THE X-RAY M_{V'}_{IV} SPECTRA OF CERIUM AND XENON

by

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ABSTRACT

Using a high-resolution curved crystal spectrometer of the Johann type with a fine focus x-ray source, the $M_{V', IV}$ absorption spectra of metallic cerium, cerium silicide, cerium fluoride, cerium oxide and xenon have been presented. Using the same spectrometer with a normal, point emission source, the $M_{\alpha', \beta'}$ emission spectrum of cerium oxide has also been examined.

For metallic cerium, by comparing the $M_{V'}$ and $M_{IV'}$ absorption lines obtained at 22°K with those obtained at room temperature, the mechanism of the $\gamma \rightarrow \alpha$ phase transition in cerium has been discussed.

Cerium oxide was found to exhibit an anomalous $M_{V', IV}$ absorption spectrum. Two extra peaks, one connected with $M_{V'}$ and the other with $M_{IV'}$, have been observed to occur in the spectrum. A suggestion has been made to account for these features. Measurements on the $M_{V', IV}$ absorption spectra of oxidized metallic absorbers have indicated that cerium oxide (CeO$_2$) results when the metal is oxidized in air, but oxidation in oxygen results in either Ce$_2$O$_3$ or a metallic sample covered with a protective layer of Ce$_2$O$_3$.

The measurement of $M_{V', IV}$ absorption in solid xenon has been performed and the resulting spectrum has been compared with that for the gas. The spectrum is dominated by two delayed, strong peaks arising from the transitions $3d \rightarrow \epsilon f$ as for the gas. In the solid, in the region of strong peaks there are also observed remarkable modulations in the absorption coefficient which are discussed as EXAFS.
ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1. X-ray Emission and Absorption Spectra

2. X-ray Absorption Fine Structure.


4. γ→α Phase Transition in Cerium Metal.

5. Present Work.
1. X-RAY EMISSION AND ABSORPTION SPECTRA.

In general, x-rays are produced by two distinct processes, either as Bremsstrahlung or as characteristic x-rays. Bremsstrahlung has a continuous spectrum and is known to arise as a result of the acceleration or deceleration of charged particles, such as electrons. The energy distribution and intensity of Bremsstrahlung from a solid, produced by electron bombardment, vary only gradually from one element to the next. Alternatively, when an atom is ionized in one of its core levels by electron bombardment or by an incident photon, a characteristic x-ray photon is emitted following the transition of an electron from an outer level into the inner hole. The x-rays produced in this way are sharply characteristic of the material. In the case of solids, valence electrons are also available for transitions to the core holes giving their excess energy away as x-ray photons. The spectra of these photons are called valence band emission spectra; they give a direct view of the density of occupied states distribution providing that the initial core level is well localized and sharp. However, the intensity of valence band emission is not only a function of the density of states, but it is also a function of the transition probability as first suggested by Jones and Mott (1); their equation is

\[ I(E) \propto P(E) \cdot N(E) \]  

where \( I(E) \) is the intensity of the emission, \( P(E) \) is the transition probability, and \( N(E) \) the density of states distribution. Therefore, the density of states distribution cannot be obtained directly from \( I(E) \) unless the function \( P(E) \) is known, or is assumed to be constant.

X-ray absorption is described as the attenuation in the intensity of the incident x-ray beam as it traverses matter of a certain thickness. In general, photo-electric absorption is the predominant absorption mechanism in which an x-ray photon gives up its energy to ionize an atom in one of its core levels, i.e., knocks out an electron from its...
orbital leaving the atom in an ionized state. Scattering processes make little contribution to the attenuation of x-rays except for wavelengths shorter than 0.5\(\AA\) and for elements of low atomic number (2).

The absorption of x-rays may be formulated in the following way: suppose that an incident x-ray beam of intensity \(I\) is reduced by an amount \(dI\) on passing through a thin homogeneous layer of thickness \(dx\). Then,

\[
- \frac{dI}{I} = \mu dx
\]

where \(\mu\) is known as linear absorption coefficient. After integration of equation (1) over the total thickness of the absorber

\[
I = I_0 e^{-\mu x}
\]

where \(I_0\) is the intensity of the x-ray beam incident on the absorber of total thickness \(x\). Equation (3) may be rewritten as

\[
I = I_0 e^{-\frac{\mu}{\rho} (px)}
\]

where \(px\) is the mass per unit area of the absorber and \(\mu/\rho\) is the mass absorption coefficient. This latter quantity is usually tabulated instead of \(\mu\) because absorbing screens are conveniently measured in terms of mass per unit area rather than thickness, especially when the thickness is very small. \(\mu/\rho\) depends on the chemical state of an element but not on the mechanical dispersion of the material.

For cerium atom, a plot of mass absorption coefficient against photon energy, \(h\nu\), is shown in figure 1.1 for a wide energy range (3). It shows a typical series of absorption discontinuities corresponding to photon energies which are equal to the binding energies of the electrons in various inner levels. These discontinuities are called absorption edges which are labelled according to the initial level involved in the absorption, such as K, L_I, L_{II}, L_{III} etc. The absorption decreases with increasing energy of incident x-rays until an absorption edge is reached where the photons have just sufficient energy to ionize electrons in this level, resulting in a sharp increase in the absorption. After
FIGURE I.1  K, L_I, L_{II} AND L_{III} ABSORPTION EDGES OF CERIUM (Ref. 3)
this edge the absorption decreases again as before the edge. In the
region between two absorption edges, the absorption is empirically
found to decrease as $\nu^{-3}$ for photo-absorption, $\nu$ being the frequency
of the incident x-rays\(^{(2)}\).

2. X-RAY ABSORPTION FINE STRUCTURE

An electron ejected from a free atom by a photon of energy $h\nu$
leaves the atom with a kinetic energy

\[ E_K = h\nu - E_B \]

where $E_B$ is the binding energy of the electron. Electrons with kinetic
energies $E_K > 0$, i.e., $h\nu > E_B$, are called "free". Such electrons from
free atoms are not subject quantization, therefore, all energies are
allowed, the result being a continuum. An electron may also go to one
of the normally unoccupied optical levels as first suggested by KOSSEL\(^{(4)}\),
providing that the selection rules for such a transition are satisfied.
The excited electron is bound in one of these states with an energy
which depends on the screening effect of the inner hole. These levels
are extremely sharp, closely spaced and form a converging series of
states in the region between the normally outermost filled level and
the ionization limit.

The above model is strictly applicable to free atoms, such as
monoatomic gases. This was first shown experimentally by PARRATT\(^{(5)}\)
for the K absorption spectrum of argon gas. As may be seen from figure
1.2, the first two members of the series corresponding to the allowed
transitions of the potassium atom 1s-4p and 1s-5p are clearly resolved,
the others are submerged in the continuum. Since the suggestion of
KOSSEL, any structure observed near the main absorption edges for
monoatomic gases, like that shown in figure 1.2, for polyatomic gases
and for solids has been known as Kossel structure.
FIGURE 1.2  K ABSORPTION EDGE OF GASEOUS ARGON (After Parratt)
In the solid state, when the atoms are close to each other, that is the interatomic distances are comparable to the orbital dimensions of the outer electrons, the interaction between atoms must be taken into account. The potential of the system now includes additional terms due to interaction with the electrons and nuclei of adjacent atoms. These additional terms in the potential of the system perturb the energy levels resulting mainly in a broadening. The most tightly bound electron orbitals are least affected, so that it can be assumed that these energy levels have the same width as in a free atom. In order to understand to what extent the outer electronic levels are affected by the neighbouring atoms, consider a solid consisting of N non-interacting atoms located in a crystal lattice. Then a given level of one of these atoms would be a member of an N-fold degenerate set of levels of the systems. As the interactions are allowed to set in, this N-fold degenerate state splits into a set of N different levels forming an energy band. The spread in energy, or the width of the band, depends on the interatomic distance, i.e., on the overlap between the wavefunctions of the interacting electrons of the respective states. The energy bands belong to the crystal lattice rather than to a particular atom. Therefore, an electron in one of these bands moves quasi-freely through the lattice.

Regarding the formation of energy bands, BRILLOUIN(6) has pointed out that an electron moving in a periodic potential, such as that formed by the atoms periodically located in crystal lattices, can only possess energies lying within certain energy intervals. This behaviour is represented in momentum space, or k space, by Brillouin zones. A point on a zone boundary indicates the direction and momentum of an electron for which there is a discontinuity in the energy, i.e., a forbidden energy. Such electrons have a wavelength and direction with respect to a set of atomic planes such that the Bragg reflection formula is satisfied.
Thus, a forbidden energy band is that for which the corresponding electrons undergo Bragg reflections at the zone boundaries. For inner core electrons, the allowed energy bands are relatively narrow and separated by very wide forbidden energy bands. As one goes from inner cores to outer, the allowed energy bands become wider while the forbidden bands become narrower until the free electron limit is reached from where all energies are allowed.

In the energy band representation of the electronic structure of solids, the highest filled band in a semiconductor or insulator is the valence band and the next higher empty band is the conduction band. The distance between these two bands is commonly known as a band gap which plays an important role in understanding the conductivity of solids. In metals, either the valence band is not completely filled or the highest filled band overlaps the first empty band. Hence no band gap exists in metals. This is, of course, the condition for good conductivity. For an insulator, however, a relatively large band gap exists. For a semiconductor, it is less than that of an insulator, being of the order of a few eV which is accessible by thermally excited electrons. It should be noted in this context that the Fermi energy is the highest energy normally possessed by an electron at absolute zero.

An x-ray absorption edge occurs when the incident photons possess sufficient energy to excite an electron from one of the inner levels of an atom into the first unoccupied energy band of the crystal. Depending on the symmetry of the electron wave functions involved in the transitions, a fine structure, corresponding to the transitions of the ejected electrons to the unoccupied states of this band will be observed near the absorption edge, as a form of Kossel structure. Because of the relative sharpness of the inner levels in solids, a study of this close in structure can yield information about the density of states distribution of the lower unoccupied energy levels. However, as in the case of emission spectra, the absorption coefficient depends on the transition probability(1) as...
\[ \mu(E) = P(E) \cdot N(E) \]

where \( N(E) \) is the density of unoccupied but allowed states, and \( P(E) \) the transition probability. \( N(E) \) may be deduced from measurements of \( \mu(E) \) if the variation of \( P(E) \) in this range can be calculated from theory. Approximations can, however, be made for \( P(E) \) due to the fact that it does not change appreciably, particularly for small energy ranges.

X-ray absorption spectra of solids, liquids, and polyatomic gases, except monoatomic gases, also show a fine structure extending for several hundred electron-volts on the high energy side of the initial rise of an absorption edge. Generally, this structure consists of numerous maxima and minima on a continuum and is obviously not related to the Kossel structure which occurs within a few tens of eV from the initial rise.

The first attempt to explain the nature of the extended x-ray absorption fine structure (EXAFS) was made theoretically by Kronig in 1931, and since then it has been known as the "Kronig structure". Kronig assumed an ejected electron to be represented by a plane wave function (Bloch function) and proposed that the Bragg reflection of the electron from the lattice planes of a crystalline solid, i.e., from the zone boundary separating allowed and forbidden Brillouin zones, is responsible for the observed discontinuities. According to this theory, maxima of x-ray absorption are expected to correspond to transitions to such allowed energy bands, and minima to forbidden bands. Kronig also argued that the zone boundaries should correspond to the inflection points between adjacent maxima and minima.

Hayasi, in 1949, offered a somewhat different interpretation for the fine structure. He assumed that the ejected electron is reflected back to the parent atom by the crystallographic planes formed by near neighbour atoms. If the reflection occurs at a Bragg angle near 90°, then...
a standing-wave pattern, called a quasi-stationary state, is set up causing the electron to remain in the vicinity of the inner vacancy. The existence of such a quasi-stationary state following the absorption of a photon results in a maximum in the absorption due to the greater overlap of the wave functions of the initial and final states. Both Kronig and Hayasi theories may be classified as "long-range-order theories"(9) from the viewpoint that they consider the solid as a three dimensionally ordered crystal.

In yet another attempt to account for the extended fine structure observed for isolated molecules, KRONIG(10) proposed that the ejected electrons are scattered by the neighbouring atoms in the same molecule and argued that the density of allowed states should vary monotonically in the energy range concerned so that the absorption fine structure should be determined by the transition probability which is probably influenced by the scattering. Several modifications to this theory have been proposed to reduce the existing discrepancies between theory and experiment. These are called "short-range-order theories" and as has been pointed out by KOSTAREV, (11) they can be applied to both finite molecules and solids.

Recently, LYTLE(12) has proposed a simple particle-in-a-box theory to explain the extended x-ray absorption fine structure in which scatterings from the first coordination shell only are taken into account. LYTLE has considered a nearly spherical polyhedron formed in the lattice to be approximated by an infinitely deep spherical hole for which solutions of the Schrödinger equation can easily be obtained. He found the possible energy values to be given by

$$E = \frac{\hbar^2}{8m \xi_0^2} Q$$

where Q are the zero roots of the half-order Bessel function forming the radial part of the solution, and $\xi_0$ is the radius of the spherical hole, i.e., the nearest neighbour distance from the absorbing atom.
The energies at which absorption maxima occur may be readily obtained from equation (7).

SAYERS, LYTLE and STERN\(^{(13)}\) have extended Lytle's theory to include scatterings from more than one coordination shell. Their results are successful in producing the true shapes of the maxima observed about 100 eV above the initial rise in absorption and agree well with the experimental data for the K-absorption fine structure. As they themselves have pointed out, the approximations used in these calculations are not expected to hold for the energies below about 50 eV. It appears, therefore, that this theory, in its present form, cannot be applied to the extended fine structure, for example, of Na and Al\(\text{L}_{\text{II}},\text{L}_{\text{III}}\) -edges reported by PETERSEN and KUNZ\(^{(14)}\).

3. OBSERVATIONS OF THE M ABSORPTION AND EMISSION SPECTRA OF THE RARE-EARTHS.

The rare-earths, from lanthanum (Z = 57) to lutecium (Z = 71), form a series of elements characterized by a gradual filling of the 4f shell. Except for the 4f shell, their electronic structure consists of a xenon core plus two or three loosely bound valence electrons (6s\(^2\) or 5d\(6s^2\)). As has been calculated by MAYER\(^{(15)}\), and COULSON and SHARMA\(^{(16)}\), the energy and spatial extention of the 4f - eigenfunctions drop suddenly at the beginning of the series. According to the calculations of MAYER, based on the Thomas-Fermi potential, the binding energy of the 4f-electron drops from 0.95 eV for lanthanum to 5 eV for neodymium (Z = 60). The study of x-ray photo-electron spectra of metallic cerium (Z = 58), praseodymium (Z = 59) and neodymium by BAER and BUSCH\(^{(17)}\) shows that the binding energies of the 4f levels are respectively 0.9, 3.4 and 4.8 eV with respect to the Fermi level. These results verify that the 4f level gets deeper on going from the beginning to the middle of the rare-earth series. In lanthanum the 4f-eigenfunction is still
essentially located outside the xenon structure, whereas in neodymium it has contracted so that its maximum lies inside the 5s² 5p⁶ closed shell of the xenon structure. No such effect occurs for the eigenfunctions of s, p or d electrons.

Although in lanthanum the normal configuration (Xe) (5d 6s²) does not contain a 4f - electron, in cerium a 4f-electron appears in the normal configuration (Xe)(4f 5d 6s²), indicating the very rapid contraction of the 4f-eigenfunction with increasing atomic number. This is due to the fact that at the beginning of the series a deep potential well develops near the nucleus due to the effect of the l-dependent centrifugal potential term in the equation for the radial part of the wave function [ราม], and the 4f-electrons are drawn into the interior of the atom. As the atomic number of the neutral atom is increased above lanthanum, electrons are added progressively to the 4f-shell until it is filled up at ytterbium (Z = 70). Table I.1 shows the electronic structures of Xe, Cs, Ba and the rare-earth elements, the bracketed numbers corresponding to the 4f populations in the trivalent ions.

As a result of the contraction of the 4f-eigenfunctions in the rare-earths, the 4f-shell becomes an inner, incomplete sub-shell. The existence of such a well localized, incomplete shell in a rare-earth element enables the Mᵥ (3d⁵/² → 4f) and Mᵥ (3d³/² → 4f) absorption transitions to occur, as allowed by the selection rules. These absorption spectra exhibit a relatively sharp, "line" structure, well removed from the observed weak absorption edges towards low energies [ราม].

It is to be expected that the Mα and Mβ emission lines, corresponding respectively to the transition 4f → 3d⁵/² and 4f → 3d³/², should occur in the rare-earth elements which have available electrons for such allowed transitions. However, RUSSELL [ราม] has observed the Mα and Mβ lines in the case of lanthanum in the trioxide which has no 4f electron and he has explained the occurrence of these lines in terms of resonance or reversible transitions. This matter will be discussed ...
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<td>71</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td>14(14)</td>
<td>1</td>
</tr>
</tbody>
</table>

TABLE 1.1 ELECTRONIC STRUCTURES OF Xe, Cs, Ba AND THE RARE-EARTH ELEMENTS (REF. 28).
The study of the $M$ emission and absorption spectra of the rare-earth elements was first initiated by Lindberg (19) in 1931, who measured the $M_\alpha$ and $M_\beta$ emission spectra of most of the rare-earths, and the $M_V$ and $M_{IV}$ absorption spectra of ytterbium and erbium. In 1945, Rule (20) studied the $M_V$ and $M_{IV}$ absorption spectra of samarium. Following Zandy's work (21) on the $M_V$ and $M_{IV}$ absorption spectra of praseodymium, neodymium, samarium and europium, an extensive survey of both the $M_\alpha, \beta$ emission and $M_{V',IV}$ absorption spectra of the rare-earths has been carried out successfully in this department (22). All these investigations have been made with Johann type curved crystal spectrometers. A photographic method of detection had been used prior to the work of Combley (23) in 1959, who first employed a proportional counter system for the detection of photons which appeared superior to the photographic method of detection.

In 1956, Stewardson and Wilson (24) studied the effect of self-absorption in the sample on the emission lines of erbium and pointed out that only under minimized self-absorption can the true shapes of emission lines be observed. Following this, in 1968, Fischer and Braun (25) studied the $M_\alpha, \beta$ emission and $M_{V',IV}$ absorption spectra of the entire series of the rare-earths. They measured the $M_\alpha, \beta$ emission spectrum under minimized self-absorption conditions and concluded that the spectrum in fact, consists of single lines for both $M_\alpha$ and $M_\beta$.

Ottewell (26), in 1969, extended the absorption studies to include barium ($Z = 56$) and caesium ($Z = 55$) in addition to the rare-earths cerium and lanthanum. By employing a Johann type curved crystal spectrometer and a proportional counter for detection, he measured the $M_V, M_{IV}$ absorption spectra of these elements in the metallic state, in the oxide and fluoride, except for caesium which was studied only in the fluoride. He also measured the $M_V$ and $M_{IV}$ absorption spectra of metallic
Ce at low temperature where $\alpha$-Ce is known to exist as a result of the $\gamma \rightarrow \alpha$ phase transition.

More recently, KARNATAK(27) has also measured the $M_{\gamma, \gamma}$ absorption and $M_{\alpha, \beta}$ emission spectra of metallic cerium, and cerium in CeO$_2$. This investigator used a photographic method of detection and an unusual method of sample preparation. Very marked discrepancies have arisen, however, from the results of the $M_{\gamma, \gamma}$ absorption spectra of metallic cerium and cerium in CeO$_2$ obtained by the three groups referred to above. Evidently, it seems that these discrepancies are due to systematic errors in some of these experiments.

4. $\gamma \rightarrow \alpha$ PHASE TRANSITION IN CERIUM METAL

At room temperature and atmospheric pressure, cerium metal is a tripositive ion in that three electrons of each atom, 5d $6s^2$, are effectively removed into the conduction band. Thus, the atoms of metallic cerium are left with a closed xenon core plus one electron in the 4f shell. Unlike the other rare-earths, cerium metal has extraordinarily rich physical properties(28) which are generally thought to be associated with the close proximity of the 4f level to the Fermi level. Recent x-ray photo-electron studies of BAER and BUSCH(17) have, in fact, shown that the 4f level lies about 0.9 ev below the Fermi level in cerium metal and is well mixed with the conduction electrons. This has also been confirmed theoretically by HERBST et al.(29)

The unusual temperature-pressure phase diagram of cerium metal is shown in Fig. 1.3(30). It may be seen from the figure that there exist five distinct solid phases: the atmospheric pressure, room temperature phase, called $\gamma$, with a face-centered-cubic (fcc) crystal structure; the double-hexagonal-closest-packed (dhcp) $\beta$-phase existing below 263 $\pm$ 10 K at atmospheric pressure; another (fcc) cubic phase, assigned $\alpha$, which exists below 96 $\pm$ 6 K; the high-pressure phase, $\alpha'$; and finally the body-centered-cubic (bcc) phase, $\delta$, existing just
FIGURE I.3 TEMPERATURE — PRESSURE PHASE DIAGRAM FOR CERIUM (after E. King et al)
below the melting point (800°C). The α-phase of cerium can also be obtained at room temperature but at pressures above 7 kbar. At a pressure of about 56 kbar, the α-phase begins to transform to the much denser α'-phase which has recently been found by ELLINGER and ZACHARIASEN to possess an orthorhombic crystal structure, contrary to the previous claims of fcc, or hcp.

The phase transformations of cerium upon cooling have been well demonstrated by McHARGUE and YAKEL using x-ray crystallographic methods, and by WILKINSON et al. using neutron diffraction methods. The results of the latter group are probably more reliable since the penetration of neutrons into matter is much higher than x-rays. The behaviour of cerium metal upon cooling is shown schematically in Fig. 1.4. It is found that an annealed cerium sample consists only of fcc Y-cerium at room temperature and atmospheric pressure. When the Y-cerium is cooled, it begins to transform to the (dhcp) β-cerium at 263 ± 10 K. The β-phase continues to be formed until 96 ± 6 K where the γ-cerium, which has not yet transformed to the β-phase, begins to transform to the (fcc) α-phase. The lattice parameter of cerium in the latter phase is 4.85 Å compared with 5.16 Å of that in the γ-phase, so that a volume contraction of 16.5% accompanies the γ → α transition. This is not so in the γ → β transition.

McHARGUE and YAKEL have observed that no β → α transition takes place between the temperatures 96 K and 77 K, but between 77 K and 4.2 K both γ → α and β → α transitions occur. These workers have also pointed out that neither γ → β nor γ → α transitions take place isothermally. This fact may be seen in Fig. 1.4.

The amount of the α-cerium to be formed at 77 K was found by GSCHEIDNER to depend upon the rate of cooling and upon the impurity present in the sample, and by McHARGUE and YAKEL to depend upon its previous history, such as thermal cycles and cold work. It appears, therefore, that a higher rate of cooling favours...
the formation of more $\alpha$-cerium.

According to figure 1.4, under optimum cooling conditions and working with a 99.9% pure sample, the amount of the $\alpha$-, $\beta$-, and $\gamma$-cerium at 77 °K is found to be of the order of 10%, 80% and 10% respectively after first cooling. At 4.2 °K the amount of $\alpha$-cerium formed after first cooling from room temperature is reported to be of the order of 50%. According to McHARGUE et al. (33), cold work done on a sample previous to cooling favours more $\alpha$-cerium to be formed at 4.2 °K.

Upon warming, $\alpha$-cerium transforms to $\beta$- and $\gamma$-cerium in about the same ratio that existed before these phases were transformed to $\alpha$-cerium. It has been observed (33) that the $\alpha \rightarrow \beta$ transformation begins at about 125 °K and ceases at 200 °K, and the $\alpha \rightarrow \gamma$ transformation begins at 160 °K and is complete at 195 °K. The $\beta \rightarrow \gamma$ transformation occurs in the temperature range between 373 °K and 425 °K.

An examination of these data indicates that all the transformations, either on cooling or warming, take place over a wide temperature range, where a wide hysteresis loop is formed for each transformation.

LOCK (36), during the measurements of the magnetic susceptibility of cerium metal at low temperatures, has observed that thermal cycling between 77 °K and room temperature favours the formation of $\beta$-cerium, and also that as the number of cyclings is increased the large hysteresis loop gradually disappears. It appears, therefore, that the effect of thermal cycling is to stabilize the $\beta$-phase in the temperature range concerned, and to suppress the $\gamma \rightarrow \alpha$ transitions.

The mechanism of the $\gamma \rightarrow \beta$ transformation consists simply of a movement of atoms and clearly no change in the electronic structure of the atoms is involved. This point is discussed in detail by GSCHNEIDNER (28). The $\gamma \rightarrow \alpha$, and $\beta \rightarrow \alpha$ transformations, on the other hand, somehow involve a change in the electronic configurations of the atoms. In order to explain the mechanism of these transformations...
and the nature of α-cerium, several models have been proposed, but none of them seem to account adequately for all of the features observed.

First, ZACHARIASEN and PAULING, working independently, suggested that during the γ → α transition the 4f electron of a cerium atom in the γ-phase is transferred or promoted to the 5d 6s conduction band, probably to the 5d. This promotion of the 4f electron to the conduction band transforms the trivalent γ-cerium to the tetravalent α-cerium and simultaneously the magnetic moment connected with the 4f state is lost. Indeed, some experimental results appeared to support this model qualitatively. However, the results of the magnetic susceptibility measurements of LOCK suggest that about one half of an electron per atom is transferred during the γ → α transition. GSCHEIDNER and SMOLUCHOWSKI have calculated the valencies of γ-, β-, and α-cerium as 3.06, 3.06, and 3.76 respectively, which are in good agreement with LOCK's data. Obviously, according to the promotional model the valence of α-cerium would be 4.

A somewhat different model of a promotional type for the γ → α transformation has been proposed by COULIN and BLANDIN. This involves essentially a compensation of the spin of the 4f electron by the conduction electrons. In the γ-phase the 4f spin would be practically uncompensated, but partially compensated in the α-phase. This model accounts for the non-integer valence and relatively small magnetic character of the α-phase. According to this model, due to complete spin compensation in the α'-phase, cerium atoms are left with no 4f character at the Fermi level, so leading to a tetravalency. This, of course, corresponds to the complete removal of the 4f electrons into the conduction band. This view is qualitatively supported by the fact that the compressibility of cerium in the α'-phase is practically zero.

GUSTAFSON et al. have carried out positron-annihilation
experiments in γ-cerium, and in α-cerium at both low temperatures and high pressures. Any rise in the valence of cerium due to complete or partial removal of the 4f electron would be accompanied by a relatively large decrease in the positron life time, and also in the angular correlation of positron-annihilation radiation. The results of these experiments show that the valence of the α-cerium is the same as that of the γ-cerium, i.e., there is no promotion of the 4f electron into the conduction band. The more recent positron-annihilation experiments of GEMPEL et al. (42), in addition to confirming the results of GUSTAFSON et al., reveal that even in the α → α' transition essentially no change in the valence is detected. Naturally, these experiments cast serious doubts on the validity of any model of the promotional type.

In agreement with the positron-annihilation experiments, JOHANSSON (43) has strongly argued, in view of the cohesive energy properties, that cerium cannot promote its 4f electron into the conduction band during the γ → α transition. He considers the γ-cerium to α-cerium transformation as a Mott transition in which the 4f-electron is localized in γ-cerium but delocalizes into a 4f-band in α-cerium. This band would then overlap the Fermi level such that a fractional number of electrons would occupy the conduction band.

Even though none of the proposed models for the mechanism of the γ → α transition provides an adequate explanation for all of the features appearing as a result of the transition, it is commonly believed that there does occur a change in the electronic configuration of the cerium atoms in which the 4f electron no doubt plays an important role. It might be expected that a modification of the electronic configuration of the 4f-level reveals itself by a change in the M4 and M4 absorption spectra of cerium. This change would
involves either a shift (called chemical shift) or a structural modification of the $M^V_\nu$ and $M^IV_\mu$ absorption lines, or both of these might occur simultaneously.

Suppose that we are working with a hundred per cent $\alpha$-cerium and the promotional model is correct. Then we would have a case similar to that of metallic lanthanum which has no 4f electron. We would still be observing a line structure as that in lanthanum. The $M^V_\nu$ and $M^IV_\mu$ absorption spectra of lanthanum are much simpler compared with those of normal cerium metal ($\gamma$-cerium), because calculations of multiplet structure reveal that the lanthanum $M^V_\nu$ and $M^IV_\mu$ lines contain two and one components respectively, while in cerium it is thirty for $M^V_\nu$ and twentythree for $M^IV_\mu$. Therefore, the observed fine structure in the $M^V_\nu$ and $M^IV_\mu$ lines of $\gamma$-cerium would be lost in the $\alpha$-phase. In addition to this structural change, it is possible that a shift of the strongest $M^V_\nu$ and $M^IV_\mu$ absorption lines of $\alpha$-cerium, relative to those of $\gamma$-cerium, would occur towards high energies similar to that which has been observed in cerium-oxide by KARNATAK who reported a shift of the order of 2eV for both $M^V_\nu$ and $M^IV_\mu$ lines. A chemical shift, as large as 2 eV, can readily be detected, but if one has to work with a sample containing, for example, 50% $\alpha$-cerium and 50% $\gamma$-cerium (or $\beta$-cerium), then a rather complicated spectrum would arise in that two spectra belonging to $\alpha$-cerium and $\gamma$-cerium would overlap. Naturally, a question arises as to what extent these spectra could be resolved.

If it is supposed, on the other hand, that the 4f electron in $\gamma$-cerium is not promoted to the conduction band, but instead the 4f level is delocalized into a band (according to the model proposed by JOHANSSON) in going from $\gamma$- to $\alpha$-cerium, then the $3d \rightarrow 4f$ (band) transition would result. Accordingly, the expected effect would be such as to broaden the absorption lines. This broadening, however, may
not be observable spectroscopically, if the width of the band is only a few tenths of an eV. The estimated values for the width of the 4f-level in γ-cerium and in α-cerium are 0.14 eV and 0.27 eV respectively, the increase being approximately 0.13 eV for the γ-α transition. Such an energy value is near the limit of resolution of the spectrometer as discussed in chapter II.

5. PRESENT WORK

In the first part of this work, an extensive study has been carried out on the $M_{IV}$ absorption spectra of both metallic cerium and cerium in oxide. FISCHER and BAUN (25) have found no significant difference between the $M_{IV}$ absorption spectra of metallic cerium and cerium in oxide. These investigators themselves pointed out, however, that the cerium sample used might not have been free from oxide. OTTEWELL (26) in this department, has reported that the $M_{IV}$ absorption lines for CeO$_2$ are of similar form to those for La$_2$O$_3$ and BaO, the three materials forming an isoelectronic sequence. Moreover, his data show a relatively large shift (about 5 eV) of the $M_{IV}$ lines in CeO$_2$, relative to those in metal, towards low energies. As has been mentioned already, the shift reported by KARNATAK (27) occurred in a direction opposite to that of OTTEWELL. If one disregards the energy scale, the data of the latter for metallic cerium agree principally with those of KARNATAK.

A very marked disagreement also arises from the data for CeO$_2$ reported by these two investigators. Detailed calculations of the multiplet splittings for La, La$_2$O$_3$, Ce and CeO$_2$ have been made by BONNELLE et al. (46) and compared with their experimental data. Good agreement has been reported for La, La$_2$O$_3$ and Ce, but not for CeO$_2$. Because of the extra peak appearing on the high energy side of the $M_{IV}$ line reported by KARNATAK, but not observed by OTTEWELL
however, the spectra of CeO₂ were found to be inexplicable in terms of their calculations which take into account the coupling between 3d and 4f electrons.

With regard to the preparation of the CeO₂ samples, it is suspected that the spectra reported by KARNATAK may not have been characteristic of CeO₂. It is clear, therefore, from the above comparisons that a further investigation into the Mₓ, Mᵧ absorption spectra of both metallic cerium and cerium in oxide has to be carried out by employing some different sample preparation methods. It has been discovered after our early recordings that the spectra reported by OTTEWELL(26) for what is called oxidized-cerium are the characteristic spectra of CeO₂. Thus, it is of great interest to try to explain theoretically these unexpected results. To do so, clearly a different approach has to be made.

To this end, a study has been made not only of the cerium oxide absorption spectra but also of the Mₓ and Mᵧ emission lines under minimum self absorption conditions. The suspicion that the method used by KARNATAK to form cerium oxide, i.e., slow evaporation of cerium metal and frequent exposure to air in between, was unreliable and led to incorrect absorption spectra, may also apply to his emission spectra.

In the second part of this work, a study of metallic cerium at 20.4⁰K (liquid hydrogen temperature) has been carried out. OTTEWELL(26), for the first time, studied the Mₓ, Mᵧ absorption spectra of metallic cerium at 77⁰K and claimed to have observed a remarkable change in the profiles of the lines compared with those at room temperature. This modification, which is more pronounced for Mₓ absorption line than for Mᵧ, is attributed to the γ→α phase transition in cerium. It would be interesting to record this spectrum under more favorable conditions for the formation of the α-phase, such as at 20.4⁰K, so that clearer evidence could be obtained for...
explaining the nature of the $\gamma \rightarrow \alpha$ phase transition in cerium.

In the third part, we have studied the $M_{\nu}, M_{\mu}$ absorption spectra of both gaseous and solid xenon. The element caesium, preceded by xenon, has been studied by OTTEWELL (26) and it was found that the $M_{\nu}, M_{\mu}$ absorption spectra show no strong lines but only edges. This is attributed to the fact that the 4f-orbital in Cs is no longer an inner orbital, but it is in the outer band. It is expected that the same argument should apply to Xe. In fact, DESLATTES (47) has reported the $M_{\nu}, M_{\mu}$ absorption spectra of gaseous xenon in which two very broad peaks occurring about 12 eV above the corresponding ionization thresholds were predominant. These are explained in terms of the transitions $3d_{5/2} \rightarrow \epsilon f$ and $3d_{3/2} \rightarrow \epsilon f$ ($\epsilon \geq 4$). It is expected that these transitions should also dominate the absorption spectra in the solid, while probably accompanied by a weak fine structure due to solid state effects, similar to that observed in the K absorption spectra of solid argon, and krypton (48).

As far as is known, the $M_{\nu}, M_{\mu}$ absorption spectrum of solid xenon have not been reported elsewhere. With this result in hand, the $M_{\nu}, M_{\mu}$ absorption spectra of the isoelectronic sequence Ce$^{4+}$, La$^{3+}$, Ba$^{2+}$, Cs$^{+}$ and Xe$^{0}$ (solid) will be complete.
CHAPTER II

EXPERIMENTAL TECHNIQUE

1. X-ray Spectroscopy with a Curved Crystal Spectrometer.

2. Additions to the Spectrometer and Source Chamber
   - The X-ray Source for Absorption Spectra
   - The Emission Source
   - The Cooling System
   - The Recording System
   - The Detector System

3. Preparation of the Absorption Foils.


1. X-RAY SPECTROSCOPY WITH A CURVED CRYSTAL SPECTROMETER.

Curved crystal arrangements, commonly known as focusing systems, are used to obtain an increased luminosity of X-ray spectrographs. The geometry of such an arrangement was first suggested by Dumond and Kirkpatrick in 1930.

There are mainly two types of arrangement; one is the Johann type in which X-rays are reflected from the surface of a curved crystal, the other is the Cauchois type in which X-rays are transmitted through the crystal. These are shown in figure 11.1. In both cases the crystal is bent to a radius R which is the diameter of the focal circle known as the Rowland circle. This method of focusing is widely used with crystals that are not readily ground, such as mica. Theoretically, Johannson's method, in which the crystal is first bent to a radius R and then ground to R/2, would provide true focusing, a point source imaging as a line.

A Johann type arrangement was used in the present investigation. If the Cauchois type were used, the X-rays with wavelengths in the region under investigation would all be absorbed as they pass through the crystal.

The focusing mechanism of the Johann type arrangement is such that the X-rays from a point source situated on the Rowland circle will be reflected in such a way as to produce a fairly sharp line at the point of the circle. Only the X-rays with the wavelength \( \lambda_1 \) from \( S_1 \) will be focused at \( P_1 \) according to the Bragg equation.

\[ n\lambda = 2d \sin \theta \]  

where \( n \) is the order of diffraction, \( d \) is the lattice spacing, and \( \theta \) is the angle between the reflecting lattice planes and the incident beam. In the same way, the X-rays with the wavelength \( \lambda_2 \) will be reflected so as to focus at \( P_2 \). For photographic detection of the reflected...
FIGURE II.1a THE REFLECTION SPECTROMETER

FIGURE II.1b THE TRANSMISSION SPECTROMETER
X-rays, a broad radiation source may be located inside the Rowland circle, say from $E_1$ to $E_2$ as in figure II.1, so that it will cover all the wavelengths lying between $\lambda_1$ and $\lambda_2$ from the points $S_1$ and $S_2$ respectively. Then, a photographic film is placed on the Rowland circle between $P_1$ and $P_2$. The use of a broad x-ray source with a photographic detection enables one to examine a wide range of wavelengths with one setting and exposure. If, however, a Geiger or a proportional counter is used as a detector, then a very small wavelength region defined by the counter window is measured. In order to examine the wavelengths lying between $\lambda_1$ and $\lambda_2$, the counter must be moved along the Rowland circle from $P_1$ to $P_2$. If a point x-ray source is used, the geometry of the spectrometer requires that the source itself has to be moved along the circle from $S_1$ to $S_2$ in accordance with the counter movement. With counter detection the range of wavelengths to be measured is, apart from mechanical limitations, limited only by the lattice spacing of the crystal employed.

The sensitivity of counters is considerably higher than that of photographic films. In the latter case, it is difficult to correct for intensity variation along the line source, and if the film is bent so as to match the Rowland circle, extra broadening of the spectral structure will arise due to oblique incidence of the reflected x-ray beam. In the case when a film is positioned normally to the reflected beam, a broadening will occur also due to defocussing, at points which are not on the Rowland circle. Interpretation of the film by a microphotometer gives rise to some broadening in the same way as does the finite width of the counter window. However, sequential recording of different wavelengths of the spectrum with, say, a proportional counter requires a very high stability in the x-ray source.

The crystal to be used in a focussing spectrometer must fulfil certain conditions. It must have a high reflectivity for the wave-
lengths of the x-rays under investigation, the lattice constant of the crystal must be such that the reflections of these wavelengths are obtained at suitable Bragg angles, and it must be bent easily to the required radius of curvature. Since the mica crystal already employed in the existing spectrometer well satisfies the above requirements, it was used throughout the present work. Because different samples of mica are thought to have slightly different lattice spacings, tests were carried out by WILLIAMS (1959)(52), and it was found that the values for the lattice spacings given by SIEGRAHN(53) were reliable. Therefore, these values were used in the present investigation.

2. ADDITIONS TO THE SPECTROMETER AND SOURCE CHAMBER

The spectrometer used throughout this work was designed by OTTEWELL(26) and constructed in this department. It is shown schematically in figure II.2. The spectrometer is enclosed in an aluminium tank and kept under rough vacuum (about $5 \times 10^{-2}$ torr) by a rotary backing pump. For the experiments which require ultra-high vacuum, however, a stainless steel chamber evacuated by a getter-ion pump was constructed and connected to the aluminium tank via a metal bellows. The ultra-high vacuum chamber is separated from the tank by a $2000 \text{Å}$ pin hole free aluminium foil or by a stretched polypropylene window. The x-ray source, $X$, is housed in the ultra-high vacuum chamber, or source chamber, and kept fixed during the experiments.

The use of a fixed x-ray source requires that, in order to vary the wavelength region incident on the counter window $D$, the crystal must move along a straight line $CP$. The movement of the crystal was achieved by means of a leadscrew operated at $M$ either manually or by a motor. In figure II.2, $P$ is the position for the samples to be exa-
FIGURE II. 2  A SCHEMATIC DIAGRAM OF THE SPECTROMETER AND SOURCE CHAMBER
mined under ultra-high vacuum conditions, and $F$ is that for the samples that may be examined in the spectrometer tank. $S$ indicates the wavelength measurement devices which consist of an electrically operated micrometer and a pair of sliding coils for electrical output to an 'X-Y' plotter. The side chamber on the main source chamber is for the preparation of the metallic samples which after evaporation may be moved to $P$. The source chamber and spectrometer tank are shown in Plate II.1.

In order to fulfill the requirements of the present work, however, some modifications had to be made to the spectrometer and the source chamber. These are described in detail in the following paragraphs.

**The X-Ray Source for Absorption Spectra.**

A new high intensity, fine focus x-ray source was designed in the present work by following the principles developed by OTTEWELL et al.\(^{(54)}\). It was observed after early runs with the existing x-ray source that some local defects appeared on the target edge which resulted in a cut-off in the x-ray beam and often a breakdown in the cathode assembly. This was attributed to inefficient cooling and it was therefore the purpose of this design to improve the efficiency of cooling and also to simplify its construction.

The mechanical construction of the source is shown in figure II.3. The anode is a tungsten blade 0.025 cm thick, 2 cm in length and about 1.2 cm wide. This is clamped in between two copper jaws, one of which is an extension of a water-cooled solid block. The knife edges of the jaws are slightly rounded so that the blade edge is left protruding about 0.05 cm above its bed. The knife edges of two stainless steel blocks one on each side of the blade serve as a focusing means for the electron beam onto the edge of the blade. The two knife edges and the blade edge are approximately in the same
plane and the gap between the latter and each of the knife edges is 0.015cm. The cathode assembly consists of two parallel thoriated tungsten wires, 0.015cm in diameter, which are secured to the front of the stainless steel filament blocks. At the rear end the wires enter two grooves in the surface of a cylinder and are secured after half a turn so that the cathode wires are given a separation of about 0.05cm. The cylinder is free to turn in ceramic washers about a horizontal axis so that, by means of a weighted arm, the wires will remain straight and parallel at all temperatures. The two stainless steel filament blocks which are at the same negative potential as the filaments are insulated by mica sheets of thickness 0.025cm from the earthed anode mount. A grooved stainless steel shield is screwed to the stainless steel filament blocks to enclose the cathode wires. Also a shield containing a thin aluminium window is attached to the front end of the water-cooled anode mount to prevent thermal heating of the absorber foil. In order to reduce the effect of space charge limitation the cathode wires are arranged as close to the anode edge as possible; the gap being 0.05cm or less. The slope of the blade edge is initially set at $4^\circ$ and by tilting the source chamber a take-off angle of $7^\circ$ is obtained for the x-rays.

As expected, the operational characteristics of this source appeared to be the same as those of the previous design, the details of which can be found in Ref. 54. The power level applied to this source is limited only by the filament current, the maximum value of which was found to be 5 amp for a safe run. Typically, an emission current of 116 mA was used with an anode voltage of 1350 volts during the measurements of the $N_{1v}$ and $N_{2v}$ absorption spectra of xenon, the value 1350 volts being below twice the excitation voltage in this energy region to avoid the effect of second order reflection.
FIGURE II.3 THE X RAY SOURCE
(scale 1/1)
Figure II.4  X-ray source power supplies and relay circuits

SWA: Safety switch
SWB: Micro switch operated by water circulation
L.A.: Water off indicator lamp
L.B.: Mains on indicator lamp
R.A.: Mains operated relay
R.B.: Transformer loaded to 5 kV
T.A.: 0.270 V, variable transformer
T.B.: X-ray tube filament
F.: X-ray tube anode
The excitation voltage for the x-ray source was supplied by an A.P.T. model 5705 stabilized, variable E.H.T. unit. The filament current was drawn directly from the mains supply via a 'variac' controlled transformer and connected in series with an A.P.T. model 5706/1 current stabilizer. With the help of this stabilizer the anode current was kept stable at a required value to an accuracy of better than 1%. A block diagram of the power supplies is shown in figure II.4

The Emission Source

This source was designed in the present work for the excitation of emission spectra under minimum self absorption conditions. It was made to fit into the ultra-high vacuum chamber in place of the x-ray source described previously for absorption work. Since, in principle, the design of the spectrometer requires a point source situated on the Rowland circle to give maximum intensity at the detector, the anode surface must be as small as possible. On the other hand, a very small anode surface would not be practical since it would be readily damaged by the electron beam due to overheating. Therefore, the copper anode was made in the form of a cylinder 0.4cm long and 0.25cm in diameter, i.e., the area of the anode surface is $0.05 \text{cm}^2$. The anode is actually an extension of a water-cooled solid block. The constructional details of the emission source are shown in figure II.5. A ring of thoriated tungsten wire 0.015cm in diameter is used as the cathode. The ring having a diameter of 0.6cm is positioned around the anode cylinder such that it is approximately in the same plane as the anode surface. A thin-walled cylindrical extension of the stainless steel filament ring mounting stands between the anode cylinder and the filament ring and protrudes 0.1cm above the anode surface. With this arrangement, the possibility of contamination due to the evaporation of the filament itself is ruled out, since the anode is not directly seen by the filament ring. The filament ring mounting block
is operated at the same negative voltage as the cathode ring and insulated from the earthed anode assembly by mica sheets 0.025cm thick. The electrons emitted by the hot filament ring are forced to follow the curved paths as shown in figure II.5 to focus onto the target surface.

The source was shielded in front with a stainless steel plate containing a hole, 0.25cm in diameter, for the x-rays to go through.

The sample to be examined was evaporated directly onto the anode surface. According to the geometry of the source, only the x-rays with a take-off angle of 90° will reach the crystal and be received at the detector, and therefore self-absorption in the sample is effectively minimized in this way.

The operational characteristics of the emission source are shown in figure II.6 where the variation of the anode current $I_a$ with the filament current $I_c$ is drawn for different exciting voltages. For the sake of comparison, the $Lα$ emission spectrum of copper has been recorded and shown in figure II.7 together with that reported by BOIJELE(55).

This source was operated from the power supplies described for the x-ray source in the preceding section.

The Cooling System

The construction of the cooling system employed in the present work is shown in figure II.8. The cryo-tip which enabled the samples of metallic cerium and solid xenon to be examined at liquid hydrogen temperature (20.4 °K) is an Air Products and Chemicals model AC 2-109, controlled by APCI control panel OC-22. The cryo-tip was so mounted on the newly constructed lid for the source chamber that when the lid is on, the cold tip of the cooler is just above the foil holder in the x-ray beam; the clearance being 0.1cm. The foil holder is pushed up by means of a lever to contact the cold tip. The lever was mounted
FIGURE II.6  ELECTRICAL CHARACTERISTICS OF THE EMISSION SOURCE

FIGURE II.7  Cu Lα EMISSION LINE. A COMPARISON
on the wall of the source chamber through a side port by means of a bellows so that it can be operated from outside. The head of the lever was made of micalex, a material possessing a low heat conductivity, and topped with a copper plate to which an iron doped gold vs. chromel thermocouple was soldered. The thermocouple was led out through a port in the lid via gas tight insulators and the temperature readings were made by a digital thermometer of Air Products and Chemicals model APD-T3.

The foil holder may be moved along the ceramic guide rails into the side chamber where samples are prepared. Here a liquid nitrogen container mounted at the top of the chamber and a lever attachment are arranged in the same way as for the cryo-tip. The nitrogen container, used as a precooler, was essential for quenching the samples since the capacity of the cryo-tip appeared to be too low to quench samples at a rate of cooling required for the phase transition of cerium metal. The foil holder is housed in a chromium plated copper shield which is located horizontally from the side chamber to the centre of the source chamber where it is held firmly by means of a copper block mounted to the bottom of a liquid nitrogen tank. This tank is welded to the lid of the source chamber and always kept full of liquid nitrogen during the low temperature experiments to keep the shield at as low a temperature as possible. The shield contains necessary openings for the x-rays, cryo-tip, lever head, etc. The movement of the foil holder is facilitated by means of an iron slug sliding inside a glass appendix and an external permanent ring magnet. A 2000 \( \Omega \) aluminium foil was used as the substrate and mounted on the foil holder which is made of copper for good heat conduction.

Figure II.9 shows a typical cool-down curve of the foil holder.
FIGURE II.8  THE COOLING SYSTEM
FIGURE II.9 COOL-DOWN CURVE OF THE SAMPLE HOLDER
Quenching from room temperature down to liquid nitrogen temperature is made by the precooler, then the foil holder is transferred to the cryo-tip where it is further quenched down to liquid hydrogen temperature. The average rates of cooling achieved by the precooler and the cryo-tip are 137 °K/min and 53 °K/min respectively. The lowest temperature observed is 24 °K. Clearly, due to the geometry of the cold tip and the temperature measuring point, the sample itself should be at a temperature between 20.4 and 24 °K when the latter is being observed. Plate II.2 shows a general view of the equipment used to operate the cryo-tip.

**The Recording System**

It may be shown that for a Johann type of curved crystal spectrometer the wavelength, \( \lambda \), of the x-rays being received at the detector is directly proportional to the distance, \( X \), between the reflecting crystal and the effective detector window. Thus, a small change, \( \Delta X \), in the distance will also be directly proportional to the corresponding change, \( \Delta \lambda \), in the wavelength, i.e., \( \Delta \lambda \propto \Delta X \). This convenient relationship was used to measure the wavelengths by a micrometer and, or by a sliding coil device. The latter was designed and constructed in the present work for recording the x-ray spectrum directly on an 'X-Y' plotter. Figure II.10 shows a schematic diagram of the sliding coils with the block diagram of its electronics. A 100 turns/cm coil, 10.5cm long and 1cm in diameter, is clamped to the crystal mount block such that it is parallel to the line that links the crystal and the detector window. Mounted on the detector arm is another coil, 15cm long and 0.63cm in diameter, which can slide in the former so that the relative displacement is equal to \( \Delta X \). The latter coil is wound on a ferrite rod which increases the mutual inductance between the coils. The displacement, \( \Delta X \), will result in a change, \( \Delta M \), in the mutual inductance coupling of the coils which
can be used as a measure of wavelength shift. The choice of sufficiently long coils and their suitable positioning provided almost a linear relationship between $\Delta \lambda$ and $\Delta M$ for the region of wavelengths concerned. Corrections have been made, however, for the minor non-linearity.

A 1500 Hz signal for the outer coil is supplied by a Wide-Range-Oscillator of Venner Electronics Ltd., type 625/2 and the output of the inner coil is rectified and applied to the X-axis of a JJ 'X-Y' plotter, type PL 100. The Y-axis of the plotter is connected to the counter via a count-rate meter so that the number of photons received at the counter will be recorded for the corresponding wavelengths. Plate II.3 shows the mechanical arrangement of the micro-meter and sliding coils.

The use of a continuous recording system requires that the movement of the crystal must be very even and slow. This is facilitated by a slow running motor, provided by Parvalux Electric Motors Ltd., which drives the manual control wheel outside the spectrometer. In order to obtain an undistorted spectrum by direct recording, the wavelength scanning speed, $v$, of the spectrometer must be such that the relation

$$v < \frac{D}{RC}$$

is satisfied\(^{(60)}\). In this relation, $D$ is the effective width of the counter window, and $RC$ is the time constant of the count-rate meter. Therefore, in accordance with the above relation, $v$ is chosen as 0.016 Å/minute. This point will be discussed in detail in section 5 of this chapter.

**The Detector System**

As already mentioned in Chapter I, a gas flow proportional counter was used successfully as a detector by OTTEWELL\(^{(26)}\) in the existing spectrometer. The same detector system was used throughout
FIGURE II.10 A SCHEMATIC DIAGRAM OF THE RECORDING SYSTEM
\[ \lambda = 2d \sin \theta \]

\[ x = R \sin \theta \]

\[ \gamma = \frac{2d}{R} x \]

\[ \Delta \lambda = \frac{2d}{R} \Delta x = 0.0401 \Delta x \]

\[ \Delta \lambda = 0.0401 \Delta x \]

\[ \frac{\Delta \lambda}{\Delta x} = 0.0401 \text{ Å/Å} \]

\[ D = \text{effective window} \]

\[ D = \Delta \lambda \sin \theta = x \Delta \theta \]

\[ \lambda = 2d \sin \theta \]

\[ \Delta \lambda = 2d \cos \theta \Delta \theta \]

\[ = 2d \cos \theta \frac{D}{x} \]

\[ = \frac{2d}{R} \cos \theta \frac{D}{x} = \frac{2d}{R} \frac{\cos \theta}{\sin \theta} D \]

\[ \Delta \lambda = 0.0401 (\cot \theta) D \]

For Ce region, \( \cot \theta = 1 \) \[ \theta = 65^\circ \]

\[ D = 70 \text{ Å} \]

\[ \Delta \lambda = 0.0401 \times 0.07 = 0.0028 \text{ Å} \]

(0.17 eV)

For Xe region at 690 eV (17.168 Å)

\[ \theta = 64.6^\circ \]

\[ \cot \theta = 0.475 \]

\[ \Delta \lambda = 0.0401 \times 0.475 \times 0.150 \text{ Å} \]

(0.11 eV)
this work since photons with energies in the regions under investigation can be best detected by a proportional counter. The counter provided by 20th Century Electronics was adapted to be used as a gas flow proportional counter and its window was covered with stretched polypropylene. A mixture of 90% argon and 10% methane served as the proportional counter gas at atmospheric pressure. By means of an adjustable slit mounted on the Rowland circle, the effective width of the counter window was set to 70μ for the wavelength region of the M_{V', IV} spectrum of cerium, corresponding to a wavelength spread of 0.028 Å (0.17 eV). In the wavelength region of the M_{V', IV} spectrum of xenon, however, the effective width was set to a value of 150μ so that the same wavelength spread as that of cerium was observed.

A block diagram of the electronic system for the proportional counter is shown in figure II.11. The counter is operated at 1.8 KV supplied by a stabilized E.H.T. unit, Isotope Developments Ltd., type 532/D. Pulses produced by the counter are fed via a preamplifier to a wide-band amplifier, I.D.L. type 652, and then to an I.D.L. type 550 count-rate meter, and a scaler unit. The count-rate meter has a choice of 1, 10 and 100 sec. time constants and provides a continuous count-rate display. The recorder output of this unit is connected to the Y-axis of the 'X-Y' plotter. Two scalers (Research Electronics Ltd.) are used, one of which, model 8042D, is used as a 0.01 sec. timer, while the other, Auto Scaler model 8041M is used as a count display. For all connections of the detector system screened cables are used to avoid the recording of spurious pulses coming from the environment of the system.

A general view of the experimental equipment is shown in plate II.4.
3. PREPARATION OF THE ABSORPTION FOILS

2000 Å thick pin hole free aluminium foils which served as substrates for all the absorption foils were prepared by a vacuum evaporation method developed by CARPENTER and CURCIO (56). A glass slide was dipped in a 10% sugar solution containing 0.5% by volume of teepol as a wetting agent, and after drying in a dust free atmosphere it was subjected to vacuum evaporation of aluminium in an Edwards model 12E6/1514 evaporation chamber. The thickness of the foil was measured by an Edwards thickness monitor. The aluminium deposit on the glass slide was scribed into the required dimensions, and then floated off and flushed with running de-ionized water in order to remove traces of sugar. A floating foil was removed from the water surface by drawing up a foil holder under the foil at a steep angle. This method of foil preparation was also used successfully to obtain carbon foils as thin as 300 Å.

The non-metallic absorption foils, cerium oxide and cerium silicide in the present case, were prepared in the evaporation chamber referred to above. The sample to be evaporated was loaded into a previously cleaned and outgassed boat, a shallow tungsten boat for cerium oxide and a tantalum boat for cerium silicide. The foil holder was mounted about 20 cm above the boat with one half of the aluminium foil being shielded from the evaporant. The quartz crystal of the thickness monitor was mounted as close to the foil holder as possible and its face was in the same plane as that of the aluminium foil. Cerium oxide was used in the form specially prepared for vacuum evaporation by BDH Chemicals Ltd. ('Vactran') while Cerium silicide of purity 99% was provided by Koch-Lights Ltd. In order to verify that the deposited cerium oxide was not affected by the substrate and, or by the method of evaporation, some tests were carried out ...
(1) Employing, in addition to aluminium foil, stretched polypropylene and 350 Å thick carbon foil substrates, the letter being supported by a nickel grid,
(2) Using an electron bombardment evaporation method as an alternative to evaporation by direct electric heating,
(3) Depositing very fine cerium oxide powder on a stretched polypropylene foil by sedimentation from a suspension in water. No significant difference was observed, however, between the $M_V$, $M_{IV}$ absorption spectra obtained from the foils of cerium oxide prepared by the above methods. Furthermore, a cerium oxide absorption foil on an aluminium substrate, after having its spectrum recorded, was compressed into a minute pellet and its crystal structure examined photographically by the x-ray powder method. The diffraction pattern obtained in this way compared well with that given in the literature for cerium oxide ($CeO_2$).

The absorption foils of metallic cerium were prepared with a moderate ultra-high vacuum (~$10^{-8}$ torr) in the source chamber so that oxidization was reduced to a minimum. The foil holder was positioned in the side chamber, as shown in figure II.2, opposite the glass appendix in which a previously outgassed, small tantalum tube containing a lump of cerium sample was housed. The cerium sample used was 99.9% pure and provided by Koch-Lights Ltd. Heating of the tantalum tube was achieved by a R.F. induction coil connected to a Radyne generator, model C 40. The quartz crystal of the thickness monitor was mounted close to the foil holder and slightly to one side of it. A screen containing a hole to define the effective area of the crystal was also arranged. Prior to actual evaporation and when
the foil holder was out of view of the sample, the tantalum tube was thoroughly outgassed by increasing slowly the power output of the R.F. generator. During the evaporations, the pressure in the system increased to $10^{-7}$ torr, compared with $10^{-6}$ torr, the normal working pressure.

The absorption foils of solid xenon were prepared in the source chamber with the foil holder positioned in the x-ray beam and at liquid hydrogen temperature. A stainless steel tube of 0.1 cm internal diameter, was brought through the lid of the source chamber near the foil holder as illustrated in figure II.8. The other end of the tube was connected via a fine control needle valve to the xenon gas supply (grade X) in a 2 litre glass flask, provided by B.O.C. Ltd. The xenon gas was slowly allowed to diffuse onto the aluminium foil, thus forming a film of solid xenon in about one minute. During the formation of the solid xenon film the pressure in the system was observed to increase to $10^{-6}$ torr from the initial value of $10^{-8}$ torr soon after the solid film was formed, the pressure returned to $10^{-8}$ torr.

The thickness of the solid xenon film was not measured directly, but estimated by comparing the absorption of x-rays by the solid xenon film with the absorption by xenon gas. In doing so, it was assumed that the mass absorption coefficient of solid xenon in the energy region about 20 eV below the $M_V$ absorption structure is the same as that of xenon gas in the same region.

For the $M_V$, $I_V$ absorption measurements of xenon gas a special cell with two stretched polypropylene windows on each side was constructed and mounted on the lid of the spectrometer tank at F in figure II.2. The construction of the cell is such that it can be moved into the x-ray beam and then out of it, thus enabling the intensity of both attenuated and unattenuated x-rays to be measured.
Before the xenon gas absorption measurements were made, this cell was used to measure the K absorption spectrum of neon gas as part of the preliminary calibration and resolution tests of the spectrometer. The path length of the x-ray beam in the cell is 3.4 cm.

Prior to the admission of xenon gas, the cell was evacuated to a pressure of $5 \times 10^{-6}$ torr and the gas pressure in the cell was measured by an EDWARDS Type C.G.3 pressure gauge to an accuracy of $2\%$.

As has been pointed out by PARRATT, HEMPSTEAD and JOSSEM (57), the directly measured details of an absorption spectrum depend upon the thickness of the absorbing foil. This "thickness effect", which is a consequence of the finite width of the spectral window of the spectrometer, decreases with decreasing absorber thickness and from this point of view the absorber should be as thin as practically possible. On the other hand, the statistical error in the absorption coefficient which occurs as a result of measuring the x-ray intensities with a photon counter increases with decreasing absorber thickness (58). Therefore, an optimum thickness for the absorber has to be determined in order to observe a spectrum with the highest contrast between its structures and with the lowest statistical error. For two different absorption coefficients, $\mu_1$ and $\mu_2$, for which the transmitted intensities are $I_1$ and $I_2$, solution of the relation $d(I_1 - I_2)/dx = 0$ with the help of equation (3) shows that the optimum thickness is

$$x_{opt} = \frac{\Delta n (\mu_1 - \mu_2)}{I_1 - I_2}$$

(10)

However, this relation is reliable only if the statistical errors involved in the measurements of $I_1$, $I_2$ and $I_0$ (the incident beam) are the same and the absorption coefficient does not vary appreciably...
over the energy region under investigation. The former was achieved essentially by measuring the time for a given number of counts for all intensities as is discussed further in the section concerning the probable errors.

An examination of the $M_V$ and $M_{IV}$ absorption spectra of cerium revealed that in order to investigate the absorption line structure in detail the absorber thickness should be of the order of 400 Å. Taking account of the $M_V$ and $M_{IV}$ absorption spectra of xenon gas and the discussion leading to equation (10), it was decided that two absorption foils of solid xenon had to be employed in the present work; a thick foil for the study of the low absorption region, i.e., the low energy side of the $M_V$ line, and a thin foil for the investigation into the high absorption region. The estimated thicknesses were of the order of 105 µg/cm² for the former and 55 µg/cm² for the latter.

4. CALIBRATION OF THE SPECTROMETER

Prior to calibration the spectrometer was optically aligned outside of the spectrometer tank by means of a point light source placed in a position coincident with the centre of the x-ray source anode. The lengths of both the crystal and the detector arms were set to 25 cm; the measurement being made by means of a cathetometer. The image of the light source reflected by the crystal was observed with a telescope at the detector slit. The curvature of the crystal was carefully adjusted as to obtain a sharp line image parallel to the slit. It was then replaced in the spectrometer tank and subjected to the final adjustment by observing the variation of the intensity of x-rays with the detector system. The position of the x-ray source was adjusted finely until the count rate reached a maximum and remained...
constant over the entire range of movement of the spectrometer.

A curved crystal spectrometer has to be calibrated in terms of suitable reference lines since only relative measurements can be made with such an instrument. For accurate measurements, therefore, it is essential to choose the reference lines of a well defined shape, well resolved from neighbouring structure and easy to produce. In the present case, the reference lines were produced with a conventional x-ray source designed to fit into the spectrometer tank, at F in figure II.2. It was made as a line source in accordance with $E_1, E_2$ in figure II.1a. Generally, $K_\alpha$ emission lines, mostly in higher orders, were employed. The energies of these lines are given together with their profiles in figure II.12 and figure II.13 for the $K_v$ and $K_{IV}$ spectra of cerium and xenon respectively. The energy values were taken from the tables of BEARDEN. In principle, two reference lines for each region are sufficient, but for confirmation some extra lines were obtained.

If $X$ is the distance between the crystal and the detector slit and $R$ the radius of the Rowland circle, then according to the geometry of a curved crystal spectrometer,

$$X = R \sin \theta.$$  \hspace{1cm} (11)

From the solution of equations (8) and (11),

$$\lambda = X \left( \frac{2d}{nR} \right)$$  \hspace{1cm} (12)

which by differentiation leads to

$$\Delta \lambda = \Delta X \left( \frac{2d}{nR} \right)$$  \hspace{1cm} (13)

From an examination of the reference lines, the ratio $\Delta \lambda / \Delta X$, the instrumental dispersion, is found to be $40.1 \times 10^{-3} \, \text{Å/mm}$ with an error of $\pm 0.25\%$. The effective radius, $R$, of the crystal may then be calculated from equation (13) using the value of $d$ ($2d = 19.89 \, \text{Å}$) for first order reflection and it is found to be 49.60 cm.
Figure II.12 Profiles and energies of reference lines for the $M_V$ and $M_N$ spectra of cerium.
**Figure II.13** Profiles and energies of reference lines for the $M_V$ and $M_{IV}$ spectra of xenon (from ref. 59)
5. DISCUSSION OF PROBABLE ERRORS AND THE RESOLVING POWER OF THE SPECTROMETER.

Discussion of Probable Errors

The errors in the measurements may be divided into two groups according to their effect on

a) the value of the mass absorption coefficient, and

b) the wavelength or energy values of the structural details.

The former may be assessed from a consideration of equation (4) which may be rewritten as

\[
\frac{\mu}{\rho} = \frac{1}{\rho x} \ln \frac{I_0}{I}
\]

(14)

It may be shown by partial differentiation of equation (14) that the maximum fractional error in \(\mu/\rho\) is

\[
\frac{\Delta (\mu/\rho)}{\mu/\rho} = \frac{\Delta I_0/I_0 + \Delta I/I}{\ln(I_0/I)} + \frac{\Delta (\rho x)}{\rho x}.
\]

(15)

When a photon counter is used to register the x-ray intensities, \(I_0\) and \(I\), the incident and the transmitted intensities respectively, may be replaced by the corresponding number of counts \(N_0\) and \(N\). As is well known, the standard deviation in counting \(N\) pulses is \(\sqrt{N}\) (and therefore \(\sqrt{N_0}\) for \(N_0\)). Hence equation (15) may be rewritten as

\[
\frac{\Delta (\mu/\rho)}{\mu/\rho} = \frac{\sqrt{N_0}/N + \sqrt{N}/N}{\ln(N_0/N)} + \frac{\Delta (\rho x)}{\rho x}.
\]

(16)

In the present work, when the mass absorption coefficients were measured by counting the incident and the transmitted photons, the number of counts recorded at each setting of the spectrometer was fixed, i.e., the time was measured to register the given number of counts. In the case of cerium, the values of \(N_0\) and \(N\) were chosen so large that the maximum statistical error is \(\pm 2\%\) for the absorption...
continuum. An examination of equation (16) reveals that in the higher absorption regions the statistical error is much lower than this value. The effect of the background on No and N was assumed to be negligible since it was kept below 1% in all measurements. The standard error made in the measurements of the thicknesses of cerium and cerium oxide is as large as ± 1%. The maximum total error in the measurements of the mass absorption coefficient is, therefore, ± 3%.

In the case of xenon, No and N were chosen such that the maximum statistical error is ± 3.2%. For gaseous xenon, the pressure in the cell was measured to an accuracy of ± 2%, thus resulting in a maximum total error of ± 5.2% in the mass absorption coefficient. As mentioned previously, the thicknesses of solid xenon absorbers were estimated from the absorption on the low energy side of the M edge, using data for the gas. With this assumption, the standard error in the thicknesses will be due to counting statistics of ± 3.2% plus the error in the mass absorption coefficient for the gas. Thus, the maximum total error in the mass absorption coefficient is ± 11.6%. It is to be noted that, essentially, the relative values of the mass absorption coefficients will be unaffected by the error made in determining the absorber thicknesses, i.e., the whole absorption curve will be shifted up or down by the same amount corresponding to the error. The standard error, S.E., was marked in the figures of the following chapter to represent the maximum error.

The wavelength of a structure in a spectrum is determined from the relation

\[ \lambda_x = \lambda_a + \frac{\lambda_a - \lambda_b}{X_a - X_b} (X_x - X_a) \]  

(17)

where \( \lambda_x \) is the wavelength to be measured, \( \lambda_a \) and \( \lambda_b \) the wavelengths...
of the reference lines, $X_a$ and $X_b$ their positions on the micrometer scale and $X_x$ the position of the structure. The error in the wavelength measurements may be calculated according to the following equation:

$$\Delta \lambda_x = \left(1 + \frac{X_x - X_a}{X_a - X_b}\right)^2 \cdot \Delta \lambda_a^2 + \left(\frac{X_x - X_a}{X_a - X_b}\right)^2 \cdot \Delta \lambda_b^2 + \left[\frac{\lambda_a - \lambda_b}{X_a - X_b}\right]^2 \cdot \Delta \lambda_a^2 + \left(\frac{\lambda_a - \lambda_b}{X_a - X_b}\right)^2 \cdot \Delta \lambda_b^2$$

(18)

In this equation $\Delta \lambda_a$ and $\Delta \lambda_b$ are taken as $\pm 0.1 \times 10^{-3}$ Å, the stated errors in Ref. 59 for the reference lines. The quantities $\Delta X_a$, $\Delta X_b$ and $\Delta X_x$ are the errors arising from the determination of the positions with the micrometer, thus being equal to 0.1 mm. By substituting these values into equation (18), $\Delta \lambda_x$, the total error in the wavelength measurements is found to be of the order of $\pm 6 \times 10^{-4}$ Å which in the middle of the wavelength ranges under investigation corresponds to errors in the energy values of $\pm 0.04$ eV and $\pm 0.03$ eV for cerium and xenon respectively.

In general, if the spectrometer is operated in a continuous scanning mode and the intensity is recorded with a synchronized pen recorder, then some distortion of the spectrum will occur. This is due mainly to the inertia of the circuit of the count-rate meter which is much greater than that of the pen recorder itself. As mentioned previously, this distortion can be made negligible, however, by a suitable choice of the wavelength scanning speed of the spectrometer with respect to the slit width, $D$, of the counter and the time constant, $RC$, of the count-rate meter. $D$ was initially set to 70 μ as a compromise between intensity and resolution, and for $RC$, 10 sec was found to be the most suitable value; the scanning speed was then chosen according to relation (9). As a check, the K absorption spectrum of neon gas was recorded continuously with...
the pen recorder and compared with that obtained by the point-by-
point method. No significant difference was observed, however, 
between them. The K absorption spectrum of neon gas taken from 
one of the present continuous recordings is shown in figure II.14, 
together with that obtained with a double crystal spectrometer 
by LIEFELD (61); the two curves being normalized for the 1s - 3p 
peak coincidence.

The Resolving Power of the Spectrometer

The spectrum obtained from a spectrometer is distorted to 
some extent by the finite resolving power of the instrument. If the 
transmitted intensity is \( I(\lambda) \) at infinite, or ideal, resolving power, 
the experimentally obtained function for the intensity, \( E(\lambda_0) \), is 
given by the folding integral (62)

\[
E(\lambda_0) = K \int_{-\infty}^{+\infty} I(\lambda) P(\lambda-\lambda_0) d\lambda
\]

(19)

where \( P(\lambda-\lambda_0) \) is the spectral window function, \( \lambda_0 \) is the wavelength 
for which the spectrometer is set and \( K \) a normalizing constant.

\( I(\lambda) \) can be calculated by solving equation (19) if the window 
function, \( P(\lambda-\lambda_0) \), is known.

The resolving power of the spectrometer is affected by the 
following main factors (63):

(a) The diffraction pattern of the analysing crystal,

(b) The Johann type curved-crystal focussing defect,

(c) The height of the focal spot in the x-ray source, and 
effective height of the crystal,

(d) The height and width of the detector slit.

With the crystal dimensions chosen by OTTLEWELL in the present 
spectrometer, the effects of the second and third of the above factors 
are small in the regions under investigation. Therefore, the spectral 
window is defined mainly by the crystal diffraction pattern and the
FIGURE II.14 A COMPARISON OF THE K ABSORPTION EDGE OF GASEOUS NEON
dimensions of the detector slit. At present no data is available for the rocking curves of plane mica crystals, so it is impossible to estimate the diffraction broadening for a curved mica crystal. An examination of figure 11.14 gives some information about the resolving power of the present spectrometer. The 1s - 3p line of the K absorption spectrum of neon gas obtained by LIEFELD with a double-crystal (KAP) spectrometer has a width at half-maximum of the order of 1 eV. Assuming the width of the initial (K) state of about 0.2 eV, LIEFELD concluded that the broadening due to the spectral window of his instrument was about 0.8 eV. The 1s - 3p line width in the present recording is also of the order of 1 eV. Assuming that the optimum neon gas pressure was used by LIEFELD (the neon gas pressure is not given in his paper), it is clear that the resolving powers of the two spectrometers are comparable.
CHAPTER III

EXPERIMENTAL RESULTS

1. The $M_{IV}^*$ Absorption Spectra
   - Metallic Cerium
   - Cerium Silicide
   - Cerium Oxide

2. The $M_{\alpha, \beta}$ Emission Spectrum of Cerium Oxide

3. The $N_{IV}^*$ Absorption Spectrum of Cerium Oxide

4. The $M_{IV}^*$ Absorption Spectra of Xenon
1. THE $M_{IV}$ ABSORPTION SPECTRA

Metallic Cerium

The $M_{IV}$ absorption spectrum of metallic cerium was recorded with great care at both room temperature and liquid hydrogen temperature ($22^\circ K$), and these spectra are shown in figures III.1 and III.2 respectively. For the sake of comparison, the former is reproduced again along with that at $22^\circ K$ in figure III.2. As summarized in tables III.1 and III.2, five different absorbers were employed and from each absorber several recordings were made. The recordings obtained at room temperature were found similar within the limits of experimental errors. Also, no significant difference was observed between the recordings made at $22^\circ K$. The purpose of using different absorbers was to rule out the possibility that the low temperature spectrum was affected by the method of preparation of the absorbers and, or by the cooling treatment.

It is to be noted that absorbers 2 and 5 form two extreme cases. In the former, the substrate temperature was $85^\circ K$ during the evaporation of the cerium sample and the rate of deposition was 5.5 Å/sec, whereas the corresponding values for the latter were $370^\circ K$ and 1.4 Å/sec respectively. In absorber 2, a very abrupt quenching to $85^\circ K$ was achieved as the cerium film was formed. With regard to the $\gamma \rightarrow \alpha$ phase transition in cerium, it is quite reasonable to expect that the amount of $\alpha$ - cerium formed at $85^\circ K$, and consequently at $22^\circ K$, should be greater than that formed by any other way of quenching.

The formation of a cerium film will be influenced by both the rate of deposition and the substrate temperature since the grain size of the film decreases with increasing rate of deposition and decreasing substrate temperature (64). Therefore, in absorber 2 the cerium film should have a small grain size compared with that in absorber 5. The influence of grain size on ytterbium lattice has been observed by...
<table>
<thead>
<tr>
<th>METALLIC CERIUM</th>
<th>SUBSTRATE</th>
<th>SUBSTRATE TEMP. DURING EVAPORATION</th>
<th>THICKNESS (Å)</th>
<th>RATE OF DEPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSORBER 1</td>
<td>2000 Å Al</td>
<td>Room</td>
<td>300</td>
<td>3.33 Å/sec</td>
</tr>
<tr>
<td>ABSORBER 2</td>
<td></td>
<td>85 °K</td>
<td>330</td>
<td>5.50 Å/sec</td>
</tr>
<tr>
<td>ABSORBER 3</td>
<td></td>
<td>Room</td>
<td>550</td>
<td>3.67 Å/sec</td>
</tr>
<tr>
<td>ABSORBER 4</td>
<td></td>
<td>85 °K</td>
<td>400</td>
<td>3.67 Å/sec</td>
</tr>
<tr>
<td>ABSORBER 5</td>
<td></td>
<td>370 °K</td>
<td>336</td>
<td>1.40 Å/sec</td>
</tr>
</tbody>
</table>

**TABLE III.1**  
**ABSORBER PREPARATION DETAILS**
<table>
<thead>
<tr>
<th>METALLIC CERIUM</th>
<th>Recordings at Room Temperature (R.T.)</th>
<th>Recordings at Liquid Hydrogen Temp. (22°K)</th>
<th>22 ° 80 °K Temp. Cycling (Recordings at 22°K)</th>
<th>Annealing (Recordings at 22°K)</th>
</tr>
</thead>
</table>
| ABSORBER 1      | ONE (before quenching) | (after quenching) | TWO (R.T. → 22°K) | ONE (after 5th cyc.) | -----
|                 | ONE (after warming up) | TWO (R.T. → 22°K) | ONE (after 5th) | -----
| ABSORBER 2      | TWO (after warming up) | (after quenching) | TWO (80°K → 22°K) | -----
| ABSORBER 3      | ONE (after warming up) | (after quenching) | ONE (after 1st) | -----
|                 | (R.T. → 22°K) | (after warming up) | ONE (after 5th) | -----
|                 | TWO (to R.T. and quenching to 22°K) | ONE (after 10th) | TWO (45 min. at 390°C) | (after annealing) |
|                 | ONE (after warming up) | (after quenching) | ONE (after 1st) | (and quenching) |
|                 | (80°K → 22°K) | ONE (after 5th) | ONE (after 10th) | (390°C → 22°C) |
| ABSORBER 5      | ONE (before quenching) | (after quenching) | ONE (370°K → 22°K) | ONE (after annealing) |
|                 | ONE (370°K → 22°K) | | | (30 min. at 320°C) |
|                 | | | | (and quenching) |
|                 | | | | (320°C → 22°C) |

**TABLE III.2** NUMBER OF RECORDINGS AND COOLING TREATMENT (R.T.: ROOM TEMPERATURE)
FIGURE III.2  $M_v, iv$ ABSORPTION SPECTRUM OF METALLIC CERIUM  
(room temp. curve raised by 2 Units)
BONNELLE, VERGAND and KARNATAK\textsuperscript{(65)}. This effect was attributed to the promotion of a 4f electron of each atom to the conduction band as the grain size gets smaller. It has been suggested by these authors that the effect might also be observed in the case of cerium. In no instance, however, was a significant difference observed between the spectra obtained from absorbers 2 and 5 at 22°K. Furthermore, temperature cyclings between 80°K and 22°K, which probably influenced the amount of α - cerium at 22°K, showed no effect on the spectrum.

The M\textsubscript{V} and M\textsubscript{IV} absorption lines of cerium shown in figure III.1 are of similar form to those reported by OTTEWELL\textsuperscript{(26)} and KARNATAK\textsuperscript{(27)}, but their energies confirm only those reported by the latter investigator. The energies of the strongest peaks C and G, corresponding to the M\textsubscript{V} and M\textsubscript{IV} lines respectively, are given in table 3, together with those of the above authors.

<table>
<thead>
<tr>
<th></th>
<th>ENERGY (eV)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M\textsubscript{V}</td>
<td>M\textsubscript{IV}</td>
<td></td>
</tr>
<tr>
<td>PRESENT WORK</td>
<td>881.78 ± 0.04</td>
<td>899.60 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>ALL AT ROOM</td>
<td>888.1 ± 0.6</td>
<td>907.6 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>TEMPERATURE</td>
<td>881.8 ± 0.1</td>
<td>899.5 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>OTTEWELL</td>
<td>881.8 ± 0.1</td>
<td>899.5 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>KARNATAK</td>
<td>881.8 ± 0.1</td>
<td>899.5 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III.3 COMPARISON OF MEASURED ENERGIES OF THE M\textsubscript{V} AND M\textsubscript{IV} ABSORPTION LINES OF CERIUM METAL.

Except for the very weak structures C\textsubscript{1} and C\textsubscript{2} on each side of the M\textsubscript{V} line, the spectrum recorded at 22°K turned out to be the same as the room temperature spectrum. It may be seen in figure III.2 that, on going from room temperature to 22°K, no energy shift of the
structures observed was detectable at all. The existence of the structures E and F of the $M_{IV}$ line at $22^\circ K$, in the same form as those at room temperature, is of great interest from the point of view that these are characteristic of cerium atoms with one 4f electron, i.e., trivalent cerium atoms. Furthermore, within the limits of experimental errors, the half widths and peak absorption coefficients of the $M_V$ and $M_{IV}$ lines remained unchanged on going from room temperature to $22^\circ K$. Therefore, these results show clearly that, whatever modification in the electronic structure of cerium takes place on going from $\gamma$ to $\alpha$ phase (100% $\gamma$ to 45% $\alpha + 55\% \gamma + \beta$ in the present case according to figure I.4), it is not strikingly evident in these $M_V$, $IV$ absorption spectra. On the contrary, OTTEWELL's spectrum obtained at $77^\circ K$, where his sample would contain only 10% $\alpha$-cerium (figure I.4), showed the following differences compared with that obtained at room temperature: (a) a shift of about 2 eV to high energy and a broadening of about 1 eV at half maximum in the $M_V$ line, the corresponding values for the $M_{IV}$ line being 0.5 eV and 0.2 eV respectively (b) the peak absorption of the $M_V$ line shows a decrease of about 15% while an increase of 10% occurs, for that of the $M_{IV}$ line, and (c) a remarkable splitting of the $M_V$ line into two components. The $M_V$ absorption line of cerium obtained in the present work and that reported by OTTEWELL are shown in figure III.3, so that a comparison may be made for the most affected line.

If these modifications were due to about 10% $\alpha$-cerium existing in the sample under examination, then the present recordings from a sample containing about 45% $\alpha$-cerium should reveal at least the same changes. Obviously, the failure of the present recordings to reproduce OTTEWELL's low temperature spectrum, even with absorbers prepared under widely different conditions and constant temperature
measurement, casts doubt on the interpretation of that spectrum as an indication of the $\gamma \rightarrow \alpha$ phase transition. One thing to be noted however is the fact that OTTEWELL did not measure the temperature of the foil during the low temperature experiments. So, there must be an uncertainty as to the temperatures actually attained by the foil when cooled and heated. Also the measurements were made on only one sample.

However, in the present work two weak structures $C_1$ and $C_2$ are evident in the $M_V$ line of the spectrum recorded at 22°K. As may be seen in figure III.3, this modification, which is different in character compared with that of OTTEWELL, can be explained by the fact that the $M_V$ line has multiplet structure. A brief discussion of this will be made in the following chapter.

Cerium Silicide

In addition to the spectrum of metallic cerium, the $M_{IV}$ absorption spectra of cerium fluoride (CeF$_3$) and cerium silicide (CeSi$_2$) were obtained in the present work. Cerium atoms in both these compounds are known to possess the same electronic configuration as metallic cerium atoms, i.e., the 4f electrons (one for each atom) are not involved in bonding (28,77). Therefore, in both cases the spectrum was, as expected, similar to that of the metal in respect of both structure and the energies of the peaks; the presence of the fluorine or silicon atoms in the sample did not modify the spectrum to a measurable extent. As an illustration figure III.4 shows the $M_{IV}$ absorption spectrum of cerium silicide. The thickness of the cerium silicide absorber used was 400 Å.

The absorption coefficients obtained for cerium silicide were corrected for absorption by silicon atoms according to the relation
FIGURE III.4 $M_{V,IV}$ ABSORPTION SPECTRUM OF CERIUM IN CERIUM SILICIDE
where \((\mu/p)_{AB}\) is the mass absorption coefficient of the compound, \((\mu/p)_A\) and \((\mu/p)_B\) are mass absorption coefficients of the metal and the silicon respectively, \(a\) and \(b\) the respective masses of \(A\) and \(B\) present in the compound. The mass absorption coefficient of silicon, as well as that of oxygen for which the same correction was made in the case of cerium oxide in the next section, in the energy region under investigation was taken from the tables of HUBBELL. Any error in \((\mu/p)_B\) should introduce an additional uncertainty in the corrected values, but since \(b\) is much smaller than \(a\) for the compounds studied and \((\mu/p)_B\) is also small compared with \((\mu/p)_A\), this uncertainty will be only a few percent of the errors discussed in chapter II.

Cerium Oxide (CeO\(_2\))

The \(M_{\text{IV}}\) absorption spectrum of cerium obtained from CeO\(_2\) absorbers is shown in figure III.5. For this, corrections were made for the absorption of the oxygen present in the compound as described above. The data for cerium oxide were verified by repeating the measurements with different absorbers as outlined in the previous chapter. It is evident that this spectrum was drastically modified compared with that of metallic cerium as may be seen in figure III.6. The strongest lines B and D were displaced about 2 eV towards high energies with respect to those of metallic cerium. In the case of oxide, two relatively strong peaks C and E emerged surprisingly on the high energy side of the \(M_{\text{V}}\) and \(M_{\text{IV}}\) lines respectively. The separation between B and C, which is of the order of 5 eV, is about the same as that between D and E, thus suggesting that C and E are somehow connected respectively with the \(M_{\text{V}}\) and \(M_{\text{IV}}\) lines. The energies of
FIGURE III.5  $M_{V,IV}$  ABSORPTION SPECTRUM OF CERIUM IN CERIUM OXIDE
Figure III.6  \( M_{V,V'} \) absorption spectra of metallic cerium and cerium oxide. A comparison.
the structures observed in this spectrum are given in table III.4 at the end of section 2 of this chapter.

This is an unexpected result not only because it does not confirm the previous data reported by OTTEWELL (26) and by KARNATAK (27), but also because it is not of the theoretically predicted form (46). Assuming that the absorption lines are due to transitions $3d^{10}4f^n \rightarrow 3d^94f^{n+1}$, the $M_V, IV$ absorption spectrum of CeO$_2$ (Ce$^{+4}$) should simply consist of two components for $M_V$ and one for $M_{IV}$ as in the case of La$_2$O$_3$ (La$^{+3}$). Assuming that the weak structure A and line B are those for $M_V$, and line D is that for $M_{IV}$ in figure III.5, then the peaks C and E are unaccounted for.

OTTEWELL had in fact obtained a similar spectrum from an oxidized cerium absorber but, at the time, the two additional peaks corresponding to C and E in the present case were thought to be due to the presence of metallic cerium in the absorber confined by an oxide layer. The present results essentially rule out this interpretation.

In addition to the measurements of the $M_V, IV$ absorption of cerium oxide, an extensive investigation into the oxidation of metallic cerium absorbers was made spectroscopically. This involved essentially the measurements of the $M_V, IV$ absorption spectra from the oxidized metallic cerium absorbers; the oxidation being carried out either in air or in oxygen atmosphere for varying periods.

After the investigations with the metallic cerium absorber 2 (Table III.1) were complete, the absorber was exposed to air for seventeen hours and subjected to $M_V, IV$ absorption measurements. The resulting spectrum is shown in figure III.7 along with that of cerium oxide. Although this spectrum is generally dominated by that of metallic cerium, there are indications that cerium oxide is also...
FIGURE III.7 $M_{V, IV}$ ABSORPTION SPECTRUM OF PARTLY OXIDIZED CERIUM
(after exposing to air for 17 hours)
present in the absorber. The two unresolved peaks appearing on
the high energy side of the M$_{IV}$ line are likely to be connected
with D and E of cerium oxide because they occur at the same energies.

The same absorber was further oxidized in air for five days,
and the resulting spectrum, which is illustrated in figure III.8 as
a copy of the original pen recording, was then indistinguishable from
that of cerium oxide shown in figure III.5. Thus, for a 330 Å thick
cerium film, five days in air were long enough for complete oxida­
tion. Clearly, there is no detectable difference between the M$_{V}$, IV
absorption spectra of cerium oxide and metallic cerium oxidized in
air, providing that the oxidation time is long enough. The same
result was also obtained from absorber 4 (Table III.1) after being
exposed to air for four days.

It is of interest to note here that the data reported by
KARNATAK for cerium oxide is most likely that of partly oxidized
metal since the peak appearing at 906.6 eV (on the high energy side
of the M$_{V}$ line) in their spectrum is in excellent agreement in
energy with peak 2 (at 906.5 eV) of the present spectrum in figure
III.7. It appears, therefore, that his absorber was not exposed
to air long enough for complete oxidation to take place.

Contrary to what was observed for the metallic cerium absorbers
oxidized in air, the M$_{V}$, IV absorption spectrum of absorber 1 (Table
III.1), which had been exposed to pure dry oxygen at a pressure of
200 mm.Hg for three hours, appeared to be identical to that of
metallic cerium. The absorber was further exposed to oxygen of 600
mm.Hg for two hours and the resulting spectrum was again similar
to that of metallic cerium. The same absorber was then left in air
for five days and still no change in the spectrum was observable,
thus indicating strongly that what was formed in the absorber upon
2/12/1975
Absorber 2 (330 Å Thick)
LEFT IN AIR FOR FIVE DAYS

FILAMENT CURRENT: 5 1/3 A
ANODE VOLTAGE: 1500 V
EMISSION CURRENT: 84 mA

I = Transmitted intensity
I₀ = Incident

I = 29 c/s
I₀ = 160 c/s

I = 26 c/s
I₀ = 167 c/s

I = 70 c/s
I₀ = 169 c/s

I = 89 c/s
I₀ = 162 c/s

I = 130 c/s
I₀ = 164 c/s

I = 121 c/s
I₀ = 171 c/s

FIGURE III.8  A CONTINUOUS PEN RECORDING
exposure to oxygen was quite stable.

The data presented here strongly suggest that a metallic cerium absorber oxidized in oxygen is different from when it is oxidized in air. Although it is to be expected that metallic cerium becomes normal cerium oxide (CeO₂) upon exposure to air, it is not so clear why the M⁴⁺ absorption spectrum of the metallic absorber is unchanged upon exposure to oxygen. However, because its spectrum is characteristic of trivalent cerium atoms, it is suggested here that the metallic cerium film either consisted completely of trivalent oxide (Ce₂O₃) or was covered with a thin, protective layer of Ce₂O₃. Obviously these two cases would not be distinguishable spectrosopically. It is to be noted here that these observations are in good agreement with those on the soft x-ray appearance potential spectrum (SXAPS) of cerium reported by SMITH et al. They found that, in both the N⁴⁺ and M⁴⁺ energy regions, the SXAPS spectrum of cerium exposed to oxygen was similar to that of metallic cerium and speculated on the formation of Ce₂O₃ rather than CeO₂. They did no work on pure CeO₂ or on cerium metal exposed to air which might give clearer evidence in support of the present results.

As mentioned previously, following the measurements of the M⁴⁺ absorption spectra, attempts were made to examine the absorbers with x-ray diffraction methods. The absorbers oxidized in air were proved successfully to be of CeO₂, but the diffraction patterns obtained from that oxidized in oxygen were too diffuse and weak to claim confidently that they were of Ce₂O₃.

2. THE Mα, β EMISSION SPECTRUM OF CERIUM OXIDE

Using the normal take-off source described in chapter II (figure II.5), the Mα, β emission spectrum was obtained from vacuum
FIGURE III.9  $M_{\alpha',\beta}$ EMISSION SPECTRUM OF CERIUM IN CERIUM OXIDE
deposited cerium oxide. The resulting spectrum is shown in figure III.9. For this particular recording, the excitation voltage of the electrons was 1500 volts and the thickness of the oxide coating was 400 Å. When a metallic cerium sample exposed to air for several days was used, as expected, the resulting spectrum was similar to that of pure oxide. In general, an emission spectrum is distorted to some extent by self-absorption in the sample. This distortion is greater in the M_{\alpha,\beta} emission spectra of all rare-earths which overlap completely the corresponding M_{\alpha'} IV absorption spectra (24, 25). However, self-absorption can be reduced to a low level if the take-off angle of the x-rays is around 90° and the excitation voltage is set at a value a few hundreds of eV above the M_{\alpha} and M_{\beta} energies. As mentioned in chapter II, the former was achieved by the special electrode design of the source, but for the latter the lowest practical value was 1.2kV. A series of recordings was made at voltages ranging up to 2.2kV. Even at 2.2kV, no significant distortion of the spectrum was observed, however, at the energies of the M_{\alpha'} and M_{\beta'} IV absorption lines where the highest self-absorption is expected (figure III.10).

The previous data on the M_{\alpha,\beta} emission spectrum of cerium oxide are those of FISCHER and BAUN (25), and KARNATAK (27). The former investigators found that the M_{\alpha,\beta} emission spectrum is similar in every respect to that of cerium metal and consists of two lines corresponding to the M_{\alpha} and M_{\beta}. Apart from the unresolved weak structures A and C, which were also detected by the latter author as giving asymmetric appearances to the M_{\alpha} and M_{\beta} lines respectively, the present result agrees well with that of FISCHER et.al. In disagreement, however, our data did not show the two weak structures occurring on the high energy sides of the M_{\alpha} and M_{\beta} emission lines in...
FIGURE III.10  A COMPARISON OF THREE SPECTRA
(metallic Ce curve raised by 3/3 scale units)
in KARNATAK's curve. These structures appeared at energies which correspond closely to those of the $M_{IV}$ and $M_{IV}$ absorption lines of cerium oxide, and they may therefore be the result of residual self-absorption. It should be noted that KARNATAK used a take-off angle of $45^\circ$ and his sample was oxidized metal which might not have been free from metal due to his method of oxidation.

In general, part of the $M_{\alpha}$ and $M_{\beta}$ emission line structure of the rare earths can be explained in terms of the reversible transitions $3d \leftrightarrow 4f$ where they overlap the corresponding absorption lines\(^{(18,24,25)}\). The most striking example of this is perhaps shown in the case of lanthanum. Lanthanum in either trioxide or in the metallic state has no electron in the 4f shell and still the $M_{\alpha}$ ($4f \rightarrow 3d_{5/2}$) and $M_{\beta}$ ($4f \rightarrow 3d_{3/2}$) transitions are produced quite easily. Since these lines are found to occur at the energies of the corresponding absorption lines, according to RUSSELL's suggestion\(^{(18)}\) the initial state of the atom involved in the $4f \rightarrow 3d$ emission transitions is the final state of the $3d \rightarrow 4f$ absorption transitions. Following the ejection of a 3d electron from an atom, a rearrangement in its electronic configuration takes place in which an outer electron is brought into the 4f shell and this is followed by the $4f \rightarrow 3d$ transition. It is clear that, under these conditions, the position of the 4f level relative to that of 3d does not change during such a rearrangement.

The same process might occur in the case of cerium oxide which is expected to form an isoelectronic sequence with lanthanum. Indeed, the $M_{\alpha}$ and $M_{\beta}$ emission lines are readily produced, but, as may be seen in figure III.10, they do not overlap the corresponding absorption lines; the $M_{\alpha}$ and $M_{\beta}$ being displaced by about 2 eV towards low energies with regard to the $M_{IV}$ and $M_{IV}$ respectively. It is to be noted here that the positions of the $M_{\alpha}$ and $M_{\beta}$ lines on the energy...
scale are found to be exactly those of the $M_V$ and $M_{IV}$ lines of metallic cerium, respectively. Hence, it appears that the resulting emission lines, presented in figure III.9, cannot be understood simply in terms of reverse or resonance transitions. This matter will be further discussed in the following chapter. In table III.4, energies of the structures observed in the $M_V$, $IV$ absorption (figure III.5), and in the $M_\alpha$, $\gamma$ emission (figure III.9) spectra are tabulated.

<table>
<thead>
<tr>
<th>CeO$_2$</th>
<th>$M_V$ (eV)</th>
<th>$M_{IV}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td></td>
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<td>883.61</td>
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</table>

<table>
<thead>
<tr>
<th>CeO$_2$</th>
<th>$M_\alpha$ (eV)</th>
<th>$M_B$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>878.20</td>
<td>881.66</td>
</tr>
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<td>*Present work</td>
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<td>*Reference 25</td>
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<td>881.8</td>
</tr>
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</table>

**TABLE III.4 ENERGIES OF STRUCTURES IN THE ABSORPTION AND EMISSION SPECTRA OF CERIUM OXIDE.**

*Accuracies are ± 0.04 eV, ± 0.08 eV and ± 0.1 eV in the present work, in Ref. 25, and in Ref. 27 respectively.*
3. THE $N_v, IV$ ABSORPTION SPECTRUM OF CERIUM OXIDE

The $N_v, IV$ absorption spectrum of both cerium metal and cerium oxide have been measured previously by HAENSEL, RABE and SONNTAG. The spectra were found to consist mainly of two parts. One is the line structure near the 4d threshold, and the other is the broad and intense peak following the line structure. The former is explained as being the result of the transitions $4d^{10} 4f^N \rightarrow 4d^9 4f^{N+1}$, while the latter as being the result of the transitions $4d^{10} 4f^N \rightarrow 4d^9 4f^N ef^{(69)}$; $N$ being 1 for metallic cerium and $\epsilon \geq 5$. The occurrence of the broad peak at about 15 eV above the 4d threshold is understood in terms of the centrifugal potential barrier occurring in the effective potential. For cerium (also for the other rare-earths) the 4f level fits inside this potential barrier and consequently gains its localized character, whereas ef levels remain well outside. Hence the transitions $4d \rightarrow ef$ become intense only if the ejected electrons receive sufficient energy to overcome the barrier.

Recently, SUGAR$^{(70)}$ has analyzed theoretically the $N_v, IV$ spectrum of cerium metal and calculated the energies and oscillator strengths of the lines which are in good agreement with the experimental results.

The $N_v, IV$ absorption spectrum of cerium oxide is found to show a marked difference as compared with that of cerium metal$^{(68)}$; the line structure being modified to a large extent and the broad intense peak shifted about 5 eV to higher energies. This is attributed to the fact that the valence of cerium atoms changes from three in the metal to four in the oxide. From this point of view, the spectrum of, say, CeF$_3$, in which cerium atoms are trivalent, should be similar in form to that of the metal, and this has indeed been
shown by SUZUKI et al. to be so. Because it appears that the observed modifications in both the $M_{\nu'} IV$ and $N_{\nu'} IV$ spectra in the oxide are due to the removal of the 4f electron in bonding, it is possible that a comparison of these spectra may be helpful in understanding the $3d \rightarrow 4f$ absorption anomaly in cerium oxide. However, this comparison is complicated by the fact that the exchange interaction between the 4d hole and the 4f electron is much stronger than that between the 3d hole and the 4f electron, thus affecting the $4d \rightarrow 4f$ transitions more than the $3d \rightarrow 4f$ transitions. It is seen that this interaction, when taken into account, redistributes the excited states of the $4d^9 4f^{n+1}$ configuration ($n = 0$ for CeO$_2$) and raises some levels above the ionization threshold.

In the present investigation, an attempt was made to obtain the $N_{\nu'} IV$ absorption spectra of cerium oxide and cerium fluoride. The grazing incidence monochromator designed by WEST et al. was used in this work with the continuous radiation of the 5 GeV electron synchrotron NINA. The resolution of the spectrometer was about 0.2 Å (0.17 - 0.30 eV) in the wavelength region under investigation. 350 Å thick carbon foils were used as substrates and the method used to prepare the absorbers was as described in chapter II. The thicknesses of the absorbers for the fine structure (low absorption) region were of the order of 800 Å, while for the high absorption region they were of the order of 150 Å.

The $N_{\nu'} IV$ absorption spectra of cerium oxide and cerium fluoride are shown in figure III.11. For the sake of comparison, the metal curve obtained by HAENSEL et al. is included in the figure. When a metallic cerium absorber exposed to air for several weeks was used, the same result as that of normal cerium oxide was obtained,
thus confirming that a metallic cerium absorber becomes normal cerium oxide after long exposure to air.

The resolution of the spectrometer (0.2 Å) was satisfactory for the broad 4d → εf maximum and good agreement between the present results and the previous data \(^{[68, 71]}\) was obtained for this part of the spectrum. However, the resolution of the spectrometer was found to be insufficient for the measurements of the fine structure, a resolution of the order of 0.1 Å (≤ 0.1 eV) being necessary. Hence the spectrum did not reveal adequately the details of the fine structure and no further comment on this is possible.

4. THE Μ_\(V^+\)_IV ABSORPTION SPECTRA OF XENON

As referred to previously, the 4f shell in xenon is no longer an inner orbital, i.e., it is a member of the εf continuum outside the complete xenon core. Hence, in xenon the 3d → 4f transitions are not expected to show line structures like those observed in the rare-earths, but only the 3d → εf (ε ≥ 4) transitions should occur. These transitions should exhibit two broad edge structures corresponding to the M\(V\) (3d\(_{5/2}\) → εf) and M\(IV\) (3d\(_{3/2}\) → εf) which are separated by some 12.5 eV, the spin-orbit splitting of the 3d levels.

Previously, DESLATTES\(^{[47]}\) has measured the absorption of xenon gas in the energy range 670 - 780 eV. He observed the M\(V\) and M\(IV\) edges as being broad maxima and occurring at about 12 eV above the 3d\(_{5/2}\) and 3d\(_{3/2}\) ionization thresholds, respectively. This absorption behaviour has been explained theoretically as being the result of a potential barrier in the effective potential which suppresses the 3d → εf transitions near the threshold \(^{[69, 73]}\). This argument also applies to the 4d → εf transitions in xenon for which the N\(V^+\)_IV absorption spectra have been obtained by HAENSEL et al\(^{[74]}\) in both ...
gaseous and solid states. They showed that the overall shape of the gas spectrum is well produced in the spectrum of solid xenon. However, some modifications, which are not present in the gas curve, are evident as being the result of solidification.

In the present investigation, the $M_{V, IV}$ absorptions of xenon gas and solid xenon were measured and compared with each other. For solid xenon, the measurements were made twice with different absorbers and no significant difference was observed in the results. Tests were made for the solid absorbers whether they were contaminated during the measurements. This was achieved simply by detecting the transmission of x-rays through the film before and after the experiment at certain photon energies. In this way, no evidence of contamination was found during the measurements which lasted about six hours.

In the energy range of the $M_{V, IV}$ absorption spectrum of xenon, the x-ray continuum was distorted to a large extent by a curious structure as shown in figure III.12. It is evident that the continuum suffers an absorption in the energy region 700 - 707 eV followed by a strong (doublet) emission line peaking at 709.6 eV. The absorption might have been due to iron probably present as an impurity in the reflecting mica crystal, but the identification of the emission line was not possible since no such emission data is found in the literature. Because of this uneven continuum, the point-by-point method was used for all xenon measurements. It was observed that when the foil holder with a solid xenon absorber (at 22° K) was left out of the x-ray beam without connecting the cooler, it took the solid xenon about 60 seconds to start to sublime (at about 50° K). A sensitive indication of this was the ion pump current which was used to measure the pressure. This time interval was about 20 sec. longer
FIGURE III.12  CONTINUUM OF THE X-RAY SOURCE IN THE XeM_{V,IV} ENERGY REGION

ANODE VOLTAGE : 1250 V
EMISSION CURRENT: 72 mA
FILAMENT CURRENT: 4.5 A

INTENSITY I, (COUNTS/SEC)

FeL_{III} edge

690 700 710 720
PHOTON ENERGY (eV)
than the longest time required for the fixed number of counts to be obtained. The incident (foil-out) x-ray intensity was therefore obtained after every foil-in intensity measurement. As mentioned in the previous chapter, the standard error in the absolute value of the mass absorption coefficient of solid xenon was ±11.6%, but the relative standard error in the adjacent regions was estimated to be ±3.2%.

The spectra obtained in the present work are shown in figures III.13 and III.14 for xenon gas and solid xenon, respectively. The arrows assigned as 3d_{5/2} and 3d_{3/2} in figure III.13 indicate the ionization threshold energies of the respective electrons for gaseous xenon as given by KRAUSE. The present results for xenon gas agree remarkably well with those of DESLATTES. Two broad peaks (M_V, M_IV) as a result of the transitions 3d → ef are prominent in the spectrum. They are separated by about 12.5 eV which compares well with 12.8 eV, the spin-orbit splitting of 3d electrons of xenon. Both the M_V and M_IV peaks are delayed by about 12 eV compared with their respective ionization thresholds.

Line structure due to the transitions 3d → ep (ε ≥ 6) is expected to appear near each ionization threshold. As may be seen in the gas absorption curve (figure III.13), even near the 3d_{5/2} threshold which is far from the strong absorption region, it is rather difficult to differentiate this structure from the continuum. In figure III.15, the present curve for xenon gas is compared with that of DESLATTES. The dashed curve in the figure is that given by this author and represents the theoretical values according to MANSON and COOPER.

For solid xenon, no experimental data concerning the binding energies of 3d electrons has so far been reported. As a matter of...
FIGURE III.15  $M_{V+4V}$ ABSORPTION SPECTRA OF XENON GAS. A COMPARISON
Figure III.16  $M_{V,IV}$ Absorption Spectra of Xenon. A Comparison
interest, these binding energies with respect to the Fermi level have been calculated by interpolation using the data for solid Te, I, Cs and Ba given by BEARDEN and BURR \((78)\). The resulting values are indicated by two arrows in figure III.14. It may be seen by examining figure III.16 that, the overall shape of the spectra is similar for both gas and solid if one disregards the fine structure. The two broad peaks as a result of the transitions \(3d \rightarrow \epsilon f\) still dominate the spectrum of solid xenon. However, this spectrum is modified to some extent by a fine structure superimposed on the broad humps. This fine structure may be regarded as an extended x-ray absorption fine structure arising as the result of a solid state effect on the outgoing photo-ejected 3d electrons. A further discussion of this matter will be made in the following chapter.

Energies of the maxima observed in the solid xenon curve are given in table III.5.

<table>
<thead>
<tr>
<th>MAXIMA</th>
<th>ENERGY (eV)</th>
<th>MAXIMA</th>
<th>ENERGY (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>682.00</td>
<td>G</td>
<td>697.01</td>
</tr>
<tr>
<td>B</td>
<td>685.84</td>
<td>H</td>
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<td>L</td>
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</tr>
<tr>
<td>F</td>
<td>692.89</td>
<td>N</td>
<td>709.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P</td>
<td>718.34</td>
</tr>
</tbody>
</table>

TABLE III.5 ENERGIES OF FINE STRUCTURE MAXIMA IN THE SOLID XENON SPECTRUM.
CHAPTER IV

DISCUSSION AND CONCLUSION

1. Multiplet Structure.

2. The Low Temperature Spectrum of Metallic Cerium.

3. Cerium Oxide.
   Analysis of the Absorption Spectrum
   Potential Barriers
   The $M_{\alpha, \beta}$ Emission Spectrum

4. $M_{IV}$ Absorption Fine Structure of Solid Xenon.

5. Conclusion.
1. MULTIPLET STRUCTURE

X-ray absorption in the vicinity of the 3d threshold in the rare-earths is principally dominated by the relatively strong and well separated \( M_V \) and \( M_{IV} \) absorption lines. The energy separation of these lines should be equal to the separation of the 3d\(_{5/2}\) and 3d\(_{3/2}\) states from which they originate. The difference in energy of these two states may be calculated by using the equation \( (20) \)

\[
\Delta E = R \alpha^2 \frac{(Z - \sigma)^4}{n^3 \ell(\ell+1)}
\]

where \( \alpha \) is the fine structure constant, \( \sigma \) is the spin relativity screening constant and \( R \) is the Rydberg constant. The other symbols in the equation have their usual meanings. For the \( M_V, IV \) doublet, \( \sigma \) is given as 13\( ^2 \). An evaluation of equation \( (20) \) for cerium yields \( \Delta E = 18.33 \) eV which is in excellent agreement with the experimental value of 17.82 eV. In the case of Xenon, a similar calculation results in a value of 12.64 eV for \( \Delta E \). This value compares very well with 12.5 eV, the separation of the broad \( M_V \) and \( M_{IV} \) absorption peaks observed in the xenon spectrum (figure III.13).

Both the \( M_V \) and \( M_{IV} \) absorption lines consist generally of more than one multiplet component giving rise to a fine structure in the spectrum. The multiplet structure arises from the coupling between the 3d hole left as a result of excitation of a 3d electron to the 4f level and the 4f electrons. Assuming that j-j coupling applies in this case and using the usual x-ray selection rules, two components are found for \( M_V \) and one for \( M_{IV} \) in the case of lanthanum which has no electron in the 4f shell. This has indeed been proved experimentally to be so (26, 46). For cerium possessing one 4f electron, a similar
calculation yields thirty and twenty three components for the
$M_V$ and $M_{IV}$ lines, respectively. Evidently, the fine structure
observed in the $M_V$ and $M_{IV}$ absorption lines of cerium arises
from this multiplicity. Assuming L-S coupling, BONNELLE, KARNATAK
and SUGAR$^{(46)}$ have calculated the energies and relative strengths
of the multiplet components for free $\text{La}^{+3}$ and $\text{Ce}^{+3}$ ions. Their data
for lanthanum are in excellent agreement with their experimental
results. In the case of cerium, the calculations have been made
only for the components which make major contributions to the
strength of the absorption lines. The resulting data tabulated by
these authors are compared in figure IV.1 with the absorption curve
of cerium obtained in the present work. As may be seen in the figure,
the weaker structures E and F of $M_{IV}$ are well accounted for by the
calculation. The broad, weak hump H can be attributed to the true
absorption edge associated with the $M_V$ line as discussed by OTTEWELL$^{(26)}$.
Clearly, H is not related with the multiplet structure being discussed
since it arises as a result of the transitions $3d \rightarrow \epsilon f$. The weak
structure B agrees approximately with the analysis but the structures
A and D ($A$ is about 8 eV on the low energy side and $D$ about 4.5 eV
on the high energy side of $C$, the strongest peak of the $M_V$) are not
accounted for by the calculations. It is to be noted however that $D$
was not observed by KARNATAK$^{(27)}$.

The spectra of lanthanum and cerium have also been analysed
theoretically by DEMEKHIN$^{(79)}$ whose results differ to some extent
from those of BONNELLE et al$^{(46)}$. This is due probably to the use
of different Slater and spin-orbit parameters in the calculations;
in the former, they were evaluated from the functions of Herman-
Skillman whereas, in the latter, they were determined directly from
the observed spectra. DEMEKHIN has applied his data (not given
FIGURE IV.1 $M_{V,IV}$ ABSORPTION SPECTRUM OF METALLIC CERIUM. A COMPARISON WITH THE CALCULATED RELATIVE ABSORPTION INTENSITIES.
(calculated values from Ref. 46)
numerically) to the experimental curves of FISCHER and BAUN\textsuperscript{(25)} which appeared to be not reliable however.

In their calculations, BONNELLE et al\textsuperscript{(46)} treated cerium in the metal as consisting of free Ce\textsuperscript{+3} ions. This is justified by the fact that the outer shell electrons (5s\textsuperscript{2} 5p\textsuperscript{6}) screen the 4f electron from the environment of the solid. Since the 3d \textrightarrow  4f x-ray absorption occurs within the radius of the 4f orbit, it makes little difference whether one considers an atom in a gas, an ion in a metal or in a compound. This was confirmed by the present data on the M\textsubscript{V}, IV absorption of cerium in cerium silicide and cerium fluoride (figure III.4) since they are essentially identical to those of metallic cerium.

Previously, OTTEWELL\textsuperscript{(26)} has shown experimentally that the M\textsubscript{V}, IV absorption spectra of Ba\textsuperscript{+2} and La\textsuperscript{+3} are similar in form. This is as expected because both are members of an isoelectronic sequence with a similar electronic configuration to that of neutral xenon. The same argument should also apply to Eu\textsuperscript{+2} and Gd\textsuperscript{+3} which belong to the isoelectronic sequence : xenon structure plus 4f\textsuperscript{7} (Table I.1 page 12). Indeed, the M\textsubscript{V}, IV spectra of these rare earths reported by KARNATAK\textsuperscript{(27)} appear to be identical. From these facts, the M\textsubscript{V}, IV spectrum of Ce\textsuperscript{+4} (in oxide) would be expected to resemble that of isoelectronic La\textsuperscript{+3}.

As our data for CeO\textsubscript{2} indicate, however, this is not the case because peaks corresponding to C and E in figure III.5 (page 70) do not exist in the lanthanum curve in Ref. 26. This anomalous behaviour may be attributed to the unusual valency (tetravalent) of cerium in the oxide where, in addition to the 5d 6s\textsuperscript{2} electrons, the 4f electron of cerium is also removed to an oxygen site in the compound. It may be seen, in fact, by examining table I.1 (page 12) that there is essentially no 4f contribution to the valencies of Ba\textsuperscript{+2}, La\textsuperscript{+3}, Eu\textsuperscript{+2} and Gd\textsuperscript{+3} referred to above, whereas the tetravalency, in the ...
case of Ce\(^{4+}\), is due evidently to the participation of the 4f electron in chemical bending. This point will be referred to in section 3 of this chapter.

2. THE LOW TEMPERATURE SPECTRUM OF METALLIC CERIUM

As outlined in chapter I, during the \(\gamma \rightarrow \beta\) phase transition the electronic structure of cerium remains unchanged; in both phases it consists of trivalent ions with one electron in the 4f shell. Hence this transition appears to be uninteresting as far as x-ray spectroscopy is concerned. In the case of the \(\gamma \rightarrow \alpha\) transition, on the other hand, the evidence that a configurational change in the electronic structure of cerium takes place is provided by the crystallographic data\(^{33, 34}\), magnetic susceptibility\(^{36}\), resistivity\(^{80}\), and Hall coefficient\(^{81}\) measurements. The \(\gamma \rightarrow \alpha\) transition is isostructural (in both phases the crystal structure is fcc) but gives rise to a volume contraction of 16.5%. \(\gamma\)-cerium is magnetic with a magnetic moment and susceptibility consistent with trivalent cerium metal whereas \(\alpha\)-cerium has a much smaller susceptibility corresponding to an almost tetravalent cerium. The \(\gamma \rightarrow \alpha\) transition is accompanied by a drop in the resistivity of cerium of approximately 50%. This is attributed to an increase in the number of conduction electrons. The Hall coefficient of \(\alpha\)-cerium is found to be about one fourth that of \(\gamma\)-cerium.

These experimental facts are commonly regarded as being in agreement with the promotional model which was first suggested by ZACHARIASEN\(^{37}\) and PAULING\(^{38}\). According to this model the valencies would simply be 3 for \(\gamma\)-cerium and 4 for \(\alpha\)-cerium. However, the calculations by GSCHNEIDNER et al\(^{39}\) give 3.06 and 3.76 for the corresponding values, thus indicating that the removal of the 4f
electron is only partial (about three quarters of an electron).
Also, the small chemical shifts reported by SHABUROV et al (83) of
the K x-ray lines in the $\gamma \rightarrow \alpha$ transition seems to be consistent
with the above model.

As shown in chapter III, the $M_V$ and $M_{IV}$ absorption lines of
cerium in cerium silicide and cerium fluoride occur at the same
energies as those of the metal, whereas a shift of about 2 eV towards
high energies is evident for both lines of cerium oxide. This shift
may be regarded as a chemical shift and appears to be observable
only if there is a difference in the valence. A similar line shift
is also observed for both europium and ytterbium (27) which can be
either divalent (in their metallic states) or trivalent (in their
compounds). That no such shift has been reported for the other rare-
earths may be attributed to the fact that they exist only in the tri-
valent form whether they are metallic or in their compounds (27).

On removing an outer electron of an atom all its core levels
are shifted by approximately the same amount because of a reduction
in the screening. In the case of the rare-earths, however, the
removal of a 4f electron causes the core levels to shift by different
amounts, as is expected because of the localized character of the 4f
electrons (FADLEY et al (82)). Some evidence for this is provided by
the $K\alpha_1, K\beta_1$ and $K\beta_2,4$ x-ray line shifts of cerium (metal-oxide)
measured by SHABUROV et al (83). Unlike an x-ray line shift which
requires consideration of two similar (core) levels, the $M_V$ and $M_{IV}$
absorption line shifts of cerium involve two qualitatively different
levels ($3d_{5/2}, 3/2$ core levels and 4f unoccupied states). The effect
of neighbouring ions (crystal field effect) upon both the 3d and
empty 4f levels should be small compared with that due to the reduced
screening (increase in the valence) because of the fact that these
levels are regarded as well localized. Reliable photoemission data for the 3d electrons of cerium would be valuable in determining the absolute shift of the 3d level in going from the metal to the oxide. One could then calculate the absolute shift, if any, of the unoccupied 4f states by using the $M_V$ and $M_{IV}$ absorption line shifts obtained in the present work. Presently, the only available photoemission data are those of NAGAKURA, ISHII and SAGAWA who reported an energy shift of 2-3 eV (to high energies) of the 3d level in the oxide relative to that in the metal. Clearly, there is a significant difference between these limits and it is hard to choose a value for a quantitative analysis.

Since it becomes evident that the $M_V$ and $M_{IV}$ absorption line shifts are associated with an increase in the valence of cerium, it would be reasonable to expect that a similar line shift would be observed if there were an increase in the valence of cerium following the $\gamma \rightarrow \alpha$ phase transition. However, considering the fact that the amount of $\alpha$-cerium in an absorber at 220K is 45% (the rest is $\gamma + \beta$) as outlined in Chapter I, the expected shift would not be as much as that observed for the oxide.

In order to gain an insight into how the $M_V$, $M_{IV}$ absorption spectrum would look if the absorber at 220K contained 45% Ce$^{+4}$ ions (corresponding to $\alpha$-cerium according to the promotional model) and 55% Ce$^{+3}$ ions, a simple analysis has been carried out. In doing this it was assumed that the known absorption data of cerium oxide and metallic cerium (at room temperature) could be used for the hypothetical Ce$^{+4}$ and Ce$^{+3}$ respectively. The resulting curve is presented in figure IV.2 and compared with the room temperature cerium curve. As a result of this analysis it is proposed here that the form of
Figure IV.2  A comparison of the hypothetical curve with the \( M_{V, IV} \) absorption spectrum of metallic cerium.
the spectrum at 220K would be similar to the hypothetical curve in figure IV.2 if the \( \gamma \rightarrow \alpha \) transition involved a transfer of the 4f electrons into the conduction band. The evident changes (a decrease in the peak absorption coefficients of about 23% for \( M\_V \) and 22% for \( M\_IV \), an increase of about 2 eV in the half-widths, and a remarkable modification of both the \( M\_V \) and \( M\_IV \) lines) could readily be demonstrated with the present spectrometer. As seen in chapter III, the fact that the spectrum obtained at 220K does not exhibit any of these modifications but rather resembles that at room temperature, appears to be against the promotional model, which was proposed to explain the mechanism of the \( \gamma \rightarrow \alpha \) phase transition in cerium (37, 38).

The results of the present investigation are in complete agreement with those of the positron annihilation experiments of GUSTAFSON et al (41). These experiments showed essentially no increase in the valence of cerium when the \( \gamma \rightarrow \alpha \) transition occurred.

From the evidence presented above it may be suggested that any model capable of explaining the mechanism of the \( \gamma \rightarrow \alpha \) transition in cerium should consider the 4f level to be strongly localized in both phases within the closed xenon core. Such a model has in fact been proposed by HILL and KMETKO (85). These workers think that the 4f electron is hybridized with the 5d 6s\(^2\) electrons and the degree of hybridization is responsible for the observed features associated with the \( \gamma \rightarrow \alpha \) transition. An alternative model is that put forward by JOHANSSON (43) according to which the localized 4f level in \( \gamma \)-cerium becomes an itinerant narrow band in \( \alpha \)-cerium. These two models seem in a sense to be similar and both predict that there is no 4f contribution to the valence of cerium in either phase, therefore in accordance with the results of the present investigation.
With regard to the widths of the occupied 4f states in y and α cerium, there have been several suggestions which differ to a large extent. Accepting the width of 0.4 eV of the 4f states in γ-cerium, the value estimated within the renormalized atom approach by HERBST et al \((29)\), JOHANSSON \((43)\) predicts that the width for α-cerium should be of the order of 1 eV, thus an increase in the width of about 0.6 eV. Recent photoemission experiments by STEINER et al \((86)\) give a width of the 4f states in γ-cerium of 0.7 eV which may be regarded as in fair agreement with 0.4 eV. These values, however, turn out to be about three times greater than those according to the relativistic augmented plane-wave calculations of MUKHOPADHYAY and MAJUMDAR \((45)\). In spite of the disagreement between the values, the data presented above agree on the fact that the occupied 4f states have a width greater in α than in γ-cerium. This broadening is attributed to an increased crystal field effect in α-cerium \((43)\).

If, in accordance with the occupied 4f states, it is assumed that the unoccupied 4f states undergo a similar broadening in α-cerium, then the magnitude of this broadening might be expected to be only a few tenths of an eV. The smallness of such a change in the width might therefore be the reason why both the M\(_V\) and M\(_{IV}\) absorption lines recorded at 220K showed no increase in their half widths compared with those at room temperature.

For the position of the occupied 4f states, the results of the valence band photoemission experiments give the values of 0.9 eV \((BAER et al \((17)\))\) and 0.5 eV \((STEINER et al \((86)\))\) below the Fermi level. As to the position of the unoccupied 4f states relative to the Fermi level, it cannot be determined directly but may be estimated, according to KARNATAK \((27)\), by using the energy of the M\(_{III}\) absorption edge in cerium metal. It may be seen in figure IV.3 that
FIGURE IV.3 PART OF ENERGY LEVEL DIAGRAM OF CERIUM. A SCHEMATIC ILLUSTRATION.
the distance, $\Delta$, between the unoccupied 4f states and the Fermi level is given by

$$\Delta = M_{\text{V}} (\text{abs}) - [M_{\text{III}} (\text{abs}) - D_1]$$

or

$$\Delta = M_{\text{IV}} (\text{abs}) - [M_{\text{III}} (\text{abs}) - D_2].$$

$D_1$ and $D_2$, the separation between the $M_{\text{III}}$ and $M_{\text{V}}$, and $M_{\text{III}}$ and $M_{\text{IV}}$ energy levels respectively, are taken from the atomic energy level tables by BEARDEN and BURR (78). An evaluation of equations (21a) and (21b), when the present data for the $M_{\text{V}}$ and $M_{\text{IV}}$ absorption lines and the energy of the $M_{\text{III}}$ absorption edge reported by KARNATAK (27) are used, reveal that the unoccupied 4f states in cerium lie about 1 eV (1.28 eV using 21a and 1.10 eV using 21b) above the Fermi level. This value, however, may vary between 0.5 and 1.5 eV due to errors in the energies of the atomic levels used, but it will, in any case, be positive, indicating therefore that the unoccupied states should lie above the Fermi level.

As to the weak structures $C_1$ and $C_2$ (figure III.2 page 63) appearing on the $M_{\text{V}}$ absorption line of cerium at 22°K, they may be regarded as being associated with the multiplet structure in the line. It is seen in figure IV.4, where the $M_{\text{V}}$ line is reproduced together with the calculated line components (46), that relatively strong components (two for both $C_1$ and $C_2$) on each side of the strongest one are likely to be responsible for the weak structures. The fact that these structures do not appear in the room temperature curve implies that the spread (in the energy scale) of the multiplet components is somehow influenced by the relatively large volume contraction of cerium in the $\gamma \rightarrow \alpha$ transition. This may be considered as follows.

Regarding the 4d $\rightarrow$ 4f transitions, because of the great overlap
FIGURE IV.4  $M_v$ ABSORPTION LINE OF CERIUM.  
A COMPARISON WITH THE CALCULATED RELATIVE ABSORPTION INTENSITIES.  
(calculated values from Ref. 46)
of the $4f$ wave function with the $4d$ wave function, the exchange interaction between the $4d$ hole and $4f$ electrons is strong \((69)\), thus giving rise to a large spread of the multiplet components arising from the $4d^94f^2$ (for $Ce^{+3}$) configuration. In the case of the $3d \rightarrow 4f$ transitions, on the other hand, the exchange interaction between the $3d$ hole and $4f$ electrons is relatively small and consequently their influence on the $3d^94f^2$ configuration is also small. Hence the multiplet components of both the $3d_{5/2}^94f^2$ and $3d_{3/2}^94f^2$ configurations are so close to each other as to produce strong and relatively sharp $M_V$ and $M_{IV}$ absorption lines. The origin of the appearance of $C_1$ and $C_2$ at $22^0K$ can now be understood qualitatively within the assumption that the overlap between the $4f$ and $3d$ wave functions is slightly greater in $\alpha$-cerium than it is in $\gamma$-cerium. The fact that the metallic radius of cerium is smaller in $\alpha$ than in $\gamma$ phase \((28)\) supports this idea qualitatively. It is therefore the effect of the slightly increased exchange interaction which gives rise to an increase in the separation between the multiplet components in $\alpha$-cerium; evidently the increase is small so that although the overall shape of both the $M_V$ and $M_{IV}$ lines was not changed significantly, $C_1$ and $C_2$ were just resolved. These modifications would, of course, be more remarkable if one obtained the spectrum of 100% $\alpha$-cerium.

It is of interest to note here that the $N_V^\prime$, $IV$ absorption spectrum of $\alpha$-cerium should undergo similar changes if the above suggestion is correct. At present, however, there is no data for the $N_V^\prime$, $IV$ absorption of cerium at low temperatures.
3. CERIUM OXIDE

Analysis of the Absorption Spectrum

As shown in figure III.5 (page 70), the $M_V$ and $M_{IV}$ absorption lines of cerium in its oxide are accompanied by the quite well resolved peaks C and E, respectively. With the latter structures which are unexpected as already mentioned, cerium oxide stands alone as there is, as far as known, no similar marked irregularity among the other rare-earths. Cerium oxide also shows its peculiarity in the $N_{IV}$ absorption spectrum (68, 87) which still remains unsolved. The emission spectrum of cerium oxide (figure III.10) also shows a departure from the familiar behaviour of the other rare-earth oxides and compounds as the $M_\alpha$ and $M_\beta$ emission lines do not appear to be of reversible or resonance type.

An attempt has been made to analyse the absorption curve of cerium oxide assuming that all the observed peaks are of Lorentzian shape (26, 27) and the result is shown in figure IV.5. It is seen from the figure that the energy separation of the peaks C and E is the same, within the limits of experimental error, as that of the stronger peaks B and D. This indicates clearly that both B and C, and D and E have essentially the same origin (initial states), i.e., $3d_{5/2}$ and $3d_{3/2}$, respectively. It means therefore that there are mainly two sets of final states separated by approximately 5 eV. Of these, the first set appears to be formed by unoccupied 4f states and gives rise to the stronger peaks B and D, the second, which we are trying to identify, results in the weaker peaks C and E. The widths of the absorption lines B and C (of $M_V$) at half maximum, measured from the analysed curve in figure IV.5, were found to be comparable. This also applies to the lines D and E of $M_{IV}$. 

/.../
Figure IV.5

Absorption spectrum of cerium in oxide.

Absorption coefficient $\kappa/\rho$ (cm$^2$/gm)

Photon energy (eV)

120000 100000 80000 60000 40000 20000
It follows from this comparison that the width of the second set of unoccupied states, corresponding to the peaks C and E, is of the same order as that of unoccupied 4f states. This close similarity between the two sets of unoccupied states indicates therefore that the second set is essentially localized inside an effective potential barrier, resembling in character the unoccupied 4f states. Transitions of 3d electrons into such localized states would then be essentially atomic in character and may be treated within the hydrogenic approximation.

In the light of the above discussion, it is of interest to consider the transition probabilities of a hydrogenic 3d electron into states possessing f-type and p-type symmetries, calculated by CONDON and SHORTLEY (86). The data given by these authors are

\[ P(3d \rightarrow 4f) = 0.137 \]
\[ P(3d \rightarrow 5f) = 0.045 \]
\[ P(3d \rightarrow 6f) = 0.0210 \]
\[ P(3d \rightarrow 6p) = 0.0007 \]

It is seen that the transition probability is large only if the final state is of f-type symmetry. Of the above data, the ratio of P (3d \( \rightarrow \) 5f) to P (3d \( \rightarrow \) 4f) yields 0.33 which appears to compare very well with 0.32, the ratio of total absorption of small peaks C and E to that of stronger peaks B and D. The latter value was obtained from figure IV.5.

Evidently, the comparison presented above implies that the unoccupied 5f states of cerium in its oxide might be responsible for the observed extra peaks C and E in the oxide curve. In other words, in addition to \( 3d^{10} 4f^0 \rightarrow 3d^9 4f^1 \), the transitions \( 3d^{10} 5f^0 \rightarrow 3d^9 5f^1 \) occur in which the 5f states are isolated somehow from the higher f states (6f, 7f, etc.) so as to be localized like the 4f states.
Potential Barriers

A well known example of potential barriers in atomic physics is the centrifugal barrier occurring in the effective potential for electronic states with high angular momentum ($\ell \geq 2$). This barrier results from the addition of a repulsive centrifugal potential to the attractive electrostatic potential acting on an electron in the field of an atomic ion. As an example and being relevant to the present work, the effective potential curve corresponding to $\ell = 3$ is shown in figure IV.6 using the Herman-Skillman potential for cerium (89). Evidently, a wide potential barrier peaking at approximately $1.4 \, \text{Å}$ and with a height of about 4 eV partitions the atomic potential into an inner well and an outer well. The localized character of the 4f states in cerium arises from the fact that the 4f wave function fits in the inner well and is screened by the barrier from the environment. Because of this, there is a strong overlap between the 4f and 3d wave functions. Hence the transitions $3d \rightarrow 4f$ (between inner well states) result essentially in strong absorption lines. The 5f states, on the other hand are outer well states (76); they are not screened and are subject to the effect of the environment, and the overlap between the 5f and 3d wave functions is comparatively small. Consequently, the spectra arising as a result of the transitions to higher f states appear as broad humps as first observed by OTTEWELL (26) for Ce, La and Ba with their maxima corresponding to transitions into continuum or cf states of positive energy.

The results of the present investigation into the $M_{V', IV}$ absorption spectra of cerium, cerium silicide and cerium fluoride are consistent with the above discussion but it appears not so for cerium oxide. As mentioned already, the 4f electron of cerium in
FIGURE IV.6

EFFECTIVE ATOMIC POTENTIAL
FOR CERIUM (Ref.89)
(dashed curve from Ref.76)
the oxide is involved in chemical bonding. This alters the distribution of states of f symmetry through the creation of an additional or so-called pseudopotential barrier in the effective potential.

The pseudopotential barrier in cerium oxide is due to the oxygen (electronegative) atoms surrounding a Ce^{4+} ion and is different in character from that due to the centrifugal repulsion term. The resulting (total) effective potential barrier which will be felt by an outgoing electron of f symmetry then equals the centrifugal barrier plus the pseudopotential barrier.

The existence of pseudopotential barriers in molecules, such as SF_{6}, has been discussed in detail by DEHMER (90). Generally, these barriers are attributed to the fact that a photo-ejected electron experiences a net repulsive interaction in the vicinity of the electronegative atoms due to three effects: (1) direct Coulomb interaction with the electrons concentrated on the electronegative atoms, (2) exchange interaction with the same electrons, and (3) the Pauli exclusion principle in regions of high electron density about the electronegative atoms. As a result, the electronegative atoms are regarded as producing a net repulsive barrier in the effective potential which is therefore partitioned into an inner and outer well. Although the relative contributions of the three interactions to, and hence the precise nature of a net potential barrier are not known, it has been successful in explaining qualitatively the K absorption spectrum of SF_{6} (91). The concept of such a barrier had actually arisen from the strong similarity of this spectrum to the M absorption spectra of the rare-earths (92).

The cerium oxide crystal is fcc (CaF_{2} type) in which a cerium ion is surrounded by eight oxygen ions, at 2.34 Å from the cerium ion, as the nearest neighbours (93). A unit consisting of a positive
Ce ion and eight negative oxygen ions can be looked upon as a molecular unit if the remainder of the lattice is ignored for a moment. Hence in this molecular unit, resembling in principle the $\text{SF}_6$ molecule, there must exist a potential barrier due to oxygen atoms. The likely position of this barrier is indicated in figure IV.6. This barrier, although its profile is not known, may be regarded as modifying the barrier due to the centrifugal repulsion term so as to result in a higher and broader total effective barrier.

In general, it may be said that a photo-ejected electron will face a different barrier than it would in the absence of oxygen atoms.

The occurrence of localized 4f and 5f states or, more correctly, bound excited states in cerium oxide may now be explained as follows.

Cerium in cerium oxide in its ground state possesses no 4f electron. Hence all states of f-symmetry lie in the outer well. Following ejection of a 3d electron by a photon of appropriate energy, the hole left behind pulls the 4f states into the inner well (94) and this leads to excitations into discrete bound 4f states. It appears, as a result of the present investigation, that a similar transfer, from the outer to the inner well, of the 5f states occurs so that the inner well transitions $3d \rightarrow 5f$, in addition to $3d \rightarrow 4f$, become possible. However, the 5f excited inner well states will not necessarily be discrete but may be described as quasi-discrete states so that an electron in these states has a finite probability of passing through the barrier into the outer well (90). In the light of the above discussion, it may be suggested that this probability is reduced to a minimum through the width of the modified effective potential barrier in cerium oxide. Hence the 5f states become almost discrete in the inner well, resembling, in principle, the 4f states.

...
In this connection, it may be pointed out that the weak structure D, observed in the $M_{IV}$ spectra of both metallic cerium and cerium silicide (figures III.1 and III.4), may be due to the transitions of 3d electrons into quasi-discrete 5f states. This structure was not accounted for in terms of the $3d^9 4f^2$ final configuration (46). It may be due to the relatively high absorption continuum that the spin-orbit mate of D was not observed on the high energy side of the $M_{IV}$ line. Another example of the above model is perhaps provided by the $M_{IV}$ absorption spectra of Eu and Gd reported recently by BONNELLE et al. Together with the results of their calculations, the weak structure labelled as 3 (in both Eu and Gd curves) was not accounted for by the calculations which are based on the transitions $3d^{10} 4f^6 \rightarrow 3d^9 4f^7$. That this structure occurs at an energy about 5 eV above the $M_{IV}$ line (as in the case of cerium oxide) indicates the possibility that it is connected with the transitions $3d \rightarrow 5f$ (quasi-discrete states). The weakness of the structures when Ce$^{+3}$, Eu$^{+2}$ (or Eu$^{+3}$) and Gd$^{+3}$ are involved may be attributed to the higher probability, compared with that in cerium oxide, that an electron in the quasi discrete states transfers to the outer well.

The $M_{\alpha, \beta}$ Emission Spectrum

As pointed out in chapter III, both the $M_{\alpha}$ and $M_{\beta}$ emission lines observed from cerium oxide samples showed shifts of approximately 2 eV towards low energies as compared with the corresponding absorption lines. This observation reveals that the $M_{\alpha, \beta}$ emission spectrum shown in figure III.9 cannot be explained in terms of reverse transitions, a model suggested by RUSSELL (18) to account for that of lanthanum. It may be seen in figure III.10 (page 79)
that the energies of \( M_\alpha \) (oxide) and \( M_\beta \) (oxide) are those of \( M_V \) (metal) and \( M_{IV} \) (metal), respectively. Furthermore, the former also coincide in energy with \( M_\alpha \) (metal) and \( M_\beta \) (metal) which are, according to KARNATAK (27), reverse transitions of \( M_V \) (metal) and \( M_{IV} \) (metal), respectively. It is evident therefore that the initial states involved in the emission transitions \( 4f \rightarrow 3d \) are essentially the same in both cases. In other words, during the emission process, cerium in the oxide simply behaves like that in the metal.

In order to explain this anomalous behaviour, it is suggested that, in the course of electron bombardment, a structural change in the sample takes place in which cerium oxide is either decomposed so as to form a metallic sample or is converted into trivalent cerium oxide (\( \text{Ce}_2\text{O}_3 \)). In both cases, cerium will be trivalent and that the resulting emission spectrum will be the same.

If, according to the above suggestion, such a change in the sample occurred, then the \( M_\alpha, \beta \) emission spectrum obtained in the present work would not be relevant to cerium oxide (\( \text{CeO}_2 \)), but rather characteristic of trivalent cerium. However, we have always referred to this spectrum as that of cerium oxide since the experiments were commenced with pure cerium oxide (\( \text{CeO}_2 \)).

Finally, it is pointed out that further experiments are necessary to test the above suggestion. It is likely that x-ray diffraction methods will give information about what goes on in the sample during electron bombardment, i.e., detection of a change in the crystal structure would be good evidence.

4. \( M_{IV} \) ABSORPTION FINE STRUCTURE OF SOLID XENON

The results of the present investigation into the \( M_{IV} \) absorption spectra of both solid and gaseous xenon have been...
presented comparatively in figure III,16 (page 92). A close examination of these curves reveals that, except for the fine structure in the solid xenon curve, the overall shape of the spectrum observed in the gas carries over substantially unchanged to that in the solid. This feature can also be seen in the N\textsubscript{V}, IV region when the strong absorption peak in solid xenon is compared with that in gaseous xenon (74). The occurrence of the M\textsubscript{V} and M\textsubscript{IV} absorption peaks at energies several eV above their respective ionisation thresholds is now known to be due to an effective potential barrier which exists in xenon for photo-ejected f symmetric (\(\ell = 3\)) electrons (76). The \(\text{ef}\) wave function at threshold has very little overlap with the 3d wave function, but the overlap becomes appreciable however only at energies some 12 eV above the threshold. In other words, 3d electrons in xenon have to receive energies enough to overcome the barrier so that the transitions 3d \(\rightarrow\) ef become prominent. This argument holds also for the analogous transitions 4d \(\rightarrow\) ef.

It is seen in figure III,16 that the solid xenon curve exhibits a fine structure which does not exist in the case of gaseous xenon. Evidently, this fine structure, appearing as modulations in the absorption coefficient, arises as a result of solidification in which the effect of neighbouring atoms on an absorbing atom has become appreciable. Remembering that, in this case, a photo-ejected electron is to a large extent free from the field of the absorbing atom, the effect can only be due to scattering of the photo-ejected electrons. In other words, the outgoing electron wave is backscattered at neighbouring atoms. As a result, the outgoing wave is subject to interference with the backscattered wave which, depending on the electron energy, can be either constructive or
destructive at the position of the absorbing atom. Such constructive and destructive interferences appear therefore as maxima and minima, respectively. Hence the structure due to the maxima and minima in the absorption coefficient is known as extended x-ray absorption fine structure (EXAFS). This argument follows essentially the original theory proposed by Kronig (10) to explain the EXAFS observed for isolated molecules.

In accordance with the above discussion, the fine structure in the solid xenon curve observed in the present investigation is most likely to be connected with the interference, at the absorbing atom, between the photo-ejected (3d) electron wave and that back-scattered from the neighbouring atoms, i.e., the structure can be regarded as EXAFS. In support of this conclusion, it is to be noted that a similar suggestion has been made by Koch, Kunz and Sonntag (94) for the modulations in the N_{IV} absorption spectrum of solid xenon (74) which might have the same origin. However, the fine structure in this spectrum is not sufficiently well resolved for it to be compared with that in the M_{IV} spectrum. It is possible that such a comparison would show whether the relative energies of the fine structure maxima of both spectra are the same, within the limits of experimental error, at energies equally separated from their respective thresholds. This is expected because the environment of the absorbing atom and the final state wave functions are the same in both cases. Actually, a further complication in analysing the M_{IV} spectrum comes from the fact that the M_{IV} peak overlaps the M_{V} to a large extent in a region where modulations in both should occur. This might be the reason why the fine structure of M_{IV} was washed out more than that of M_{V}. A similar complication exists also in the case of the N_{IV} spectrum...
in which an even greater overlap of the $N_V$ and $N_{IV}$ peaks occurs as result of the smaller 4d spin-orbit splitting.

From a theoretical point of view, the absorption coefficient which is a result of contributions of both the dipole transitions and backscatterings of the photo-ejected electrons may be formulated in terms of the appropriate matrix element (94)

$$\int \left[ \Psi^* (r) + \Psi_{SC}^* (r) \right] \hat{\varepsilon} \cdot \nabla \Psi_V (r) \, dr. \tag{22}$$

In this equation $\Psi_V (r)$ is the initial state wave function, $\Psi^* (r) + \Psi_{SC}^* (r)$ represents the final state as a superposition of an outgoing wave $\Psi (r)$ with $\Psi_{SC} = \sum_i \Psi_i$, a sum over the backscattered waves from the neighboring atoms located at positions $i$, and $\hat{\varepsilon}$ is the unit vector in the direction of polarization of the incoming radiation. Since the absorption cross section is proportional to the square of the matrix element, one obtains from equation (22):

$$\sigma = \left| \int \Psi^* (r) \, \hat{\varepsilon} \cdot \nabla \Psi_V (r) \, dr + \int \Psi_{SC}^* (r) \, \hat{\varepsilon} \cdot \nabla \Psi_V (r) \, dr \right|^2. \tag{23}$$

The first term in this equation corresponds to the dipole transition cross section and gives an absorption coefficient varying smoothly with energy, while the second term stands as a contribution which oscillates as a function of the final state energy.

The exiting calculations of the second term in equation (23) are those of SHIRAIWA et al (96) and SAYERS et al (13) whose results appear to be in fair agreement with the K absorption fine structure of, say, Cu and Fe observed at energies about 100 eV above the threshold. The approximations used, such as omitting the multiple scattering and the details of the potential of the absorbing atom, make the above model calculation inapplicable...
to the fine structure occurring within about 50 eV from the threshold (94). This is because in this energy region multiple scattering of the electron by first and second nearest neighbours become appreciable as does the effect of interaction between the electron and the core hole in the absorbing atom. Without taking account of these facts, PETERSON and KUNZ (14) have attempted a calculation, in a manner similar to that of SHIRAIWA et al (96), of the observed L\textsubscript{II, III} absorption fine structure of aluminium occurring in the region about 50 eV above the threshold. They claimed limited success in reproducing the spectrum qualitatively and pointed out the need of a more advanced EXAFS theory for a quantitative analysis.

As far as is known, no theoretical treatment concerning M\textsubscript{V, IV} absorption edge fine structure has been reported. In fact, the present experimental work appears to be the first to demonstrate clearly the existence of EXAFS in the M\textsubscript{V, IV} absorption spectrum of solid xenon.

Finally, it may be pointed out that a discussion of this EXAFS in terms of the band calculation on solid xenon by RÖSSLER (97) is impossible since this calculation is restricted to a region only up to 8 eV above the Fermi level, i.e., it does not cover the region of delayed strong absorption peak where the EXAFS occurs.
5. CONCLUSION

The measurements on the $M_V$, $IV$ absorption spectrum of metallic cerium at $22^\circ K$ have shown that the $\gamma$-$\alpha$ phase transition in cerium does not involve a change in the number of $4f$ electrons; the valence of cerium remains unchanged. These results, in agreement with those of the positron annihilation experiments (41), are regarded as providing evidence in support of the recent models (43, 85) proposed for explaining the nature of the $\gamma$-$\alpha$ phase transition in cerium.

It has been shown conclusively that the $M_V$, $IV$ absorption spectrum of cerium in cerium oxide is strikingly different from those reported previously (26, 27). Two relatively strong peaks, one connected with $M_V$ and the other with $M_{IV}$, are found to occur in the spectrum. These extra peaks are attributed to the transitions of $3d$ electrons into quasi-discrete $5f$ states in cerium oxide.

The study of the $M_V$, $IV$ absorption spectra obtained from oxidized metallic cerium absorbers has provided evidence that metallic cerium becomes normal cerium oxide ($CeO_2$) when oxidized in air (at atmospheric pressure), whereas oxidation in dry oxygen yields trivalent cerium oxide ($Ce_2O_3$). However, in the latter case, the possibility that the metallic absorber is covered with a protective, thin layer of $Ce_2O_3$ was not ruled out by the present experiments.

The observed $M_\alpha$ and $M_\beta$ emission lines of cerium in cerium oxide do not occur at the energies of corresponding absorption lines and therefore appear not to be of reverse or resonance type.
This inconsistency is attributed to a change in the electronic structure of cerium (tetravalent → trivalent) in the oxide sample in the course of electron bombardment.

The comparison between the $M_{V, IV}$ absorption spectra of solid and gaseous xenon has provided evidence that the transitions $3d \rightarrow 4f$ are predominantly atomic in character with both spectra showing similar delayed strong absorption peaks. However, striking modulations, regarded as an $M_{V, IV}$ EXAFS, have been observed in the solid xenon curve and these are attributed to interference between the outgoing electron wave and the backscattered wave from the neighbouring atoms.
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