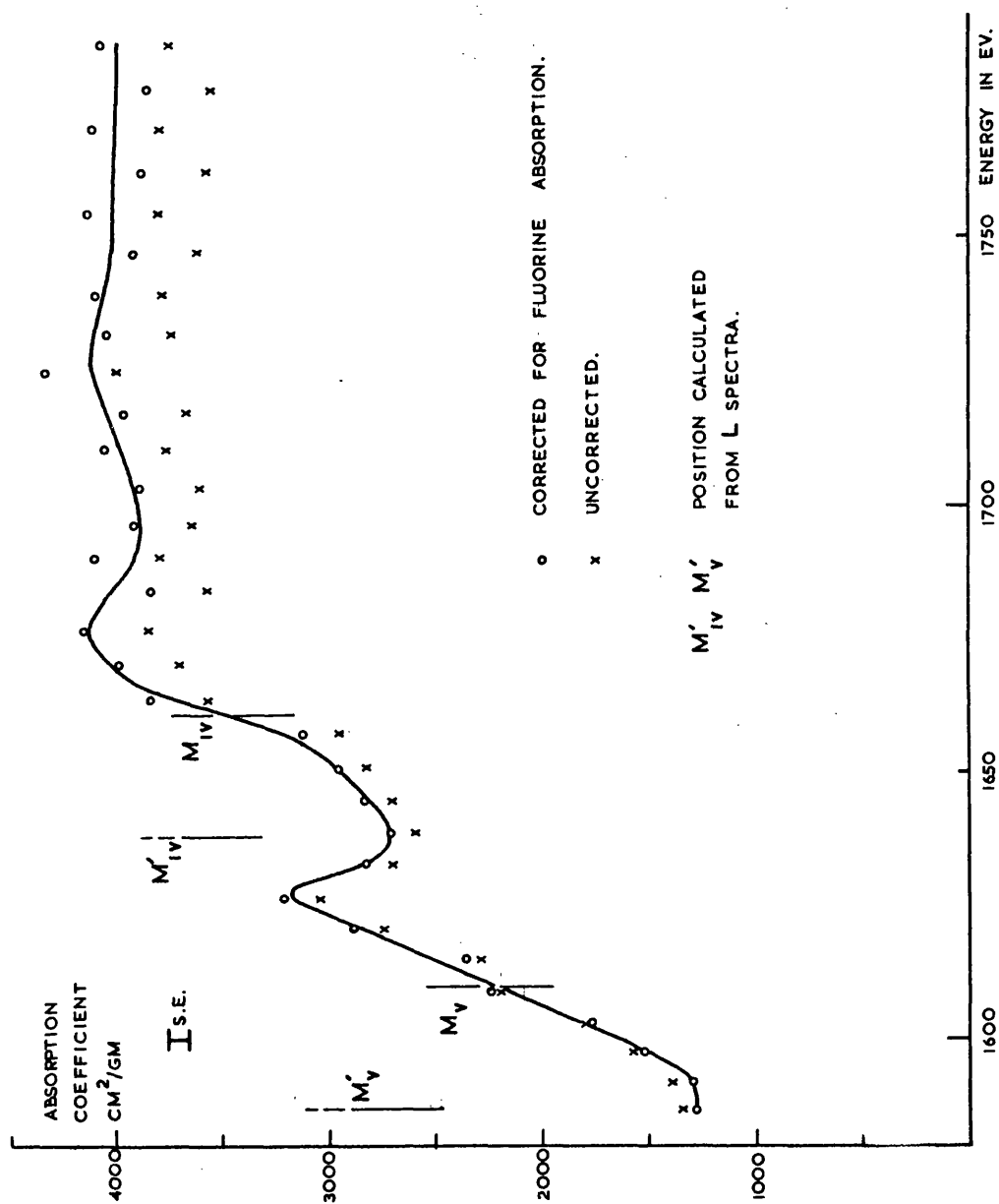


FIGURE 3.12 M_{IV} M_V EDGES OF LUTECIUM OXIDE SHOWING TANTALUM CONTAMINATION.

FIGURE 3.13 M_{IV} M_V EDGES FOR LUTECIUM FLUORIDE.

an absorption screen of the fluoride of this metal was prepared. This compound evaporates at a much lower temperature than the oxide, being similar in this respect to ytterbium fluoride. The variation of absorption coefficient with photon energy for lutecium fluoride and the curve obtained after correction for the fluorine absorption are plotted in Figure 3.13. In this it can be seen that there is no longer evidence of tantalum absorption.

Hafnium.

This metal could not be obtained in a form suitable for the preparation of absorption screens by evaporation. The oxide has melting and boiling points similar to those of tantalum or tungsten and this rules out any evaporation technique similar to the one described above. With the metal this situation is only slightly improved. A suitable compound would be the tetrafluoride but this substance proved to be unobtainable commercially. In view of this difficulty, absorption screens were prepared by the method set out in the last chapter. A measurement of the transmission of the foil only reveals the general structure in the variation of absorption with wavelength. The wavelength position of any such structure can be determined but no measure of the absolute or even relative values of the absorption coefficient may be obtained. The absorption equation for such a foil may be written as

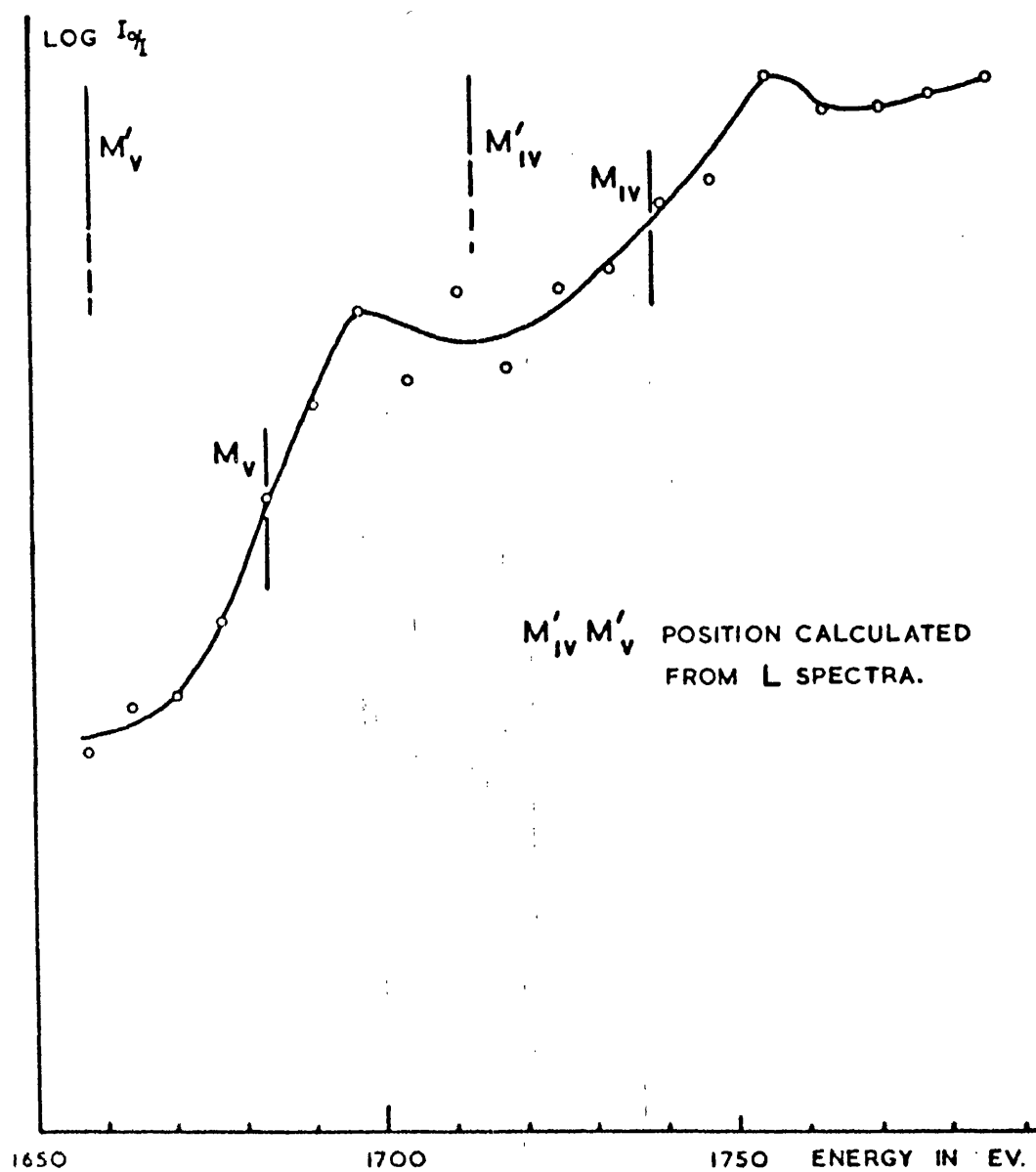
$$\log_e \frac{I_0}{I} = A\mu + B$$

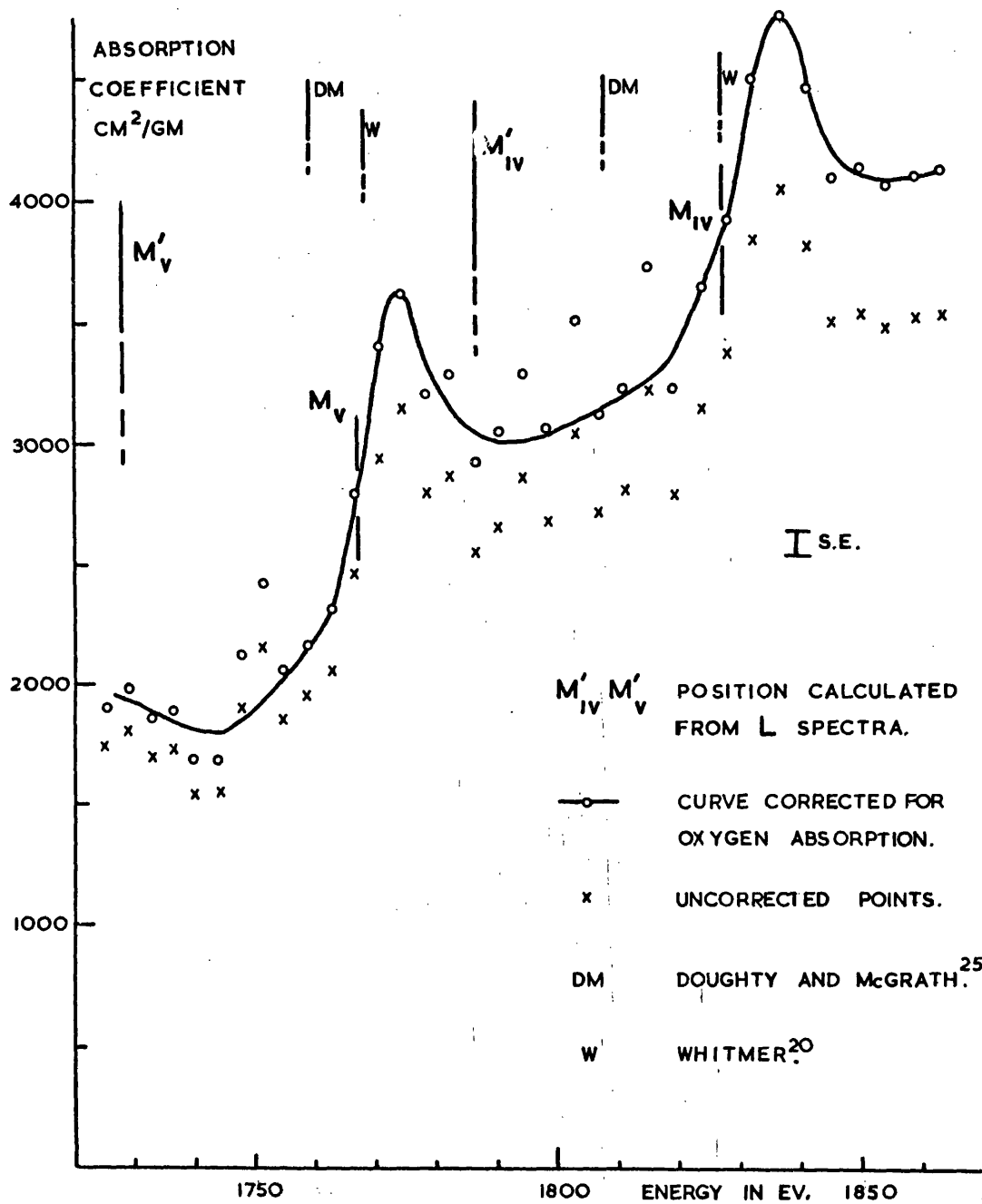
where A is the mass per unit area of hafnium, μ its mass absorption coefficient and B the sum of all such products for the other substances making up the foil. The term B will be a function of wavelength but an examination of a clear collodion film showed that this function was fairly uniform in the range of the hafnium edges. As both A and B are indeterminate for this absorption screen the value of μ cannot be obtained. A plot of the variation of the quantity on the left hand side of this equation is given in Figure 3.14.

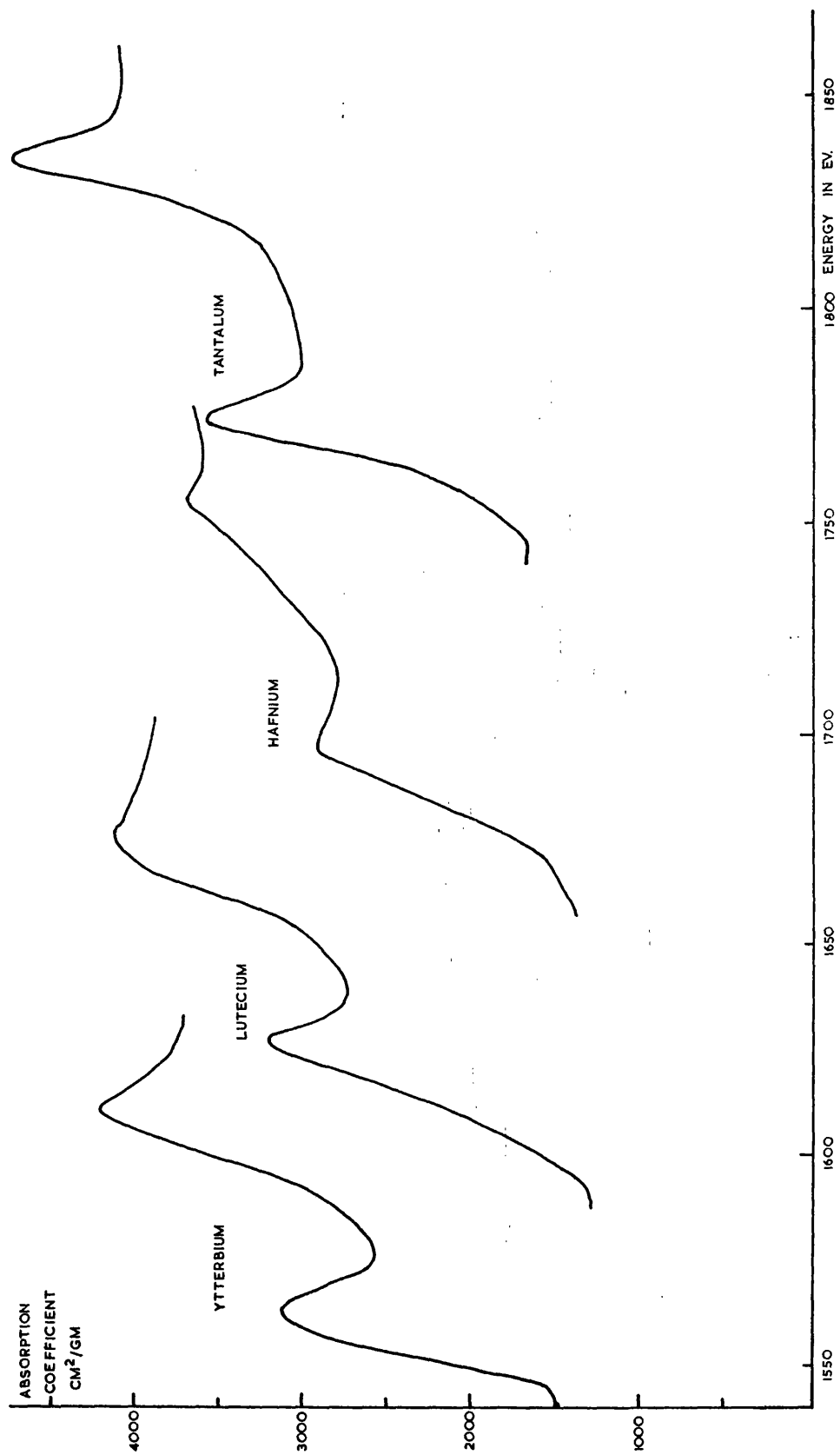
Tantalum.

The tantalum M_{IV} and M_V edges had been previously detected photographically by Whitmer²⁰ and by Doughty and McGrath²⁵; in each case metallic foils were prepared, but different wavelength values for the positions of the edges were obtained. In this investigation, tantalum oxide was used as absorber, being easier to evaporate than tantalum itself. The absorption curve for this compound and the curve corrected for oxygen absorption are shown in Figure 3.15. The positions of the edges as given in the two investigations referred to above are also indicated in the figure and the discrepancy between the three sets of results is discussed in the next chapter.

The M_{IV} and M_V edges of all four elements are plotted on a common energy scale in Figure 3.16. The scale of the ordinate

FIGURE 3.14 $M_{IV} M_V$ EDGES OF HAFNIUM OXIDE.

FIGURE 3.15 M_{IV} M_V EDGES OF TANTALUM.



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FIGURE 3.16 $M_{IV}M_V$ EDGES OF YTTERBIUM LUTECIUM HAFNIUM AND TANTALUM.

does not apply to the hafnium absorption curve which has been drawn in for completeness.

Foil Thicknesses.

The mass per unit area of each of the foils is listed below together with the standard error arising from the weighing technique.

Ytterbium fluoride	0.17	$\pm$	0.017	mgm/cm ²
Ytterbium metal	0.19	$\pm$	0.019	mgm/cm ²
Lutecium oxide	0.14*	$\pm$	0.017	mgm/cm ²
Lutecium fluoride	0.12	$\pm$	0.017	mgm/cm ²
Tantalum oxide	0.10	$\pm$	0.017	mgm/cm ²

*This figure includes an unknown mass of tantalum.

The standard errors in the weighing process are based on a survey of the weight of discs of melinex punched at random from a large sheet. However, a systematic study of discs cut from adjacent areas of plastic showed that short range fluctuations would give an error in the foil thickness of 0.01 mgm/cm². Thus it can be seen that the errors quoted in the list given above are probably somewhat exaggerated.

Wavelength and Energy Values.

The energy values quoted below were calculated from the wavelengths by means of the following equation

$$E = \frac{12372.44 \times 10^3}{\lambda(\text{in xu})} \text{ ev.}$$

in which the constant term is that given by Chupp et al⁵².

The method of calibration has been described above but it should be noted here that no account has been taken of the anomalous dispersion of the mica crystal. To correct for this effect the Bragg equation should be written

$$\lambda = \frac{2d_n}{n} \sin \theta + \frac{\Delta \lambda}{n^2}$$

For a particular crystal the term $\Delta \lambda$ is a function of wavelength only, which rises in sharp peaks in the vicinity of the absorption edges of the constituent elements of that crystal. However it does not rise above 0.5 xu and when divided by n^2 this factor becomes small by comparison with other errors.

The position of the absorption edge has come to be defined as its first point of inflexion. Although such a definition may seem somewhat arbitrary there has been some experimental justification in the work of Soules and Shaw⁵⁸ who found that for the K absorption of argon the inflexion point of the edge for the solid coincided with the peak of the first sharp absorption line for the gas. However estimation of this inflexion point is not always easy and so the error involved in determining the

wavelength position of the edge is probably much larger than the error in calibration. The wavelength and energy positions of the absorption structures measured in this study are given below together with the results of previous workers.

Ytterbium M_V line

This absorption line was found to be extremely sharp and so its position could be established as accurately as the calibration would allow. The estimated error in the wavelength is ± 0.5 xu which is equivalent to ± 0.2 ev for the energy.

Substance	Wavelength	Energy
Fluoride	8140.3	1519.9
Oxide	8139.6	1520.0

Previous measurements of this line were all made on the oxide and the following values were obtained:

Lindberg¹⁰ 8138 ± 1 xu : Zandy²⁸ 8136 ± 2 xu : Phakey²⁹ 8138 ± 1 xu.

Ytterbium M_{III} edge.

For the values stated for all edges the estimated errors are 2 xu for wavelength and 0.5 ev for energy.

Substance	Wavelength	Energy
Fluoride	6364	1944
Metal	6369	1942.5

The M_{IV} and M_V edges.

Substances	M_{IV}		M_V	
	λ	E	λ	E
Ytterbium Fluoride	7746	1597.3	7980	1550.4
Ytterbium Oxide	7749	1596.7	7987	1549.0
Ytterbium Metal	7815	1583.0	8055	1536.0
Lutecium Fluoride	7447	1661.7	7683	1610.3
Lutecium Oxide	7444	1662.0	7685	1610.0
Hafnium Oxide	7117	1738.5	7349	1683.5
Tantalum Oxide	6772	1827.0	7002	1767.0
Previous Results				
Whitmer ²⁰ Tantalum Metal	6773*	1827	6997*	1768
Doughty and McGrath ²⁵ Tantalum Metal	6854 ^x	1808	7033 ^x	1759

* ± 10 xu^x ± 5 xu

CHAPTER FOUR: DISCUSSION AND CONCLUSION

Ytterbium M_{γ} Absorption Line.

Ytterbium M_{III} Absorption Edge.

The M_{IV} and M_{γ} Absorption Edges.

Conclusion.

In this investigation both line and edge absorption have been studied. The difference in character between these two types of structure is determined by the degree of influence of the surrounding ions upon the ejected electron. In the first case the final state of the electron is an inner state which is shielded from the field of the other ions but in the second the final state is one which is associated with this field. For the rare earth elements the M_{IV} and M_V spectra consist of both line and edge absorption since for that series both inner and outer f type states exist. Mayer⁵³ has calculated the atomic eigenfunctions of 4f and 5f electrons and has shown that the effective potential in which such electrons move possesses two separate minima, one at a radial distance of the order of 6 Angstroms from the nucleus and the other much closer at about 0.2 Angstroms. For elements low in the Periodic Table the inner trough is hardly formed and consequently the lowest level for an f electron is situated in the outer trough. Here the potential is similar to that for hydrogen and hardly varies with atomic number. For heavier elements however the inner trough deepens until at the beginning of the rare earth series its first electron level becomes the lowest level of the whole system and so at this point there is a sudden shrinkage of the radius of the 4f orbit bringing it physically inside the atom which has a radius of about 1.8 Angstroms. Progressing to heavier elements the inner trough in the potential continues to sink until

at the beginning of the actinide series it is sufficiently deep to also contain the 5f electron states. Thus at this point a second rare earth series commences. Between these two series the 5f wave function for the free atom is similar to the 4f function for hydrogen with a mean radius of about 7 Angstroms. In a solid such functions will overlap considerably, producing a band of states belonging to a group of ions rather than just to one. The extent of this group is a matter for some debate which has given rise to two distinct theories; the long range order theory of Kronig⁷ and the short range order theory which has been reviewed by Kozlenkov⁵⁴. Discussion of these theories is taken up again below but for the present it can be concluded that the calculations of Mayer result in a picture of the f type states which is qualitatively consistent with the observations made in the present experimental investigation.

Ytterbium M_V Absorption Line.

The theory of the natural shape of absorption lines as presented by Condon and Shortley⁵⁹ shows that the transmitted intensity after traversing a thickness x of the absorber is given by

$$I(\sigma) = I_0 \exp. - \frac{\xi}{1 + (\frac{\sigma}{\sigma_0})^2} \quad (1)$$

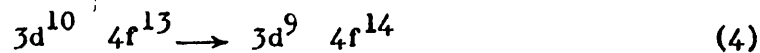
in which σ is the wave number of the radiation measured from the centre of the line, σ_0 a constant term characteristic of the particular line and ξ is given by

$$\xi = \frac{h\nu}{c} \frac{B(ba)}{\pi \sigma_0} N(b) x \quad (2)$$

In this expression $B(ba)$ is the probability of a transition from state b to state a , $N(b)$ the density of atoms in the initial state and $h\nu$ the energy of the absorbed quantum. Now the mass absorption coefficient is defined by the equation

$$I = I_0 \exp. -\mu m \quad (3)$$

where m is the mass per unit area of the absorber. In the region of the M_V line absorption this coefficient can be divided up into two parts; one related to the transition



and the other covering transitions from the N, O shells etc. The observed absorption coefficients once corrected for the absorption of fluorine (or oxygen) may be analysed into these two components (see Figure 4.1.) and if the maximum of the line absorption is considered, ξ may be evaluated from the following expression

$$\mu_{\max. m} = \xi \quad (5)$$

since $\sigma = 0$ in the middle of the line. A measurement of the width of the line at half maximum will yield the value of σ_0 and knowing these two quantities $B(ba)$ may be determined. However to make such a process meaningful a careful survey of the effect of absorber thickness on the dimensions of the absorption

line would have to be carried out in conjunction with a detailed analysis of the spectral response of the spectrometer. Work of this kind was not included in the scope of the present study and so the above is to be taken as an indication of the results that further investigation would achieve. The main purpose of the measurements on the M_V line was to demonstrate its magnitude for ytterbium in compound and its absence for ytterbium metal.

The electronic configurations of the rare earths have been summarised by Meggers⁵⁵ and more recently by Cabezas et al³⁷. From optical spectroscopic data it is concluded that the neutral atom of ytterbium has an outer configuration of $4f^{14} 6s^2$ whereas the triply ionised atom has only thirteen 4f electrons. In most compounds ytterbium is trivalent but magnetic studies on the metallic substance have shown that it is non paramagnetic indicating that there are no unpaired electrons. Thus in the metallic state the 4f shell is complete and only the two 6s electrons contribute to the band structure of the solid. However the above argument should only be taken to apply to the majority of atoms for in all the magnetic studies carried out so far some trace of paramagnetism has been detected. Spedding⁵⁶ concludes from his work that there is about one atomic percent of tripositive ions whereas Leipfinger⁵⁷ quotes 2% and Lock⁵⁰ estimates that only one atom in 270 possesses any permanent magnetic moment. An estimate of the number of tripositive ions in the pure metallic foil prepared during the present work may be obtained by an

analysis of its absorption curve. An examination of the equations (2) and (5) stated above shows that for the absorption line the maximum value of the mass absorption coefficient is proportional to the number of atoms in the initial state (b) required for the transition (ba), where the states for the transition discussed here are indicated in (4). If it is assumed that in the fluoride foil all the ytterbium atoms have only thirteen 4f electrons then a comparison between the maximum of the line absorption for the corrected fluoride foil and the maximum of that for the metal foil will give the fraction of triply ionised atoms in the latter. Thus

$$\frac{N(\text{Yb}^{3+})_{\text{metal}}}{N(\text{Yb})_{\text{metal}}} = \frac{N(\text{Yb}^{3+})_{\text{metal}}}{N(\text{Yb}^{3+})_{\text{fluoride}}} = \frac{x}{y}$$

where x and y are indicated in Figure 4.1.

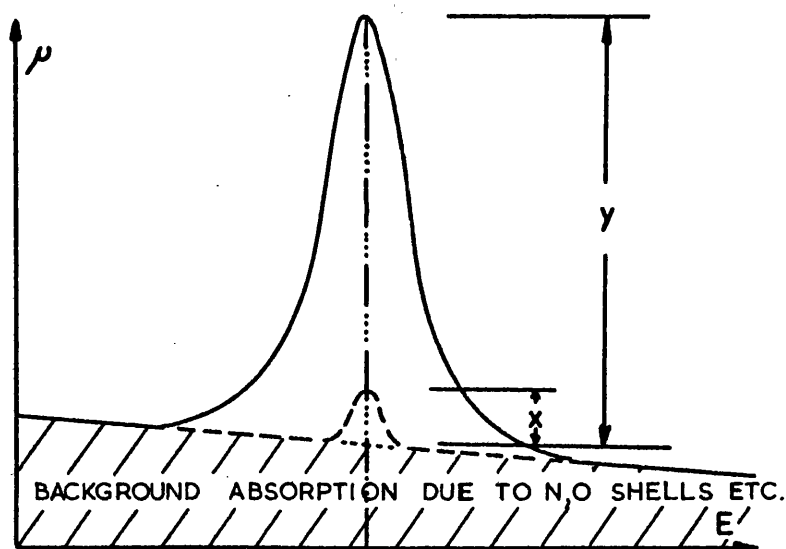


FIGURE 4.1. ANALYSIS OF M_v ABSORPTION LINE.

From equations (2) and (5) it can be seen that N refers to a number per gramme of ytterbium. The above process assumes that the general background absorption for the triply ionised atom is the same as that for the doubly ionised; however, from the absorption curves shown in the last chapter it can be seen that such an assumption is reasonable. An analysis of this type was carried out on these absorption curves and the values of x and y obtained were as given below

$$x = (1940 - 1750) \text{ cm}^2/\text{gm}$$

$$y = (20028 - 1750) \text{ cm}^2/\text{gm}$$

These results indicate that about one atom in a hundred of the metal foil contained a gap in the 4f shell, a figure which is consistent with those obtained for other samples of metallic ytterbium in the magnetic studies mentioned above.

Ytterbium is also found to be divalent in some compounds, for example YbS, YbSe and YbTe. However, the only one of these to be studied in detail is YbS and for that Domange et al⁶⁰ have found by chemical analysis that its stoichiometry should be written $\text{Yb}_{0.9}\text{S}$ which would require that 39% of the ytterbium atoms were tripositive. From magnetic measurements they conclude that 41% of the atoms are in this state. The magnitude of the M_V absorption line of trivalent ytterbium makes its measurement for a particular compound an extremely sensitive test for the presence of atoms in such a state. If it is possible to prepare

them in a suitable form this test could be usefully applied to the compounds mentioned above.

The classical dispersion theory applied to Xrays⁴⁶ predicts that absorption should take the form of resonance lines and, although this prediction is generally untrue in the case of ytterbium M_V absorption, it has some value. From this theory it can be seen that associated with such an absorption line is an anomaly in the refractive index. Such phenomena are common in optical spectra, but rare in the Xray region and of considerable interest by virtue of the fact that in a narrow wavelength range the refractive index of the absorbing medium, which is normally almost equal to one, becomes appreciably less than unity and in consequence the critical angle for external reflection increases to as much as five degrees. Thus an Xray beam reflected at such an angle would be monochromatic to an extremely high degree since very little reflection of other wavelengths would take place. Preliminary measurements on the reflection of Xrays by ytterbium fluoride carried out by Underwood⁶¹ in this laboratory indicate that such an increase in the critical angle does in fact occur.

For the absorption profile of ytterbium metal in the region of the M_V absorption line a small structure was observed to the high energy of the position of this line. This structure consisted of one very small maximum adjacent to the line at an energy of

1520.4 ev and a larger maximum further removed at 1522.1 ev.

Calculations of the energy of the $3d \rightarrow 5d$ and $3d \rightarrow 6p$ transitions, based on the position of the M_{iii} edge ($3p \rightarrow 5d$) obtained in this investigation, were made in the following manner. The observed position of the M_{iii} absorption edge of ytterbium metal indicated that the energy of the $3p \rightarrow 5d$ transition was 1942.5 ev. The calculated energy of this edge was obtained using data on the L spectra of ytterbium given by Sandström³⁶. For such a calculation the $M_{iii} \rightarrow L_i$ (β_3) emission line must be used in conjunction with the L_{iii} absorption edge. Thus, in order to obtain the energy of the $3p \rightarrow 5d$ transition, the energy difference between the L_i and L_{iii} levels must be found. This can be done in several ways, but of these the two involving the α_1 , β_9 and α_2 , β_{10} L emission lines were chosen as most reliable. The energy of the M_{iii} edge was then found by means of the following equations.

$$\beta_9 \qquad \alpha_1 \qquad \beta_3$$

$$(M_{iii})_{abs} = (L_{iii})_{abs} + (M_{iv} \rightarrow L_i)_{em} - (M_{iv} \rightarrow L_{iii})_{em} - (M_{iii} \rightarrow L_i)_{em}$$

and

$$\beta_{10} \qquad \alpha_2 \qquad \beta_3$$

$$(M_{iii})_{abs} = (L_{iii})_{abs} + (M_{iv} \rightarrow L_i)_{em} - (M_{iv} \rightarrow L_{iii})_{em} - (M_{iii} \rightarrow L_i)_{em}$$

In electron volts these equations become

$$8944.15 + 8959.69 - 7415.57 - 8536.84 = 1951.43$$

$$8944.15 + 8910.01 - 7367.09 - 8536.84 = 1950.23$$

giving a mean value for the $3p \rightarrow 5d$ transition of 1950.83 ev.

The difference between this value and the present experimental value is 8.33 ev and so in order to bring the calculated energy of the $3d \rightarrow 5d$ transition into agreement with the observed M_{iii} edge, this quantity was subtracted as indicated in the equation below

$$\begin{aligned} (3d \rightarrow 5d) &= (L_{iii})_{\text{abs}} - (M_v - L_{iii}) - 8.33 \text{ ev} \\ &= 1520.26 \text{ ev.} \end{aligned}$$

The energy of the $3d \rightarrow 6p$ transition was obtained from this value by adding the 5d, 6p energy difference, which was taken as the difference between the observed L_i edge ($2s \rightarrow 6p$) and that calculated on the basis of the observed L_{iii} edge (ie. equivalent to $2s \rightarrow 5d$). This difference was found to be 2ev. Thus the calculated energies for the two transitions are

$$(3d \rightarrow 5d) = 1520.3 \text{ ev}$$

$$(3d \rightarrow 6p) = 1522.3 \text{ ev}$$

The agreement between these values and those observed for the

two small maxima indicates that this structure represents the onset of the M_V edge absorption. However, the transition probability is here very small, especially for the first (quadrupole) transition, and so this absorption is dwarfed by that due to transitions into the f states.

Ytterbium M_{III} Absorption Edge.

The M_{III} edge is due to the transition of a $3p$ electron into d type states and so in the case of ytterbium the energy of the edge should be governed by the transition $3p \rightarrow 5d$. The position of this edge was investigated and a comparison made between the structure found with a metallic absorber and that found with one of ytterbium fluoride. One reason for this study was connected with the interesting conduction properties of ytterbium metal. An isolated neutral ytterbium atom has a closed shell structure and so in the metal some overlap of bands must occur to provide carriers for conduction. Anderson et al⁶² have shown that this metal has a positive Hall coefficient which indicates that the principal conduction carriers are holes. A possible explanation of this observation is that overlap occurs between the $6s$ and $5d$ states leaving an s band with about 0.7 holes per atom and a d band with the same number of electrons per atom. This would lead to the possibility of some slight absorption due to the transition of $3p$ electrons into the holes in the s band. Such absorption would occur immediately to the low energy side of the M_{III} edge. The absorption curves shown in Figure 3.10 indicate

that there is a slight difference between the structure on the low energy side of the edges of the two substances. However the work on this aspect cannot be taken as conclusive. In order to gain comprehensive information about the filled and unfilled outer s and d states a much more detailed study of the absorption structure is required together with a measurement of the emission profile associated with the M_{iii} edge.

The M_{iv} and M_v Absorption Edges.

In the survey of previous work, which was given in the first chapter, mention was made of the discrepancy between the observed wavelengths of M_{iv} and M_v edges and those calculated from L spectra. Such calculations are usually based on the L_{iii} edge since its wavelength position is probably established with greater accuracy than the other two. For the elements studied in the present work the L_{iii} edge commences with a transition of a 2p electron into the 5d level. The validity of this statement can be seen from the points plotted in Figure 4.2. In this graph the ordinate is $\Delta \nu_R$ calculated from the following expression

$$\Delta \nu_R = \left[\nu_R \right]_{(L_{iii}) \text{ abs.}} - \left[\nu_R \right]_{(X_{iv,v} \rightarrow L_{iii}) \text{ em.}}$$

where X is successively N, O, and P. By this means it is shown that for elements of atomic number in the range 40 to 47 the end level of the L_{iii} absorption transition is $N_{iv,v}$ (4d); for elements in the range 63 to 79 it is $O_{iv,v}$ (5d); and for those

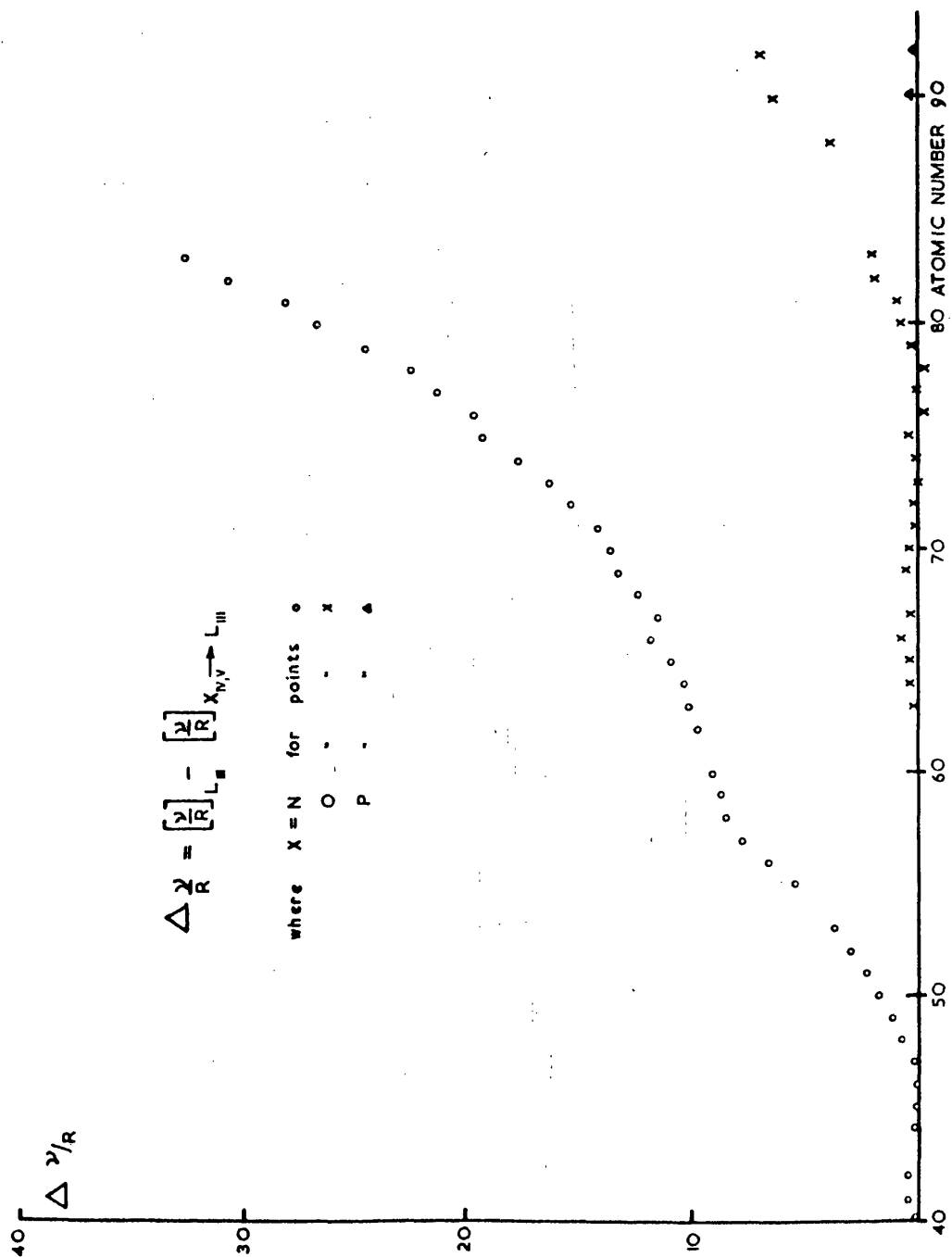


FIGURE 4.2 GRAPH ILLUSTRATING END LEVEL OF L_{III} ABSORPTION PROCESS.

above 90 it is $P_{iv,v}$ (6d). In the case of the M_{iv} and M_v spectra of ytterbium, lutecium, hafnium and tantalum, however, the probability of a transition into the $O_{iv,v}$ level is extremely small as is the probability of a transition into the next outer level (6p). In fact a transition from the 3d level will only be appreciable if the end level is f type and apart from ytterbium the first level of this symmetry, for the elements listed above, will be the band which is formed from the 5f atomic levels. For trivalent ytterbium there is an inner 4f vacancy giving the line absorption discussed above but the edge absorption will arise from the transitions into the 5f band. In this way the discrepancy between the observed and calculated positions of the M_{iv} and M_v edges has been qualitatively explained in the works of Phelps²², McGrath²⁴, Cauchois⁶⁴, and Friedel⁶³. For elements heavier than osmium (76) this discrepancy decreases until at about radium (88) it vanishes and then goes negative as would be expected since here the second rare earth series commences and the 5f level becomes an inner level in the same way that the 4f level is an inner level for lanthanides. For this latter series Stewardson and Zandy²⁹ have reported that measurement of the discrepancy with respect to spectra associated with 3d $\rightarrow$ 4f transitions also gives negative values. The wavelength values from previous measurements on the M edges of the heavy elements are given in Table 1. From the most recent results on the M_{iv} and M_v edges values of the discrepancy have been calculated in electron volts, employing the

TABLE 1. Wavelengths in K x u of M edges of heavy atoms.
A survey of previous results.

Element	M _v	M _{iv}	M _{iii}	M _{ii}	M _i	Reference
73 Ta	6.997	6.773	5.647			20 *
	7.033	6.845				25 *
74 W		6.487	5.427			10
	6.708	6.475	5.418	4.800	4.365	16 *
76 Os	6.194	5.975	5.027	4.412	4.037	17 *
77 Ir	5.961	5.754	4.851	4.270		17 *
78 Pt	5.736	5.541	4.674		3.738	17
	5.747	5.545	4.676			10 *
	5.711	5.506	4.677	4.085	3.742	18
79 Au	5.529	5.330	4.508			10
	5.506	5.315	4.501		3.603	18
	5.529	5.336	4.516			21
	5.579					23
	5.522	5.318				24
	5.521	5.321	4.509			26 *
80 Hg	5.331	5.139	4.340			10 *
81 Tl	5.136	4.936	4.185			10
	5.137	4.934	4.187			21 *
	5.147					23
82 Pb	4.945	4.747	4.033			10
				3.469	3.219	24

TABLE 1. (continued)

Element	M _v	M _{iv}	M _{iii}	M _{ii}	M _i	Reference
82 Pb	4.944	4.750	4.030			21 *
	4.954					23
83 Bi	4.762	4.569	3.894			14
	4.762	4.568	3.893			10
	4.763	4.574	3.889	3.342	3.100	22 *
	4.762	4.567	3.897			21
	4.763					23
90 Th	3.721	3.552	3.058			13
	3.721	3.552	3.058	2.571	2.388	15
	3.715	3.545	3.062			10
	3.722	3.549				23 *
				2.571	2.388	14
91 Pa	3.601	3.429				30 *
92 U	3.391	3.326	2.873			13
	3.382	3.320	2.877			10
				2.385	2.228	14
	3.491	3.326				23 *
94 Pu	3.278	3.117	2.709	2.229	2.087	31
	3.320		2.716		2.113	38

* values used in the calculation of $\delta(h\nu)$. (see below)

conversion factor given in the last chapter. For this calculation the general expression given below was used.

$$\delta(h\nu) = (M_{IV,V}) \text{ abs.} - (L_{III}) \text{ abs.} + (M_{IV,V} \rightarrow L_{III}) \text{ em.}$$

This expression is illustrated schematically in Figure 4.3. The values of $\delta(h\nu)$ obtained from the previous results are given in Table 2 together with those obtained from the present work. The data on the L spectra was taken from the tables given by Sandström³⁶.

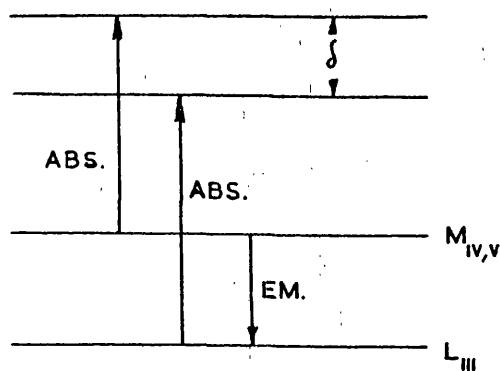


FIGURE 4.3. SCHEMATIC ILLUSTRATION
OF DISCREPANCY.

Very little theoretical work on this discrepancy is to be found in the literature. To date the calculations of Friedel⁶³ stand alone. This author used the Wigner-Seitz method to compute the energy difference between the top of the conduction band and the bottom of the 5f band for tungsten, gold, lead and radium. The values so obtained are plotted in Figure 4.4 in comparison with those listed in Table 2, and it can be seen that there is good agreement between the theoretical and experimental values.

TABLE 2. The M_{IV} , M_V edge discrepancies in ev.

Element	$\delta(h\nu) M_V$	$\delta(h\nu) M_{IV}$
Present Work		
Yb (compound)	+21.1	+20.0
Yb (metal)	+ 7.4	+ 5.9
Lu	+23.4	+24.1
Hf	+24.8	+25.4
Ta	+38.6	+40.6
Previous Work		
Ta ²⁰	+39.8	+40.1
Ta ²⁵	+30.8	+20.9
W	+40.2	+44.1
Os	+42.8	+45.4
Ir	+39.8	+37.9
Pt	+38.6	+36.6
Au	+34.7	+33.9
Hg	+23.2	+18.4
Tl	+20.8	+23.9
Pb	+13.9	+13.7
Bi	+14.4	+13.6
Th	- 6.4	- 2.2
Pa	- 7.5	- 2.0
U	- 5.9	- 5.3

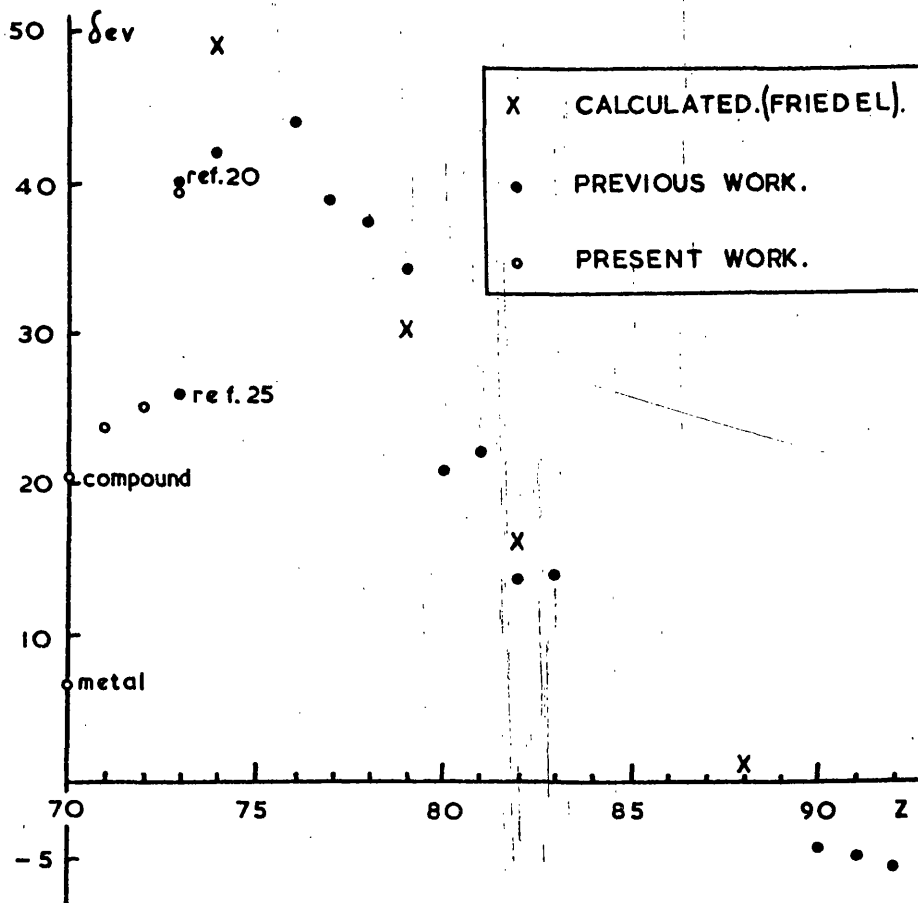


FIGURE 4.4. EXPERIMENTAL VALUES OF $\delta(h\nu)$.

The method adopted by Friedel amounts to the treatment of the observed M_{IV} and M_V edges as Kronig structure on the real edge, where the real edge is taken to commence with a transition into the first available level. The transition probabilities are such that the magnitude of this structure is far greater than that of the so called real edge. Such an argument seems to be valid as far as the present measurements on ytterbium are concerned, for as has already been mentioned a small structure in the position of the real edge was in fact observed. There is some doubt

however that structure in the absorption profile so near to what has been described as the real edge can be thought of as Kronig structure. That is to say that the final state of the electron is probably not a lattice state but one in a much more localised region. In this case the short range order theory should be applied. In this theory the ejected electron is described by a wave packet rather than by an unlimited plane wave passing through the lattice. It is considered that this electron wave is scattered by the potential of the absorbing atom and its surrounding ions and interference between the primary and scattered wave produces variations in the amplitude of the final state wave function in the vicinity of the absorbing atom. This amplitude, which governs the magnitude of absorption, is dependent upon the nature of the potential of the absorbing atom, the potential and distance of the surrounding ions and the symmetry of the initial state function. As Kozlenkov⁵⁴ has pointed out, in this theory a spherical approximation is made whereby the scattering potential is regarded as radially symmetric. Thus the ions surrounding the absorbing atom are smeared out over the surface of a sphere and the total potential then becomes the sum of that due to the absorbing atom and that due to all the surrounding concentric layers. From this it can be seen that in such a theory the final energy state of the electron is independent of the direction in which it is ejected. This is not the case for the long range order theory of

Kronig⁷ and, with regard to this fundamental difference between the two theories, Boster and Edwards⁶⁵ have performed some interesting experiments of the K absorption edge of a single crystal of copper. As they have pointed out, the theory of Kronig predicts that the use of a metallic single crystal absorber and polarised Xradiation should result in a more pronounced extended structure on an absorption edge than would be observed with a polycrystalline absorber and unpolarised radiation. Further, rotation of the crystal in the plane of the polarised Xrays should, according to this theory, produce a shift in the energy positions of the absorption maxima and minima. However the results obtained with copper showed that these two effects were only appreciable at energies over 230 ev higher than the actual edge. Thus it appears that the long range order theory is only really applicable to absorption structure well removed from the edge. Nearer to the edge the short range order theory seems to produce results more in agreement with experimental observations (Kostarev⁶⁶, Shiraiwa et al⁶⁷ and Hayasi⁶⁸). In the long range order theory it is assumed that the ejected electron moves freely within the crystal, an assumption which does not seem justifiable except for electrons with fairly large kinetic energy. Less energetic electrons fail to really escape from the field of the absorbing atom. Shiraiwa et al⁶⁷ attributed the restriction of the free path of the ejected

electron to inelastic collisions with the surrounding ions and Kozlenkov⁵⁴ suggested that further limitation may arise from interactions with the lattice electrons. It is this difference in the physical basis of the two theories which appears to define their range of applicability. At first sight the good agreement between Friedel's calculations and experimental observations may be taken to indicate the validity of the long range order theory in this region, but although this author suggested that the M_{IV} , M_V edges were Kronig structure he did in fact employ the tightly bound electron approximation in his calculation. This approximation is based on atomic wave functions and consequently closer to the short range order theory. As has been pointed out above there is need for more theoretical work on the absorption structure in the region of the M_{IV} and M_V edges of the heavy elements and from this discussion it seems that in the performance of such work the short range order theory of X-ray absorption structure should be used.

It is of interest to note that a discrepancy similar to the one discussed above would be expected to occur for the elements just below the rare earth series. For these elements the 4f level is an outer level just as the 5f level is an outer level for the elements before the actinide series. Very few absorption measurements have been made on the M_{IV} and M_V edges in this region but it is possible to find some indication of

the discrepancy in the work of Prins and Taken⁷³ and of Russell²⁹. The values of $\delta(h\nu)$ obtained from their results are given below in Table 3.

Table 3.

M_{IV} M_V edge discrepancy below rare earths (in eV)

	Prins and Taken				Russell	
	47Ag	48Cd	50Sn	53I	56Ba	57La
M_{IV}	+30.4				+1.6	-6.0
		(+32.5)	(+21.8)	(+3.5)		
M_V	+32.2				+9.9	-3.3

From this table it can be seen that the discrepancy decreases towards the rare earth series, going negative at lanthanum.

The most important factor contributing to the field in which an ejected electron moves is the potential of the absorbing atom, and consequently an indication of the behaviour of the absorption coefficient may be obtained from calculations based on the free ion. Calculations of this type have been carried out for ytterbium in the region of the M_{IV} and M_V edges by Weinmann⁶⁹. In this work the self consistent field and wave functions for 69 Tm^{3+} given by Ridley⁷⁰ were used, the field

being modified to approximate to that of ytterbium. The curve obtained from these calculations indicates that, passing through the region in the direction of increasing photon energy, the absorption coefficient gradually increases until midway between the M_{III} and M_{IV} edges where it goes through a maximum. The curve is without structure, but this is to be expected since such structure arises from the influence of the surrounding ions which here have been neglected. A comparison between the theoretical and experimental curves is shown in Figure 4.5 which also shows the curve calculated by Weinmann⁶⁹ from a screened hydrogenic approximation. From this figure it can be seen that, for the approximations made in the modified Tm^{3+} curve, the agreement between theory and experiment is good.

The energy difference between the M_{IV} and M_V levels of an atom can be calculated from L emission spectra by use of the following energy equation

$$\Delta M_{IV,V} = L\alpha_1 - L\alpha_2$$

and the values so obtained, compared with those from direct measurement of the position of the M_{IV} and M_V edges. Such a comparison is made for the results of the present study in Table 4.

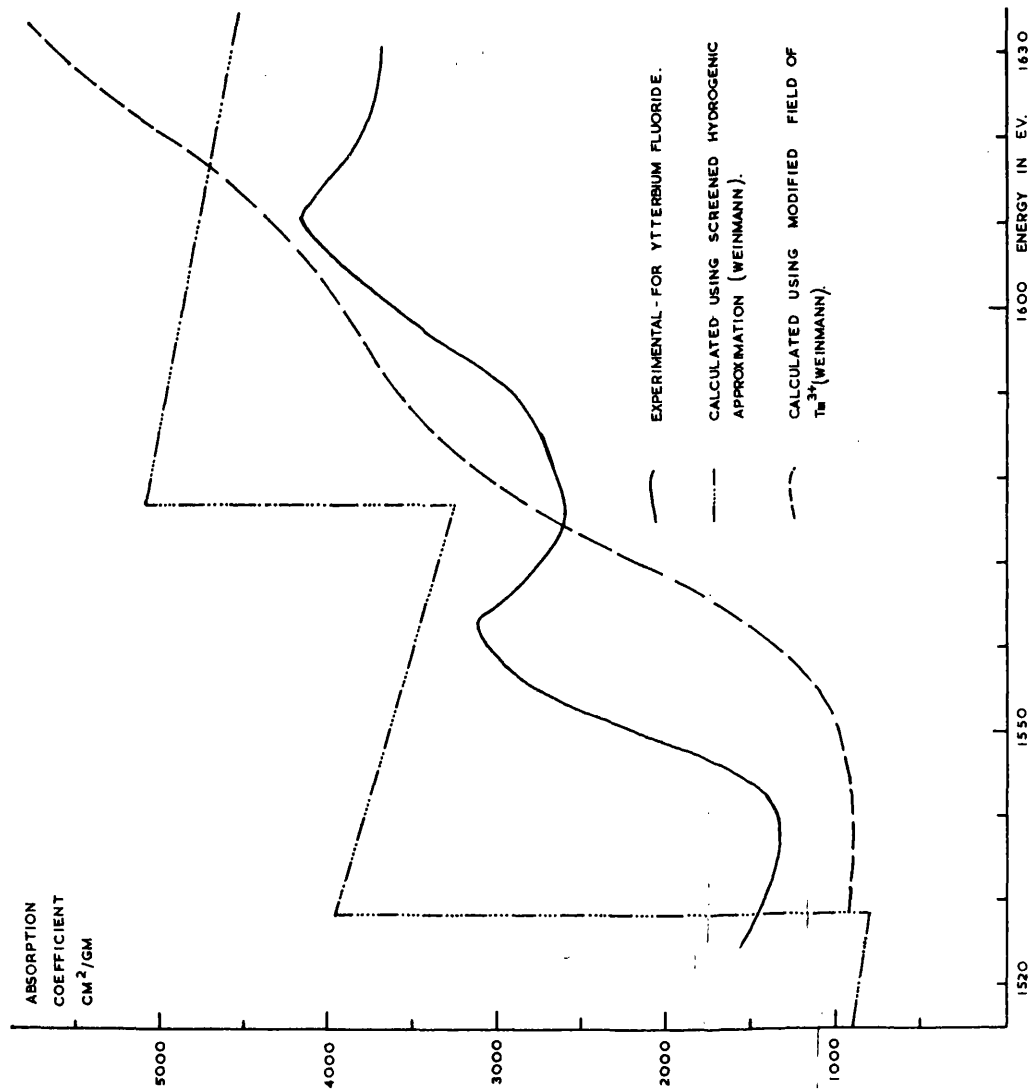


FIGURE 4.5 COMPARISON BETWEEN THEORY AND EXPERIMENT FOR YTTERBIUM ABSORPTION

Table 4.

The energy difference between the M_{IV} and M_V levels.

Substance	$\Delta M_{IV,V}$ (ev)	
	Experimental	Calculated
Ytterbium fluoride	46.9	
Ytterbium oxide	47.7	48.5
Ytterbium metal	47.0	
Lutecium fluoride	51.4	
Lutecium oxide	52.0	51.0
Hafnium oxide	55.0	54.4
Tantalum oxide	60.0	58.2

The error in both experimental and calculated results is of the order of ± 1 ev. In making this comparison it is assumed that the end levels for the M_{IV} and M_V absorption processes are the same, but from the agreement between the two sets of values this assumption seems to be justified.

In the measurement of the M_{IV} and M_V edges for ytterbium metal it was found that they were placed some 14 ev to the low energy side of those observed for the fluoride. For the energy of an absorption edge in a crystalline substance Pauling⁷¹ has written the following expression

$$h\nu_{\text{abs}} = h\nu_0 + e\phi - E_{\text{crystal}}$$

The three terms on the right hand side are respectively the energy

of the edge in the free ion; the energy of an electron in the field produced at the centre of the absorbing atom by the surrounding ions; and the electron affinity of the crystal. This equation is really only of use in comparing the energy of an absorption edge of the same ion in different compounds, whereas the essential difference between the absorption for ytterbium metal and that for the fluoride is a difference in the first term of this expression. For, as has been indicated above, the ions in the metal are dipositive while those in the fluoride are tripositive. Considering the observed M_{IV} and M_V absorption edges on the basis of the short range order theory such a change in the field of the absorbing atom can be expected to have a considerable effect on the position of these structures. A similar shift in absorption edge has been observed by Beeman et al.⁷² for copper in the divalent and monovalent states. The K absorption edge of hydrated Cu^{++} was compared with that for the cuprous halides and a shift of about 10 ev observed. Between individual halides however the variation in position was less than 2 ev. The comparison between copper and ytterbium in this respect is a good one since in both cases, going from the lower to the higher state of ionisation involves removing an electron from an otherwise filled shell, the 3d shell of the former and the 4f shell of the latter. For ytterbium it was also observed that the difference between the position of the edges for the fluoride and the oxide was only of

the order of 1 ev, and so it can be seen that the nature of the field of the absorbing atom is the principal factor governing the position of absorption structure.

The measurement of the tantalum edges was carried out in order to compare the structures observed in this work with those of previous experiments. The position of the edges was found to be fairly close to those reported by Whitmer²⁰ and consequently in disagreement with those observed by Doughty and McGrath²⁵. In the present study tantalum oxide was used as absorber whereas in both of the previous investigations foils of tantalum metal were prepared by evaporation. It is extremely difficult, however, to prepare an oxide free tantalum foil and so it is to be expected that in both these cases some oxide was present. A possible explanation of the different results is that the positions of the edges for the metal and oxide differ and that Whitmer's foil contained a considerable amount of oxide whereas that of Doughty and McGrath was comparatively pure metal. This explanation can only be tested by a study of carefully prepared metallic foils. It should be noted here however that the $\Delta M_{iv,v}$ for the results of Doughty and McGrath is of the order of 10 ev smaller than the value calculated from L emission data, which seems to indicate some uncertainty in the placing of the edges in that investigation. In view of the observed shift in the edges for ytterbium and the possibility of a similar shift for tantalum an extensive

metal-compound comparison for the elements in this region is obviously desirable. Unhappily the preparation of such metal foils presents an extremely difficult problem.

Conclusion.

The results of the present experimental work on the M_V absorption line of ytterbium in the pure metal and in compound are consistent with the theory that for the rare earth elements these lines are due to transitions into vacancies in the 4f shell. The more directly quantitative qualities of counter, as opposed to photographic, detection have enabled a comparison to be made between these results and those of the magnetic studies of Lock⁵⁰ and others^{56,57}. Such a comparison clearly indicates the validity of the above theory.

The measurements on the M_{IV} and M_V edges of ytterbium show that edge absorption does occur for the rare earths but that the magnitude of this structure is much less than that of the absorption lines. From these measurements and those on the M_{IV} and M_V edges of lutecium and hafnium it was found that, in agreement with the previous work on other heavy elements, there was a discrepancy between the observed positions of the edges and those calculated from L spectra, and that this discrepancy decreased from tantalum to ytterbium. The detection of these edges for ytterbium, lutecium and hafnium is a measure of the sensitivity of the counter technique since in previous

photographic work carried out in this laboratory these structures had proved undetectable.

An examination of the M_{IV} and M_V edges for ytterbium metal has revealed a shift in position with respect to those observed for ytterbium fluoride and this shift has been attributed to the difference in the valency of the ytterbium atom in these two substances. Bearing this shift in mind it has been possible to suggest an explanation for the different results for the positions of the tantalum edges which have been reported.

A study was made of the M_{III} absorption edge for ytterbium metal and fluoride and some indication of the validity of the theory that the conduction carriers in ytterbium metal are holes in the 6s band was obtained.

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