1982

A photoemission study of the 4f character in gamma and alpha cerium

David Michael Wieliczka

Iowa State University

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A PHOTOEMISSION STUDY OF THE 4F CHARACTER IN GAMMA AND ALPHA CERIUM

*Iowa State University*  Ph.D. 1982

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A photoemission study of the 4f character in gamma and alpha cerium

by

David Michael Wieliczka

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

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Iowa State University
Ames, Iowa

1982
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INTRODUCTION

The element cerium was first discovered in 1803, in the form of an oxide (1). In 1827, metallic cerium was isolated using sodium to reduce cerous chloride (2). Since that time, cerium has been the subject of many experiments. The fascination with this element is due to its varied properties in each of its five allotropic forms.

The pseudo-equilibrium pressure-temperature phase diagram is shown in Fig. 1. The boundaries drawn as dashed lines do not necessarily represent the true equilibrium phase boundaries due to the large hysteresis associated with these transformations. Studies by Hull (3) in 1921 at room temperature and atmospheric pressure indicated that cerium had both a face-centered cubic (fcc) and a hexagonal closed packed structure (hcp), labeled γ- and β-Ce, respectively. Subsequent studies showed that γ-Ce existed solely in an fcc structure. The next phase to be identified was the α-phase. It was observed at both high pressure and room temperature by Lawson and Tang (4) in 1949 and at atmospheric pressure and low temperature by Schuck and Sturdivant (5) in 1950. The α-phase was also identified to be fcc in structure, but the volume was found to be about 17% less than that of γ-Ce. In 1957, β-Ce was identified by McHargue et al. (6) to have a double-hexagonal closed packed structure (dhcp). This phase is produced by cooling γ-Ce below 270K. A few years later in 1961 Spedding et al. (7) identified a high temperature phase, δ-Ce, to be body-centered cubic (bcc). The last phase to be identified was α'-Ce which exists only at high pressure (greater than 50 kbar) (8). Due to the complex phase diagram at low
Figure 1. Pseudo-equilibrium pressure-temperature phase diagram. Boundaries between γ, β, and α phases are not necessarily equilibrium boundaries. Phase boundary between α and α' is questionable. C.P. is critical point.
temperatures (T 300K), many of the early experiments were performed on samples containing two or more phases. Recent experiments are more reliable due to new techniques that have been developed to prepare pure single phase samples (9). These experiments have shown a wide range of physical phenomena. In 1957, Lock (10) suggested antiferromagnetism in β-Ce on the basis of magnetic susceptibility measurements and this was confirmed by neutron diffraction by Wilkinson et al. (11); the existence of a critical point between γ and α-Ce was first observed by Ponyatovski (as cited in Ref. 2); Wittig (12) discovered superconductivity in α'-Ce; and most recently Gschneidner et al. (13) observed the Kondo effect in β-Ce. Reliable measurements of the properties of the cerium allotropes are of interest in their own right, but much of the experimental work has been motivated by the isostructural γ-α phase transition.

Physical Properties

Shortly after the discovery of the γ-α phase transition, Zachariasen (14) and Pauling (15), working independently, suggested that the valence of metallic cerium changes from 3 to 4 when transforming from γ to α-Ce. To test this theory, many experiments were performed in an attempt to determine the 4f population in each phase. In Table 1, are presented some of the physical properties associated with the two phases.

The electronic specific heat constant is related to the density of states at the Fermi level. This value is normally obtained by plotting \( C_v/T \) vs. \( T^2 \) at low temperatures. The electronic contribution to the heat capacity is the linear extrapolation of this curve to \( T = 0 \)K.
Table 1. Physical properties of γ- and α-Ce

<table>
<thead>
<tr>
<th>Property</th>
<th>α-Ce</th>
<th>γ-Ce</th>
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<tbody>
<tr>
<td>Crystal structure</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>4.84 @ 90K</td>
<td>5.16 @ 300K</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>8.24 @ 90K</td>
<td>6.77 @ 298K</td>
</tr>
<tr>
<td>Electronic specific heat const. (mJ/g-at K$^2$)</td>
<td>12.8 @ 90K</td>
<td>7.5 @ 300K</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>179 @ 0K</td>
<td>138 @ 300K</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>Pauli</td>
<td>Curie-Weiss</td>
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Since the γ-phase does not exist at low temperatures, an alternative procedure must be used. Gschneidner (16) has approximated this value using the heat capacity at constant pressure measured at room temperature. A value of 7.5 mJ/g-at K² for the γ value of γ-Ce was obtained by subtracting contributions due to the lattice specific heat, the thermal excitation of the 4f electrons, and the difference between the heat capacity at constant pressure and at constant volume from the heat capacity as measured at 300K. The value obtained for α-Ce by extrapolating Cᵥ/T to OK is 12.8 mJ/g-at K² (17). Assuming the value for the electronic specific heat of γ-Ce is valid, the large increase accompanying the phase transition would indicate an increase in the density of states at the Fermi level. This increase is possibly due to the promotion of the 4f electron to the conduction band.

The magnetic susceptibility of γ-Ce, measured above 300K, shows a Curie-Weiss dependence (18,19). The results indicate that γ-Ce probably has one localized 4f electron with an effective moment of 2.52 μₜ in good agreement with theory. On transforming to α-Ce, the susceptibility departs from the Curie-Weiss law and becomes Pauli paramagnetic (17). This departure can be interpreted as the loss of the localized moment due to the 4f electron. Although the susceptibility is nearly temperature independent, it has a value 4.5 times the Pauli contribution predicted from the electronic specific heat constant. This discrepancy can be attributed to an exchange enhancement arising from a partially occupied 4f level.

The possibility of an exchange enhancement in the magnetic susceptibility has led to a search for a T² term in the low temperature
resistivity (20,21,22). Such a term should exist due to the scattering of s electrons from the spin fluctuations of the f electrons. It has been shown by Brodsky and Friddle (22) that the appearance of such a term is largely dependent on the sample preparation and, therefore, there has been no definite answer to this question. At higher temperatures, the electrical resistivity increases dramatically at the α-γ phase transition.

Recently experiments have been performed which probe the electronic structure directly. In 1969, Gustafson et al. (23) performed positron-annihilation experiments on both the γ and α phases of Ce. The angular correlation of the positron-annihilation radiation and positron lifetimes have been shown to be sensitive to the valence of the metal in which they annihilate. By comparing the annihilation measurements in both phases, Gustafson et al. were able to conclude that the valence of Ce does not change from 3 to 4, but they were not able to identify the nature of the 4f level. Their results were more consistent with a valence of approximately 3 in both phases.

Although the positron annihilation measurements are sensitive to the valence of the metal, they do not provide information on the angular momentum composition of the valence band. Kornstädt et al. (24) have employed Compton-scattering to investigate the electronic structure of both γ- and α-Ce. The advantage of Compton-scattering is that it is equally sensitive to all electrons in the crystal and thus can probe the 4f character on both sides of the transition. Employing renormalized free atom wavefunctions, they were able to discount the promotion model,
but due to the simplified nature of the wavefunctions, they could not be specific about the disposition of the 4f level, i.e., localized or band-like. A better fit to the Compton profile was obtained by Glotzel and Podloucky (25) using Bloch functions in the linear muffin-tin orbitals representation and self-consistent local-density potentials. Their calculations gave an angular momentum decomposition of \(6s_{0.53}6p_{0.22}5d_{2.06}4f_{1.19}\) and \(6s_{0.63}6p_{0.27}5d_{1.93}4f_{1.17}\) for \(\alpha\)- and \(\gamma\)-Ce, respectively. Again the results indicate no appreciable change in the 4f population.

To test further, the promotion model x-ray absorption measurements of the two phases have been taken. With the premise that the 4f electron is promoted to the conduction band, the screening of the nuclear charge will be decreased and subsequently core levels should be shifted to a deeper binding energy in \(\alpha\)-Ce. Results by Lengeler et al. (26) on the L-edge do not show a change in the threshold of either the \(L_1\) or the \(L_{2,3}\) edges on transforming from \(\gamma\)- to \(\alpha\)-Ce. Their data for these edges only show minor differences in the absorption spectra. Besides a decrease in the white line intensity between the \(L_{2,3}\) spectra of \(\gamma\)- and \(\alpha\)-Ce, the most outstanding difference is the appearance of another peak 9 eV above the white line in \(\alpha\)-Ce. They interpret this feature as due to a double excitation process that involves both the 4f and the 2p core electrons. It is concluded that this process can only occur in \(\alpha\)-Ce because the 4f electron is less localized and, therefore, hybridizes with the empty 5d states.

A more direct measure of the electronic states in Ce can be obtained by use of bremsstrahlung isochromat spectroscopy (BIS) and x-ray
or ultraviolet photoemission spectroscopy (XPS, UPS). Several of these experiments have been performed on γ-Ce, independently. These results give energies for the 4f level ranging from just below the Fermi level to a binding energy of 1.9 eV.

From both UPS and XPS on γ-Ce, Platau and Karlsson (27) identified a feature in the valence band at a binding energy of 1.9 eV as due to the 4f^1 level. Since their measurements were restricted to two photon energies, they used oxygen exposures to help interpret their results. The energy distribution curves (EDC) show that part of the valence band vanishes after appropriate oxygen exposure. With exposure to oxygen, Ce initially forms a 3+ compound. Therefore, the part that vanishes was identified with the (5d6s)^3 electrons. The feature which remained was shifted to a slightly deeper energy and was identified as the 4f^1 level. A comparison of the oxide with the metal leads to the identification of the feature at 1.9 eV as 4f related.

In corroboration of the results of Platau and Karlsson, are the UPS results of Johansson et al. (28). These investigators were able to vary the photon energy through the 4d absorption threshold. In so doing, they used the enhancement of the Ce valence band emission in this photon energy range to locate the 4f level. Their results indicate two prominent features in the valence band located at binding energies of about 0.5 and 1.9 eV. The peak at 1.9 eV was identified as emission from the 4f^1 level while the feature closest to the Fermi level was identified as mainly 5d states.
Contrary to these results are the XPS data of Steiner et al. (29). Although the EDCs show the same general features, the interpretation is different. They argue that since the s-d interaction is stronger than the s-f interaction, the feature deeper in binding is due to the d-band and the feature near the Fermi level is the f level.

A similar conclusion was reached by Baer et al. (30) by comparing XPS and BIS measurements. These two complementary techniques provide information of the occupied, as well as the unoccupied, states. Their BIS results indicate a distinct maximum just above the Fermi level. Since they were able to identify the $4f^2$ final states as being located at approximately 4.0 eV above the Fermi level, they concluded that this feature was due to a weak contribution from empty $4f^1$ states just above the Fermi level. This requires placement of occupied $4f^1$ states just below the Fermi level. Since the emission from a single $4f$ level is approximately 0.5 that for the three 5d and 6s electrons, it is not possible to assign unambiguously the $4f$ states in the XPS valence band spectra. They do, however, conclude that the $4f$ states are localized and have a Coulomb correlation energy of about 4-5 eV.

Due to the experimental difficulties involved in preparing the \( \alpha \)-phase, very little work has been done in the area of photoemission on this phase. The most relevant work has been done by Martensson et al. (31) on the Ce\(_{0.9}\)Th\(_{0.1}\) system. It was found that the presence of Th in concentrations of at least 10% stabilized the fcc phase and the phase transition. These authors found two features in the valence band located at 2.1 eV and just below the Fermi energy. On transforming
to the low temperature phase, the relative intensities of these features changed with the deeper feature losing intensity and the other gaining intensity. These features were interpreted in terms of a double well potential for the 4f state, one being broad and shallow lying near the radius of the 5d distribution and the second being narrow and at the usual 4f position.

As can be seen by the varied nature of the experimental results, the simple model proposed by Zachariasen and Pauling is not adequate to explain the $\gamma$-$\alpha$ phase transition.

Theories of the $\gamma$-$\alpha$ Phase Transition

With the failing of the simple promotion model, many other attempts have been made to describe adequately the $\gamma$-$\alpha$ phase transition. These models can be placed in one of three categories: 1) promotion type; 2) Mott transition; and 3) band model. Those theories that fall under the category of the promotion model involve localized 4f levels, but include interaction or hybridization terms. The Mott transition theory is taken from the metal-insulator phase transition and describes the delocalization of the 4f levels. The most recent calculations involve band calculations with the 4f levels expressed as narrow bands in both phases.

The Promotion Model

The several promotional models that have been proposed have as a common assumption the coexistence of localized 4f levels along with itinerant conduction electron states, derived from s and d bands.
Blandin et al. (32) have used the formalism for localized magnetic impurities as developed by Anderson (33). Consider the case with conduction electrons of energy $e_k$ and a localized $f$ state with energy $E_o$ located above the Fermi level ($E_o > E_F$). The Hamiltonian in the Hartree-Fock approximation becomes:

$$H = k, s \sum e_k a_{ks}^+ a_{ks} + E_s \sum a_{fs}^+ a_{fs} + U_{fs} n_{f-s} + \sum V_{fk} (a_{ks}^+ a_{fs} + a_{fs}^+ a_{ks})$$

where $k$ and $s$ are the wavevector and spin indices, respectively. The first term gives the energy of the conduction electron with wavevector $k$ and spin $s$, the second term is the energy of the localized $f$ state, the third is the Coulomb energy required to place two electrons of opposite spin in a localized state on a single atom, and the last term is an interaction term between the localized $f$ state and the conduction band. This leads to a virtual bound state whose density is in the form of a Lorentzian as given below:

$$p_s(E) = \frac{1}{\pi} \frac{D}{(E - E_s)^2 + D^2}$$

where

$$E_s = E_o + U_{n-s}$$

and

$$n_s = p_s(E)dE$$

Equations (3) and (4) represent a set of self-consistent equations which
give a relation between the population of the localized state and the energy location of that state. This relation is given in Eq. (5) and has both magnetic and nonmagnetic solutions.

\[
\cot(\pi n_s) = \frac{E_o + U_n - E_F}{D} 
\]

When \( E_o - E_F \) is large, the solution is nonmagnetic. As \( E_o - E_F \) decreases, a magnetic solution appears when \( U_p(E_F) = 1 \). This criterion is similar to that found in band magnetism. Therefore, a transition from the magnetic to the nonmagnetic state can be found if, by some means, e.g., pressure, the energy of the localized state is moved relative to the Fermi level.

This model can be extended to include degenerate orbital states. The results are similar to those previously shown with the exception that the magnetic states are split into the spin and orbital components. Thus, we have a model which gives a description of a first-order transition with an abrupt variation in the magnetic moment and in the number of localized electrons. This model has explained the existence of the critical point in the phase diagram and the nonintegral valencies associated with the two phases. The major drawback with it is that it uses the Hartree-Fock approximation which neglects f-f interactions.

An alternative approach has been suggested by Ramirez and Falicov (34), who have based their model on the short range electron-electron interaction between the f states and the conduction band states. The energy of the system is then a sum of the energy of the conduction electrons, the conduction holes, the energy of the localized f state,
and the interaction energy as given below:

\[ E = E_e + E_h + NE_0 n_f - NGn_f^2 \]  \hspace{1cm} (6)

where \(-G\) is the interaction between an \( f \) electron and a conduction hole, \( N \) is the number of atoms in the system, and \( n_f \) is the occupation probability for the localized \( f \) states. The entropy can also be written for the system.

\[ S = S_e + S_h + S_f + Nk_B n_f \ln(2J + 1) \]  \hspace{1cm} (7)

The first three terms are due to the conduction electrons, holes, and localized \( f \) states, respectively. The last term is the spin entropy associated with the \( f \) states. From Eqs. (6) and (7), the free energy for the system can be evaluated and minimized to obtain the occupation probability for the conduction electrons, holes, and localized \( f \) electrons. Since the model produces some rather complex expressions, it is better to give a qualitative discussion of the results.

At a given energy for the localized states, the occupation of these states can be found as a function of temperature. As in the theory of Blandin et al. (32), a critical energy, \( E_c \), exists which defines the critical point in the phase diagram. Above this energy, there is no first order phase transition, whereas below, the system experiences one. Although we have a model which describes the main features of the phase diagram, it does not account for several of the experimental facts. This model does not account for the nonintegral valence, the weak temperature dependence of the magnetic susceptibility, or the large electronic specific heat found in \( \alpha \)-Ce.
The most recent work in this area has combined the ideas of the two models previously presented. Alascio et al. (35) have described the problem with an Anderson type Hamiltonian which includes a term for the highly-correlated f states, as well as an interaction term between the localized f states and the band states. The initial description is very similar to that by Blandin et al. (32), but the development departs from theirs since the Hartree-Fock approximation is not employed. This is essential to the work since the spin entropy associated with the Ce$^{3+}$ ions cannot be described in the Hartree-Fock scheme. The calculations are carried out in the limit that the Coulomb energy for two localized electrons on the same atom is infinitely large.

The results give good agreement with the phase diagram as it is shown that a linear relationship between the lattice constant and the f level occupation gives a reasonable fit to the experimental data. This model is also shown to give a Curie-type magnetic susceptibility at high temperatures and almost temperature-independent susceptibility at low temperatures, in good agreement with the experimental data. The problem of the high electronic specific heat in $\alpha$-Ce is also addressed and shown to be due to the high correlation of the localized f states.

The three promotional type models presented here are dependent on the fact that the f level lies very close to the Fermi level in energy. This leads to a description of the phase transition in terms of the occupation of the 4f level. As the temperature is lowered or the pressure is increased, the Fermi level moves further from the f level and thus the f population decreases. When hybridization between the f
level and the valence band and correlation effects between f levels on nearest neighbors are included, the experimental specific heat, magnetic susceptibility, and variation in the lattice constant are adequately described. The difficulty arises when one considers the evidence of photoemission ($E_{4f} = -2$ eV) and that of Compton scattering (no 4f population change).

The Mott Transition

The label Mott transition was first given to the metal-insulator transition found in some transition metal-oxides. The conductivity was measured as a function of temperature and showed a large increase at the transition temperature. This increase was as large as $10^6$ for VO.

This can be understood qualitatively in terms of a simple model (36). First consider two atoms with one electron per atom. When the atoms are infinitely separated, we have two energy levels $E$ and $E + U$ corresponding to single and double occupancy, respectively. As the distance between the atoms decreases, at some point bands will form. Since the atoms are still widely separated, the wavefunctions can be considered to be localized on the atomic site. These wavefunctions can be expressed in terms of Wannier functions, as they will decay exponentially from the atomic site. Although there may be some overlap between neighboring atoms, it is still too small to form polar states (2 electrons on an atom).

As the atoms are brought together even further, true bands will form. Now the wavefunctions can be expressed in terms of true Bloch
states. When the Coulomb energy, $U$, is approximately equal to the bandwidth, $W$, the band due to the higher atomic level may be more energetically favorable and polar states will form. Therefore, the condition for the Mott transition to occur is that $U \approx W$.

In the case of cerium when two atoms are infinitely separated, a value of 16.56 eV is obtained for the energy separation between the $f^1$ and $f^2$ configurations (37). As the atoms are brought together to form a solid, we do not have the simple picture previously presented due to the three $s$ and $d$ electrons that cerium possesses. The role of these $s$ and $d$ electrons is to screen the Coulomb force between the electrons and, therefore, to reduce the value of $U$.

To obtain a value for $U$ in the solid, we examine the following reaction: $2(4f^15d^16s^2) \rightarrow 4f^05d^26s^2 + 4f^26s^2$. From tabulations of Brewer (38), we find that the energy to form an $f^0$ and $f^2$ state in the solid is on the order of 5 eV. This value is substantiated by the use of photoemission and BIS where a value of 4-5 eV is obtained, depending on the position of the $f^1$ level.

We are then left with the problem of determining the bandwidth of the $4f$ levels. The first band calculations showed that the $4f$ levels were very sensitive to the initial conditions used. Therefore, self-consistent calculations must be used to obtain reliable results. The most recent of these give a bandwidth in $\gamma$-Ce of $\approx 0.8$ eV and that the bands broaden in $\alpha$-Ce to $\approx 1.2$ eV (39).

Since the Coulomb energy and bandwidth are the same order of magnitude, there is evidence that the $\alpha$-$\gamma$ phase transition is a Mott
transition. This is a viable interpretation of the experimental results. With the formation of polar states, one would expect a loss of localized magnetic moments. The Mott transition is also in agreement with the results of Compton scattering and positron annihilation, that there is no loss of $f$ character in forming the $\alpha$ phase. In describing the phase transition as a Mott transition, there is no need for the $4f$ level to be located near the Fermi level. This fact reconciles the problem brought up by the photoemission data.

**Band Structure**

The nature of the $4f$ state has also been studied using band structure calculations. The earliest calculations, which were nonself-consistent, showed that the $f$ band position was strongly dependent on the atomic configuration and the exchange-correlation functional (40,41). From this, it was concluded that self-consistency was necessary to obtain reliable band structure results.

The earliest self-consistent calculations were performed by Kmetko (42) using the augmented plane wave method (APW). Although these calculations are self-consistent, they do not include relativistic effects or spin-orbit interactions. To include the effects on the "core" charge of a spatially localized $f$ electron, they allowed the "core" charge to vary after each iteration. The results showed two responses to the compression of the lattice. The first was a simple distortion of the wavefunctions and second, and more important, a redistribution of charge among the various components was observed.
The charge distributions analyzed into s, p, d, and f components for La and Ce are given in Table 2 (42). From these values, we see that under compression, charge flows out of the more compact f distribution and into a more extended d-like one. This result seems to be contradictory to the fact that the lattice has been compressed, but can be understood when one considers the effect of the 4f population on the atomic radius. The empirical radii of rare earth atoms are approximately 20% greater in the divalent than the trivalent form. Using their results, Kmetko (42) showed that the outermost 5d maximum is reduced 14.8% per f-electron removed. Thus, the high compressibility of La and Ce are apparently due to the softness of the atom which in turn is due to the instability of the 4f bands.

These results are similar to those of the promotional models in that d-character is gained at the expense of 4f character. They also show the f-level moving higher in energy relative to the Fermi level in the α phase. The major difference between this and the promotional models is that here the f levels are treated as band states even when occupied.

Recently Pickett et al. (39) studied the γ-α phase transition by means of a self-consistent APW energy band calculation. These calculations included relativistic effects and spin-orbit interactions. To simplify the calculations, the spin-orbit interaction was treated as a perturbation after self-consistency had been reached.

The band structures for γ and α-Ce are given in Figs. 2 and 3, respectively. Notice that the band structure for both phases are quite
Table 2. Angular momentum decomposed charge distribution from Kmetko

| Metal and Structure | Unit Cell Dimension A | Charge Inside APW Sphere s | p | d | f | Total Charge Inside APW Sphere s | p | d | f | Total Charge Outside APW Sphere s | p | d | f | Total Charge Per Atom s | p | d | f |
|---------------------|-----------------------|----------------------------|---|---|---|----------------------------------|---|---|---|---------------------------------|---|---|---|--------------------------|---|---|---|--------------------------|
| β-La fcc            | 5.285                 | 0.286                      | 0.113 | 1.341 | 0.547 | 0.669                          | 0.161 | 0.066 | 0.389 | 0.053 | 0.447 | 0.179 | 1.730 | 0.600 |
| β-La fcc            | 5.021                 | 0.130                      | 0.126 | 1.657 | 0.384 | 0.651                          | 0.098 | 0.059 | 0.462 | 0.032 | 0.328 | 0.185 | 2.120 | 0.416 |
| γ-Ce fcc            | 5.161                 | 0.281                      | 0.103 | 1.294 | 1.653 | 0.662                          | 0.155 | 0.057 | 0.375 | 0.075 | 0.436 | 0.159 | 1.669 | 1.730 |
| α-Ce fcc            | 4.660                 | 0.150                      | 0.109 | 1.673 | 1.280 | 0.775                          | 0.090 | 0.041 | 0.547 | 0.120 | 0.140 | 0.150 | 2.210 | 1.400 |
Figure 2. Self-consistent band structure, including the spin-orbit interaction for γ-Ce. The Fermi energy lies near the bottom of the flat 4f bands. The energy scale on the left is relative to the average interstitial potential (Ref. 39)
Figure 3. Self-consistent band structure, including the spin-orbit interaction for α-Ce. The Fermi energy lies near the bottom of the flat 4f bands. The energy scale on the left is relative to the average interstitial potential (Ref. 39)
similar. Both consist of very wide 5d bands and narrow 4f bands (1 eV). The Fermi level is pinned to the bottom of the 4f band. In transforming to α-Ce, the 4f bandwidth increases by about 60% with a corresponding 5d bandwidth increase of about 40%. Since the Fermi level is effectively pinned to the bottom of the 4f bands and these bands broaden in the α phase, the 4f band center must rise relative to the Fermi level. Although the f band center does move further above the Fermi level, the amount of 4f character does not change appreciably between the two phases. This is due to the increased hybridization of the 4f levels which results in longer tails in the 4f density of states on both sides of the main 4f band region.

The charge decomposition is given in Table 3 with specific irreducible representations used for d and f contributions. Again there is very little change observed in transforming from γ to α-Ce. The total 4f charge remains approximately 1 in both phases. These results are contradictory to those found by Kmetko and suggest a change in localization of the 4f rather than a loss of 4f character as the mechanism for the γ-α phase transition.

Purpose

The purpose of this work is to use ultraviolet photoemission spectroscopy to study the electronic structure of both γ- and α-cerium. The two questions that need to be addressed in resolving the problem of the γ-α phase transition are: 1) Where is the 4f level located with respect to the Fermi level? and 2) How does the 4f level change in transforming from γ- to α-Ce? The first question leads to a photon-
Table 3. Angular momentum decomposed muffin-tin density of states at $E_F$, $N_1(E_F)$, and corresponding charges $Q_1$ from Pickett et al.

<table>
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<tr>
<th>Unit Cell Dimension A</th>
<th>Density of States or Charge</th>
<th>Angular Momentum Components</th>
<th>Interstitial Charge</th>
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<td>0.14</td>
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energy dependent study of the energy distribution curves while the latter leads to a study of the yield spectra of both phases.
PHOTOEMISSION

The photoelectric effect was first observed in 1887 by Hertz. Not until the work of Einstein in 1905 was this effect understood in terms of the quantization of light, i.e., the photon. Originally the photoelectric effect was limited to the measurement of a material's work function. When techniques became available to measure accurately the energies of the emitted electron, much more information on the solid became available.

The basic photoemission apparatus consists of a beam of monochromatic light incident on a clean surface of a solid, and an electron energy analyzer. The resulting scan of the emitted electron energies shows several features, as shown schematically in Fig. 4. This shows an energy distribution curve (EDC) for a metal. The highest electron energy possible corresponds to an electron emitted from the Fermi level, giving a large step in the EDC. Besides locating the Fermi level, the valence band can be studied and compared to band structure calculations. At lower electron kinetic energies, corresponding to deeper energy levels in the solid, core levels can be identified provided the photon energy is greater than the core level binding energy. The inelastic secondary electrons account for the remainder of the spectra. These electrons have experienced at least one inelastic collision before leaving the solid.

The experimental valence band spectra can be understood in a qualitative sense by using the "three-step" model of photoemission (43,44). In this model, photoemission is treated as a sequence of
Figure 4. Representative energy distribution curve for a metal. Electronic kinetic energy increases from left to right.
1) optical excitation of an electron, 2) transport of the excited electron through the solid, and finally 3) the escape of the electron through the sample surface into vacuum. Included in the second step is the possibility for inelastic scattering by the other electrons in the solid. The photoemission intensity is, therefore, a sum of a primary distribution of electrons $I_p(E, \omega)$ and a secondary distribution $I_s(E, \omega)$ which have suffered an energy loss due to inelastic scattering. We then have

$$I(E, \omega) = I_p(E, \omega) + I_s(E, \omega).$$  

(8)

The primary distribution can then be factored according to the "three-step" model in terms of a photoexcitation process $P(E, \omega)$, a transport function $T(E, \omega)$, and an escape function $D(E)$:

$$I_p(E, \omega) = P(E, \omega) \times T(E, \omega) \times D(E).$$  

(9)

The first step is to determine the photoexcitation spectrum. This involves the optical excitation of an electron from an initial occupied state, $i$, to a final unoccupied state, $f$. The intensity of this transition is determined by the dipole matrix element. In golden rule form:

$$P(E, \omega) = \sum |<f|p|i>|^2 \delta(E_f - E_i - \hbar \omega) \delta(E_f - E)$$  

(10)

where $p$ is the momentum operator, the first delta function assures conservation of energy and the second selects the emitted electrons whose energy corresponds to that set by the electron analyzer.
After excitation, the electron must be transported to the surface. A first approximation of the transport function was given by Berglund and Spicer (43). They consider the simplest case where: 1) the inelastic scattering is isotropic; 2) only inelastic scattering need be considered; and 3) the probability of inelastic scattering can be described in terms of an electronic mean free path \( \lambda_e(E) \) dependent only on the energy \( E \). Integrating over the semi-infinite depth of the sample gives for the transport function:

\[
T(E, \hbar \omega) = \frac{\lambda_e(E)/\lambda_{ph}(\hbar \omega)}{1 + \lambda_e(E)/\lambda_{ph}(\hbar \omega)}
\]

where \( \lambda_{ph}(\hbar \omega) \) is related to the absorption depth of the photon. This is a slowly varying function of the electron energy and should not give rise to any structure in the EDC.

In the semi-classical picture, the escape of the electron from the solid can only be accomplished if the electron kinetic energy is large enough to overcome the potential barrier \( E_p + \phi \), where \( \phi \) is the work function of the material. Using a free-electron model for the excited photoelectron, an escape cone can be defined as

\[
\cos \theta = \left( (\phi + E_p)/E \right)^{1/2}
\]

with \( \theta \) measured from the surface normal. For an isotropic distribution of electrons in the solid, the escape function becomes

\[
D(E) = \begin{cases} 
\frac{1}{2} \left( 1 - (\phi + E_p)/E \right)^{1/2} & \text{if } E > E_p + \phi \\
0 & \text{elsewhere}
\end{cases}
\]
Notice that \( D(E) \), like \( T(E, \hbar \omega) \), is a smooth function of the photoelectron energy \( E \).

The "three-step" model then shows that any structure in the EDC is due to the optical excitation process. Since this process is governed by the dipole matrix element, the intensities of various features will depend on the initial and final states involved. At low photon energies, the observed features are due to excitations from valence band to low lying conduction band states. Since we are restricting ourselves to direct transitions, \( \vec{k}_f = \vec{k}_i \), a change in photon energy requires both a new initial state and a new final state. This can cause drastic variations in intensity of the individual features. At higher photon energies, valence band states are excited to nearly-free-electron-like final states. In this case, the matrix element can be approximated by the atomic cross section of the levels that contribute to that region of the EDC. The EDC can then be interpreted in terms of the valence band density of states of the solid.

Although the "three-step" model is used widely and has given good agreement with experiment, it does have some deficiencies. These deficiencies fall into two categories: 1) the neglect of surface effects; and 2) the use of one-electron eigenfunctions to determine the possible transitions. A proper description of the photoemission process as the response of a multielectron system to electromagnetic radiation would contain these effects. Several more rigorous descriptions of the photoemission process have been given by Schalich and Ashcroft (45), Feibelman and Eastman (46), and Caroli et al. (47).
Rather than present the more rigorous formulation, it is easier con­ceptually to amend the "three-step" model to account for these effects.

The surface effects arise from the loss of the three-dimensional nature of the solid. This loss in translational symmetry perturbs the bulk energy bands and can produce some completely different states at the surface. It also places new restrictions on the $k$-vector component normal to the surface and changes the $k$-vector selection rule.

In the original "three-step" model, the wavevector is conserved in all three dimensions. To account for the loss in translational symmetry in the direction normal to the surface, a small imaginary part, $k_{\perp}^{(2)}$ is added to the real $k$-vector component that is perpendicular to the surface, $k_{\perp}$ (46). This replaces the $\delta$ function in the wavevector with a Lorentzian distribution

$$
\Delta(k_{\perp}, k'_{\perp}) = \frac{k_{\perp}^{(2)}}{[(k_{\perp}^{(2)})^2 + (k'_{\perp} - k_{\perp})^2]} \quad \text{(14)}
$$

This relaxed selection rule has different effects for three different ranges of the photon energies. For $K_{\omega} < 20 \text{ eV}$, the mean free path of the electron is greater than the dimension of the unit cell. Equation (14) then represents a sharply peaked function around $k' = k$. In this range, the $k$-conserving "three-step" model is a good approximation. As the mean free path approaches its minimum around 40 to 100 eV and the relaxed selection rule is used, surface effects become more prominent. Beyond 100 eV, the mean free path again increases and the uncertainty in $k$ decreases. At these energies, the separation of final states also
decreases. This leads to a situation where the requirement of quasi-direct transitions is readily fulfilled due to both a small freedom in $k$ and the abundance of final states. We then observe the initial density of states in the EDC.

The "three-step" model also does not address processes that involve more than one electron. The simplest of these is the 2-electron or Auger process. This is normally associated with the excitation of a core electron. After excitation, the core hole is filled with an electron from the valence band and another electron is emitted from the solid. The emitted electron leaves with an energy corresponding to the difference between the core hole state and the state from which the electron was in that filled the hole. Since this process relies only on the presence of the core hole, a feature will be present in the EDC above the threshold energy corresponding to the excitation of the core level. The energy associated with this process is independent of the photon energy and will, therefore, always appear at the same kinetic energy.

The emitted electron energy can also be changed due to the response of the system to the excitation. This response can be in the form of relaxation or screening (48). After excitation of the electron, the system is in an $N-1$ electron state with a positive hole remaining. The surrounding electrons tend to relax around this hole, thus lowering the energy of the system. This energy is transferred to the emitted electron which leaves the solid with a slightly higher kinetic energy. The relaxation energy is calculated in the adiabatic limit corresponding to an excitation just above threshold. In this limit, the time scale
for which the excited electron leaves the region is long and, therefore, the atom can remain in its ground state configuration. This configuration is determined by the instantaneous charge density. The relaxation energy depends greatly on the local extent of the initial electron state. For localized levels, the relaxation energy is greatest with the energy decreasing as the state becomes more band like.

Departure from the adiabatic limit introduces a nonvanishing probability that the target will be left in an excited state, causing the electron to be emitted with less energy than in the adiabatic limit. The emitted electrons are referred to as shake-up satellites and leave excited electrons in the solid. If the amount of energy transferred to the system from the photoexcited electron is large enough, a second electron may be excited to a high enough energy to leave the solid. The feature due to this process is called a shake-off satellite.

It is convenient to think of the photoexcitation process as switching on a time-dependent potential due to the positive hole (49). Suppose the potential is instantly switched on at $t = 0$, i.e., $V_0(r,t) = V_0(r)\delta(t)$. This potential has Fourier components at all frequencies and, thus, can transfer energy to the electron gas leading to a satellite structure. On the other hand, if the electron is excited closer to threshold, it remains in the vicinity of the hole longer and the electron gas sees no net potential. The short-time Fourier components are small resulting in low intensity shake-up satellites. With a very long switch-on time, the adiabatic limit is reached. Depending
upon the photoelectron kinetic energy, the switching can span the entire time domain with the satellite intensity varying accordingly.

In terms of energy eigenstates, the shake-up satellite corresponds to an excited state of the N - 1 electron ion. These states could be thought of as excitation of an electron to a higher orbital by the sudden loss of a core electron and the accompanying sudden change in the potential. Although this is an incorrect physical picture of the shake-up feature, since it uses a one electron picture, it does give some qualitative insight into the problem. In reality, the shake-up states are simply eigenstates of the N - 1 electron ion. Transitions to these states are allowed in exactly the same way as to the primary hole state.

Amending the "three-step" model to include the many-body and surface effects gives a reasonable qualitative theory of the photoemission process. Admittedly this procedure is not rigorous and does contain some unjustified approximations, but has been shown to be quite adequate in describing the experimental features.

The second step of the "three-step" model involves the transport function. As the electron moves through the solid, it may experience an inelastic collision. Those electrons which are emitted from the solid after scattering contribute to the secondary electron distribution. The number of secondary electrons at energy E is proportional to the number of excited electrons with energies greater than E. This is due to the fact that any electron with energy E', greater than E, can be inelastically scattered in some manner to give it a final energy of E.
The scattering can be either a single or multiple event and can be an electron in either the primary or secondary distribution. The most important inelastic scattering mechanism is electron-electron scattering. The scattering event may take place between two excited electrons or more likely between an excited electron and a valence electron. The probability of the latter process is much greater than the former since the fraction of electrons excited is small. Since scattering depends on the density of occupied states, under "ideal" conditions, information concerning the band structure can be obtained even from these electrons (50). The "ideal" conditions refer to the use of a single crystal as the sample. When using polycrystalline samples, the features in the secondary distribution are broadened and contribute a smooth background, which increases with decreasing electron energy, to the EDC.

Although the secondary electrons may not provide any information in terms of the energy distribution, they do play a role in terms of the yield spectrum. The total yield spectrum at a given photon energy is given by the total intensity of the energy distribution curve. This is the sum of the primary, secondary, and Auger distributions. Since the number of secondary electrons, at energy E, is proportional to the total number of electrons with energy greater than E, the same information in the total yield spectra can be gained by determining the intensity at very low kinetic energies. The spectra obtained by scanning the photon energy while sampling electrons with kinetic energies of 2 eV is the partial yield spectra. Both this and the total yield spectra have been shown to be similar to the absorption spectra (51). Therefore, through
photoemission, we can not only observe the energy levels of the solid in direct emission, but can also get a measure of the matrix elements involved in the photoemission process.
EXPERIMENTAL PROCEDURE

Data Acquisition System

All experiments were performed at the Synchrotron Radiation Center located at Stoughton, Wisconsin. A schematic representation of the photoemission experiment is shown in Fig. 5. Much of the experimental chamber has been left off for clarity. The geometry of the components was such that the foci of the cylindrical mirror analyzer (CMA) and the light source were coincident at the sample position.

The light source was the storage ring Tantalus I, in conjunction with a grazing-incidence monochromator (grasshopper). The effective energy range of the grasshopper was from 40 to 170 eV. The resolution varied from 0.1 to 0.5 eV, depending upon the photon energy and the entrance and exit slit widths.

A commercial double-pass cylindrical mirror analyzer was used to determine the emitted electron energies. The band pass of the electron analyzer ($\Delta E$) was proportional to the kinetic energy ($E$) of the electrons as they were emitted. Therefore, as the electron energy increases, the band pass of the analyzer would increase. To overcome this, the analyzer can be run using spherical retarding grids. The grids are used to change the kinetic energy of the emitted electrons to a previously set value, the pass energy. The potential applied to the grids is equal to the difference between the pass energy and the electron energy. In this way, the energy of the electrons which pass through the analyzer is kept constant, keeping the resolution constant over the range of the scan. We have used a pass energy of 30 volts as a compromise between
Figure 5. Schematic representation of the data acquisition system

- HV + 0-3KV
- Pulse Counting Electronics
- X-Y Recorder

Equations:

\[ V_2 = \text{Pass Energy} \]
\[ V_2 = 1.70 \times V_3 \]
\[ eV_1 = \text{Electron Energy} \]
improved resolution and good count rates. To sample different kinetic energies of the electrons emitted from the sample, the potential applied to the grids is varied by adjusting the potential, $V_1$.

Operating the analyzer in the retarding mode solves the problem of varying resolution, but introduces a problem with the count rates. There are two factors which affect the count rate at a given energy: 1) the lens characteristics of the spherical retarding grids, and 2) scattering from the grids. The lens characteristics of the grids essentially reduce the accepted specimen area. This reduction is given theoretically by:

$$\frac{\text{Reduced diameter}}{\text{Original diameter}} = \left( \frac{\text{Pass energy}}{\text{Initial kinetic energy}} \right)^{1/2}$$  \hspace{1cm} (15)

In reality this transmission function is difficult to determine. However, as long as features close in energy are compared, the transmission function should not introduce a large source of error.

When dealing with a flooded source, we can also neglect the effect of grid scattering. This can be seen by the fact that the number of electrons scattered out of the proper trajectories are compensated for by electrons scattered into those trajectories. The definition of a flooded source is one in which the radiation spot size on the sample is greater than the photoelectron sampling diameter without the retarding grids. Comparing the spot size of the light leaving the monochromator to the largest sample diameter, we can assume that we are dealing with a flooded source. Again, if this criterion does not hold, it will
introduce only small errors, provided that spectral features close in
energy are compared.

The signals associated with this technique are usually small and
must be detected using pulse counting techniques. After the electron
passes through the CMA, it is in a positive potential which attracts it
to the opening of the channeltron (labeled - in the figure). The
opposite end of the channeltron is at yet a higher positive potential
so that the electron moves to the other end (+). In traversing the
length of the channeltron, the original electron is amplified to a large
pulse of electrons at the opposite end. This pulse is collected (C)
and sent to the pulse-counting electronics. The pulse-counting elec­
tronics consist of either a computer in conjunction with a scaler, or a
ratemeter with a built-in digital-to analog (D-A) converter. After
passing through the D-A, the signal is sent to the vertical input of
the x-y recorder. The horizontal input is connected to the potential
which varies the electron energy sampled. The resulting scan is an
energy distribution curve. The partial yield data were taken by setting
the electron energy to 2 eV and scanning the monochromator through the
desired photon energy range. The constant-initial-state spectra was
obtained by scanning both the electron energy and the photon energy so
that the energy of the initial state was kept constant.

Sample Preparation

The samples were thick films evaporated from bulk cerium obtained
from Ames Laboratory. An analysis of residual elements is given in
Table 4. The most important impurities are those due to other rare
Table 4. Chemical analysis of cerium used (impurity levels are in atomic ppm)

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Conc.</th>
<th>Impurity</th>
<th>Conc.</th>
</tr>
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<td>Lu</td>
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earths, with the largest being La with a concentration of 17 atomic parts per million (ppm).

The cerium had been electro-polished and sealed in an evacuated ampoule. The seal was not broken until just before placement of the cerium in the evaporator basket and subsequent closing of the vacuum chamber. The cleanest films were obtained only after a prolonged degassing procedure of the evaporator. After mounting the basket in the chamber, the chamber was sealed and evacuated to approximately $10^{-7}$ Torr. The basket was then heated until the pressure recovered to the value prior to the heating of the basket. The system was allowed to cool and the chamber brought up to atmospheric pressure using dry nitrogen gas. The cerium was then placed in the basket and again the chamber was sealed. The chamber was baked for a period of about 24 hours to reach minimum pressures. With the pressure less than $10^{-9}$ Torr, the degas procedure began. Heat was applied slowly to the evaporator, keeping the pressure less than $10^{-9}$ Torr, until the cerium melted. After melting, the pressure was kept below about $5 \times 10^{-10}$ Torr until evaporation began to take place. Following this procedure, we were able to obtain a high percentage of clean films. If an evaporation produced a dirty film, a new film was evaporated over the old one. Film thicknesses varied from one evaporation to the next, but were in the range of 50 to 200 Å.

The $\gamma$-phase samples were obtained by evaporating onto a substrate at room temperature. To obtain $\alpha$-phase samples, two procedures were used. The first was to cool a room temperature film to about 40K. In
some instances, this did not produce a phase transition. In these cases, the films were dirty which probably prohibited the transition from occurring. Provided a clean film was produced at room temperature, direct cooling did produce a phase transition to the α-phase. The second procedure was to evaporate cerium onto a low temperature substrate. In this way, the cerium was quenched upon contact with the substrate and produced films with a greater percentage of the α-phase than those that were directly cooled. The low temperatures were produced with a closed-cycle helium refrigerator, and the temperatures were monitored using a Au-0.07% Fe vs. Chromel thermocouple.

The appearance of the α-phase was confirmed by measuring the electrical resistivity as a function of temperature. This showed the characteristic drop in resistivity at about 110K. Since we were unable to obtain temperatures below 40K, we could not determine the amount of β-phase present in the sample. At low temperatures, the antiferromagnetism of β-Ce produces a feature in the resistivity.
PARTIAL YIELD

Introduction

The absorption spectra of the rare earths show a rich multiplet structure in the region of the 4d core energy. This structure has been shown, experimentally and theoretically (52,53,54,55,56), to be dependent on the 4f occupancy in the ground state configuration. In Figs. 6 and 7 are the absorption spectra for LaF$_3$ and CeF$_3$, respectively (57). Notice that both spectra are composed of a region of low magnitude with sharp features and a region higher in energy and magnitude with much broader features. Other than this gross similarity, the spectra are strikingly different in the amount of structure present.

This multiplet structure observed in the rare earth elements can be understood in terms of dipole transitions of the type $4d^{10}4f^N - 4d^{9}4f^{N+1}$, ignoring possible transitions to shells with $n > 4$. The ground state configuration consists of a filled 4d core level and $N$ electrons occupying the spin-orbit and multiplet split 4f shell. The low-lying 4f orbits are trapped inside the centrifugal potential barrier and overlap with the 4d wavefunctions. The neglect of the higher energy nf orbits ($n > 4$) is due to the more expansive wavefunctions, so almost no overlap with the 4d levels occurs. Therefore, essentially all the absorption strength from the 4d shell in the rare earths should go to the 4f shell.

After excitation of the 4d electron, the large overlap induces a strong exchange interaction between the $4f^{N+1}$ subshell and the 4d hole. This interaction splits the $4d^{9}4f^{N+1}$ levels by about 20 eV, pushing
Figure 6. Absorption spectrum of LaF$_3$ from Ref. 57. The three vertical lines represent calculated absorption lines (energy and oscillator strength) for the free La$^{3+}$ ion (Ref. 54).
Figure 7. Absorption spectrum of CeF$_3$ (solid) and of Ce metal (dashed). The former is from Ref. 57 and the latter from Ref. 58, but shifted 0.37 eV to lower energy.
some levels well above threshold. These then autoionize to various channels leaving the configuration $4d^{10}4f^{N}$. Those levels still below threshold do not decay rapidly and thus exhibit sharp features in the absorption spectra.

The $\text{LaF}_3$ spectrum shows two sharp features located at 97.66 and 102.09 eV. These values are in good agreement with those calculated by Sugar (54). The calculated spectrum also is shown in the figure, with the height of the tick mark corresponding to the relative magnitude of the features. Above threshold, the theory predicts one feature which is observed at an energy of 117.65 eV.

As we go from $\text{LaF}_3$ to $\text{CdF}_3$, one electron is added to the electronic structure so that the ground state configuration changes from $4f^0$ to $4f^1$. The addition of this $f$ electron increases the number of structures observed in this region. Below threshold, the number of sharp structures exceeds that of La, with many peaks having shoulders. The large autoionization feature above threshold has become more complex and the entire spectrum is located at higher energies. The shift in energy is due to the change in binding energy of the $4d$ level between La and Ce. The energy positions are given in Table 5 along with the calculated positions.

**Results and Discussion**

Insofar as the absorption spectrum is similar to the partial yield spectrum, we can use that aspect of photoemission to examine the structure in the $4d$-$4f$ transition energy region. In Fig. 8 are the partial yield spectra for $\text{CeF}_3$, $\gamma$-Ce and $\alpha$-Ce. Notice the similarities
Table 5. Energies (eV) of structures in the measured spectra of cerium and cerium trifluoride

<table>
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<tr>
<th>Calculated Energy Positions</th>
<th>Absorption CeF$_3$</th>
<th>Partial Yield CeF$_3$</th>
<th>Absorption γ-Ce</th>
<th>Partial Yield γ-Ce</th>
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Figure 8. Partial yield spectra of CeF₃ (solid), γ-Ce (dashed), and α-Ce (dot-dashed). The vertical axis is different and offset for each curve.
between the partial yield and the absorption of CeF$_3$. We do observe more structure in the low energy range than Olson and Lynch (57) due to improved resolution. Several of the features in this range may be resolution limited and, therefore, artificially broadened.

Calculations carried out by Sugar (54) assume the rare earth atom exists in the trivalent state. In making this assumption, Sugar has ignored effects due to the valence electrons and considered the problem from a purely atomic viewpoint. For the case of CeF$_3$, this assumption is well justified due to the isolation of the cerium ions. CeF$_3$ is a large bandgap insulator with the (5d6s)$^3$ electrons filling the fluorine 2p shell. The subsequent fluorine 2p level corresponds to the top of the valence band with the cerium 4f level lying in the gap. The crystal structure is such that the cerium ion has fluorine ions as nearest neighbors. Therefore, the cerium ions are essentially isolated in real space from each other. Due to these effects, the 4f level is nearly ionic like and, therefore, the calculations by Sugar should give reasonable agreement. Comparison of the fine structure in the yield to that calculated gives very good agreement as shown in Table 5. Above threshold, only two features are observed. This does not necessarily disagree with the theoretical results, since the line shape seen in this region is very sensitive to the amount of overlap between the excited state configurations and the continuum states (59,60). If several of the excited states can autoionize into the same continuum state, the line shape observed will be drastically different than if they were independent processes. This effect of configuration interaction makes
it very difficult to interpret the line shape of the autoionization feature. There has been very little work in the area of autoionization and none in regard to the 4d-4f transitions in the rare earths.

The partial yield for γ-Ce is also shown in Fig. 8 with the zero intensity shifted vertically for clarity. The fine structure is very similar to that of CeF$_3$, but shifted slightly in energy and broadened. The natural broadening causes the loss of many of the features that were observed in CeF$_3$, but the structure still corresponds to a 4f$^1$ ground state configuration. We no longer have the simple atomic representation that was used to describe the 4f level in CeF$_3$. The (5d6s)$^3$ electrons which are lost to the fluorine atoms in CeF$_3$ are now present in the valence band of γ-Ce. The other major change is that cerium atoms now have other cerium atoms as nearest neighbors. With cerium atoms as nearest neighbors, the 4f wavefunctions can now overlap slightly with the possibility of a large overlap and the formation of a 4f band. The larger the overlap of the 4f wavefunctions, the more the 4f level moves away from an atomic-like state. This departure affects the overlap of the 4d and 4f levels and will be seen as a loss of structure and a shift in energy of the multiplet features.

The presence of the valence band can have two effects on the observed multiplet features. If the 4f levels from neighboring atoms do interact, the resulting state is then more likely to hybridize with the s-d valence band, further increasing the departure from the atomic state. Again, this would be seen as a variation in intensity and a shift in energy. Independent of the nature of the 4f state, the
presence of the valence band will provide an increased number of decay channels for the excited electron. This will decrease the lifetime of the excited state and, thus, broaden the observed features. Above threshold, the features observed in CeF$_3$ are no longer seen as peaks, but form a shoulder on the low energy side of the autoionization feature. The peak in the autoionization feature occurs at an energy of 127.7 eV. This value disagrees with that given by absorption measurements on thin films of cerium, although the positions of the fine structure show good agreement. The peak positions determined by Haensel et al. (61) are given in Table 5 along with those from the current investigation. The disagreement in the autoionization peak could be due to oxide contamination on the films studied by Haensel et al. An indication of this is from the pressures at which the samples were prepared. The films studied by Haensel et al. were evaporated at pressures of about 10$^{-6}$ Torr while those used in the present investigation were prepared at pressures less than 2 x 10$^{-10}$ Torr. Although this does not give conclusive evidence for contamination of the films studied by Haensel et al., we were able to show that our films were very nearly oxide free. The oxide contamination was monitored by examining the magnitude of the oxygen 2p level in the EDCs. Once oxide contamination was observed, a new film was prepared. Again, as in cerium trifluoride, the line shape of the autoionization feature is very dependent on the configuration interaction of the excited states and the continuum states. The broadening of this feature at the onset introduces an increasing background through the fine structure region.
On transforming to \( \alpha \)-Ce, two changes are observed in the partial yield. The fine structure broadens from that observed for \( \gamma \)-Ce, although it is still consistent with a \( 4f^1 \) configuration. The broadening is probably due to an increased hybridization of the \( 4f \) levels with the valence band states. The second change occurs in the autoionization region. The peak now appears at 130 eV shifted from the position of 127.7 eV in \( \gamma \)-Ce. Several partial yield spectra were taken at various temperatures. Upon cooling, the broadening and the growth of the new peak did not occur until after passing through the \( \gamma \)-\( \alpha \) phase transition. When warming the sample, these two features were persistent until the temperature passed above 190K, the \( \alpha \)-\( \gamma \) transition temperature. Due to this temperature response, we can conclude that these effects are due to the phase transition and not to the temperature change. A comparison of a cooled film with one evaporated onto a low temperature substrate is shown in Fig. 9. The enhancement of the feature at 130 eV seen in the sample evaporated at low temperatures indicates that this sample preparation procedure produces a sample with a higher percentage of \( \alpha \)-phase present.

The growth of the peak at 130 eV in transforming from \( \gamma \) to \( \alpha \)-Ce may be due to a loss of \( 4f \) character. If cerium were to lose the \( 4f \) electron and transform to a \( 4f^0 \) ground state configuration, we would see a change in the structure of the partial yield. The yield would resemble that of La but shifted in energy, i.e., 2 peaks in the fine structure. This effect is observed in CeO\(_2\) which does have a \( 4f^0 \) ground state configuration (61).
Figure 9. Partial yield spectra of γ-Ce (solid) and two samples of α-Ce produced by different techniques. Direct cooling from room temperature to 50K (dashed) and evaporation onto a substrate held at 50K (dot-dashed). The vertical axis is different and offset for each curve.
A series of oxygen exposures were used to observe the transition from the $4f^1$ to the $4f^0$ configuration. The partial yield curves are shown in Figs. 10 and 11 and corresponding EDCs are given in Fig. 12. The lowest curve in each figure represents the film before any deliberate exposure to $O_2$. Notice the EDC of Fig. 12 shows a considerable amount of contamination present, as shown by the large feature at -6.0 eV. The numbers labeling the subsequent curves are related to the intensity of the $O_2$ exposure and are given in units of Langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr-sec}$).

In Fig. 10 is shown the autoionization feature of the partial yield after $O_2$ exposure. The partial yield of the film as evaporated shows a peak in the autoionization feature at an energy at 126 eV. This value is in better agreement with that observed by Haensel et al. and adds further weight to the argument for oxygen contamination in their data. As the film is exposed to successive amounts of $O_2$, the main intensity of the autoionization feature shifts from 126 eV to about 131 eV.

This change in structure is similar to that seen in $\alpha$-Ce, but along with the change in the autoionization feature is one in the fine structure which does not occur in $\alpha$-Ce. After an exposure of 5 L of $O_2$, the EDC in Fig. 12 no longer gives the spectrum of a metal, but that of an insulator. The binding energies are determined by using the value of the Fermi level from the first curve, before $O_2$ exposure. The EDC at 5 L shows a shift in the 4f level from -2.15 to -1.7 eV. There is also an apparent enhancement of the 4f level. This is due to the increased electron escape depth in an insulator compared to that in a metal.
Figure 10. Partial yield of cerium at room temperature after exposure to O$_2$. The numbers to the right correspond to the O$_2$ exposure in Langmuirs. The vertical axis is offset for each curve.
Figure 11. Fine structure of the partial yield spectra for O₂ exposures. Numbers on the left correspond to those of Fig. 10. The vertical axis is offset for each curve.
Figure 12. Energy distribution curves, after O2 exposure, using 40 eV photons. The Fermi level of the lowest curve is used to determine the energies of the higher curves.
The fine structure associated with the $4f^1$ configuration begins to decrease and two new features begin to appear. One appears as a shoulder on the high energy side of the peak at 103.4 eV. The other feature is still small and only affects the background seen around 108 eV.

With increased oxygen exposure, the EDCs in Fig. 12 show that the intensity of the $4f$ level begins to decrease in magnitude. Accompanying the loss of $4f$ character is the loss of the structure in the partial yield associated with the $4f^1$ configuration. With an exposure of 160 L of $O_2$, the magnitude of the $4f$ level falls to about 0.1 times the magnitude seen in the 5 L curve. The partial yield associated with 160 L of $O_2$ shows two main features in the fine structure located at 103.85 and 108.25 eV. Those features still seen for the $4f^1$ configuration are most likely due to an underlying layer which is still $3+$. This is seen because of the large electron mean free path in the insulating material. The autoionization feature, as stated earlier, is now located at 131.25 eV and has a much smaller width. This indicates a reduction in the number of possible states in this region and along with the fine structure, we conclude that the oxide formed has a $4f^0$ configuration.

Summary

The theoretical work of Starace (53), Sugar (54), and Dehmer and Starace (55) has been shown to be quite adequate in describing the multiplet structure in the absorption spectra of the rare earths in the region of the 4d core energy. We have shown by comparing CeF$_3$, $\gamma$-Ce, and $\alpha$-Ce that a $4f$ occupancy of 1 is consistent for all three samples studied. The ionic picture used in the theoretical work
describes the spectrum of CeF$_3$ very accurately due to the isolation of the cerium ion in this compound. Leaving the ionic solid and examining the metal introduces possible hybridization with the s-d valence band and f-f overlap between nearest neighbors. These solid-state effects change the 4f wavefunction so that the atomic picture for the 4f level begins to break down. In transforming from $\gamma$- to $\alpha$-Ce, we have explained the observed broadening in terms of somewhat increased hybridization rather than a major loss of 4f character. The increased hybridization provides more channels for the excited state to decay and thus shortens the lifetime. The decrease in lifetime is then seen as a broadening of the spectral features.

Although we have postulated that the observed broadening in the fine structure is due to the breakdown of the atomic picture, it still remains to be seen to what extent this can occur before the fine structure is changed drastically. If the 4f electron were to become totally band-like, the 4d-4f overlap would decrease substantially and the resulting fine structure would resemble that for a 4f° configuration. The other possibility is that the fine structure would remain as for the 4f$^1$ configuration but broadened and shifted in energy, since the energy values are also dependent on the magnitude of the 4d-4f overlap. These questions cannot be answered at this time since the theoretical work has been done only in the atomic approximation.

We are also puzzled as to the causes behind the changes seen in the autoionization region. We have ruled out any structure due to direct emission by comparing yield at several electron energies. If
any structure were due to direct emission, it would shift as we changed the energy sampled. The data taken after oxygen exposure show similar structure in the autoionization region, but the appearance of this structure is accompanied by a change in the fine structure, which is not seen in the yield of α-Ce. The origin of this feature is still not understood and, as in the fine structure, needs a great deal of theoretical work before a complete understanding is available.
ENERGY DISTRIBUTION CURVES

Introduction

The second purpose of this investigation was to determine the position of the 4f level with respect to the Fermi energy. This can be accomplished by tuning the photon energy to regions where the 4f contribution to the EDC is small and then comparing those EDCs to those taken when the 4f contribution dominates the spectrum. It was found that there are two photon energy ranges where this comparison can be made. For each range, the surface effect changes and the 4f electron emission mechanism varies so that identification of the 4f level can be made using complementary results.

Results and Discussion

The energy distribution curves for γ-Ce are given in Figs. 13 and 14. These have been normalized to the intensity at the center of the valence band (−1.0 eV). The photon energy is given to the right of each curve. With 40 eV photons incident on the sample, the EDC shows three features in the valence band, located at binding energies of −0.25, −0.9, and −2.05 eV. Notice the very small intensity above background level at a binding energy of −6.0 eV. This indicates a very small contamination of the sample. The two extremal features begin to increase in intensity as the photon energy is increased, and dominate the spectra above 60 eV. The maximum amplitude, compared to the center of the valence band, is reached at about 65 eV and remains relatively constant until above 80 eV. The intensity of these features
Figure 13. Energy distribution curves of $\gamma$-Ce in the photon energy range of 40-80 eV. The photon energy is given to the right of each curve. The curves have been normalized to the intensity at an energy of -1.0 eV.
Figure 14. Energy distribution curves of γ-Ce in the photon energy range of 90-150 eV. The photon energy is given to the right of each curve. The curves have been normalized to the intensity at an energy of -1.0 eV.
decays until it reaches a minimum near 115 eV. Further increasing the photon energy, we see the two peaks reappear and continue to increase in intensity.

Upon cooling γ-cerium, the relative intensities of various features change as shown in Fig. 15. The temperature is given at the right of each curve. The data were taken continuously while cooling with a temperature change during the scan of about 10K. The inset plots the ratio of the peak heights of α to β. The solid line is drawn as an aid in observing the changes in this ratio. Notice that above 100K, the ratio is fairly constant in magnitude, then decreases between 100 and 80K, and then levels off again below 60K. This change in intensity occurs below the γ-α phase transition temperature. Insofar as the ratio is nearly constant above the γ-α phase transition temperature, it would indicate that the variation in intensities is related to the phase transition.

As indicated by the phase diagram, direct cooling does not produce a pure sample of α-Ce, but produces a multiple-phase sample. The amount of α-, γ- and β-phase present depends on the cooling rate as well as the quality of the film. In Fig. 16 are shown EDCs taken with 50 eV photons for γ-Ce and two samples of α-Ce. The partial yield of these samples was discussed in Fig. 9. As in the partial yield, the observed spectral changes associated with the phase transition are enhanced in the sample prepared by evaporation onto a low temperature substrate. This indicates that a higher percentage of the α-phase is
Figure 15. EDCs during cool down of $\gamma$-Ce. The inset is a plot of the ratio of the magnitude of the feature at -2.0 eV to that near the Fermi level. The line is only an aide to observe the change in this ratio with temperature.
Figure 16. EDCs comparing $\gamma$-Ce to two samples of $\alpha$-Ce. One prepared by direct cooling to 50K and another prepared by evaporation onto a substrate held at 50K.
present in the sample, but we cannot determine whether the amount of
the $\gamma$ or $\beta$ phases, or both, are reduced.

The EDCs of $\alpha$-Ce are remarkably similar to those of $\gamma$-Ce as shown
in Fig. 17, again normalized to the emission at -1.0 eV. The data
shown were taken on films evaporated onto a low temperature substrate.
At 40 eV, three structures are visible in the valence band, as in $\gamma$-Ce,
located at 0.15, -1.1, and -2.0 eV. Other than the slight energy dif­
ference of the center feature, the only other change concerns the
relative magnitudes. The two features nearer the Fermi level are both
enhanced, while the feature located at -2.0 eV has decreased in
intensity.

The general trends of the features as a function of photon energy
are the same for $\alpha$-Ce, as previously discussed for the $\gamma$ phase. The
two extremal features are enhanced with increasing photon energy to
about 70 eV. Above 90 eV, the relative magnitudes begin to decrease
and reach a minimum near 115 eV. Above this, the intensities of the
two features again increase. The major différence between $\gamma$ and $\alpha$-Ce
is that the deepest feature dominates the EDCs in $\gamma$-Ce, whereas in
$\alpha$-Ce both that feature and the one near the Fermi level are nearly
equal in magnitude.

With the photon range accessible by the grasshopper monochromator,
we were only able to obtain spectra of the 5p core levels, shown in
Fig. 18. The binding energies were found to be -17.4 and -20.5 eV for
the $5p_{3/2}$ and $5p_{1/2}$ state, respectively. Within experimental error,
no change in binding energy was observed for this core level in $\alpha$-Ce.
Figure 17. Energy distribution curves of α-Ce in the photon energy range of 40-130 eV. The curves have been normalized to the intensity at an energy of -1.0 eV.
Figure 18. Energy distribution curves of $\gamma$- and $\alpha$-Ce with 60 eV photons, showing the 5p core level. The spin-orbit splitting is 3.1 eV.
The valence band spectra for cerium may be composed of several types of electrons, i.e., s, d, and f. From a purely atomic picture, we know that the cross sections for photoabsorption of these three levels are all different functions of energy. Provided all three levels have nearly the same threshold, which is the case for the valence band electrons, we would see the s and d cross sections reaching a maximum value very near threshold and then decreasing rapidly above this value. The cross section of the f level is small at threshold and just above and reaches a maximum value far above threshold where the s and d cross sections are small. Using this, we should be able to tune the photon energy so that the 4f cross section is large and the 5d and 6s cross sections are small.

In Fig. 19 is shown a constant initial state (CIS) spectrum of the feature at -2.0 eV in \(\gamma\)-Ce. This has been corrected for the analyzer transmission function. The spectrum is essentially a measure of the 4f cross section in \(\gamma\)-Ce. Notice that the cross section increases from its value at 40 eV to a local maximum at about 55 eV. Below 40 eV, the 5d cross section is much larger than the 4f, but then decreases rapidly above this energy. By comparing EDCs at photon energies of 30 and 60 eV, we can selectively probe the electronic character of the valence band to isolate the 4f contributions. The CIS also shows a maximum in the 4f cross section at 122 eV. The atomic 4f cross section is small at this energy, but the 4f emission is enhanced due to Auger-like transitions from the intermediate excited state produced from the excitation of a 4d core electron. Again, comparing EDCs at
Figure 19. Constant initial state spectrum for the 4f level in $\gamma$-Ce

$\gamma$-Ce

4f $E_B = 2.0$ eV
115 and about 120 eV will highlight the 4f contribution to the valence band.

These comparisons are shown on the left of Fig. 20 for γ-Ce. The top curves are a comparison of the 60 and 30 eV EDCs normalized at -1.0 eV. The middle set shows the comparison of the 120 and 115 eV EDCs. By subtracting, we obtain the difference curves shown on the lower left. The two sets of difference curves show very similar results; a large feature located at -2.0 eV and a smaller feature at about -0.3 eV. The feature near the Fermi level may actually be located at the Fermi level, but due to the finite resolution and the effect of the Fermi level cutoff, it may appear to peak below it. On the right is shown a comparison of γ- and α-Ce at photon energies where the 4f contribution is dominant. The α phase shows an increase of the feature near the Fermi level at the expense of the deeper feature.

Both features have been independently identified in previous investigations as being related to the 4f level (28-32). We propose that both are contributions from the 4f state. There are several possible interpretations for these two features, e.g., surface shift, shake-up, or screening. The loss of three-dimensional symmetry at the surface can induce a shift in the energy levels compared to the bulk energy levels. This is seen in CeN (62) where two 4f features, separated in energy by about 1.2 eV, are identified. The feature observed at the Fermi level was concluded to be due to the emission from the bulk 4f state. The emission at -1.2 eV has been assigned to a surface stabilized 4f$^1$ level which is shifted down in binding energy. These
Figure 20. EDCs for α- and γ-Ce. Spectra on the left for γ-Ce highlight the 4f character through variations in d/f partial photoionization cross sections (uppermost), through resonance photoemission, and through difference curves (lower most). Spectra on the right compare γ- to α-Ce using photon energies where the 4f character is most pronounced.
conclusions were based on the facts that this peak showed a contamination dependence, a characteristic electron kinetic energy dependence in the range 40 to 150 eV, and that it is very weak in XPS spectra. The two features we propose to be 4f related show none of these characteristics.

We are then left with a satellite picture. Since either screening or shake-up processes may be involved, either of the features may be due to the direct emission of the 4f electron. The shake-up process produces a satellite, located at higher binding energies with respect to the direct emission feature. We would then identify the feature at the Fermi level as being due to the direct emission and the deeper feature as the shake-up satellite.

This description fails when one considers the relative magnitude of the two features and how these magnitudes change when transforming to the \( \alpha \) phase. In the \( \gamma \) phase, the magnitude of the feature at -2.0 eV is larger than that of the feature at the Fermi level. In the description of the shake-up process, this indicates a strong coupling between the 4f state and the valence band states. As we transform to \( \alpha \)-Ce, the feature near the Fermi level increases in magnitude. This would mean the 4f electron becomes more localized and, therefore, the interaction with the valence band electrons decreases. This is contradictory to the results of the partial yield which indicates an increased hybridization of the 4f electron in the \( \alpha \) phase, and expectations based on the smaller volume of the \( \alpha \) phase.
The alternative is to describe the features as being due to a direct emission with no screening and an emission where the 4f hole is screened. The screening process has the effect of increasing the emitted electron's kinetic energy. With this in mind, we would assign the -2.0 eV feature as being the direct 4f emission and the feature near the Fermi level as being the screened emission. The difficulty arises when one considers the 4f excitation energy calculations by Herbst et al. (63-65). They have assumed a "complete screening" approximation in calculating the energy in the metal excited by emission of the 4f electron. To compensate for the loss of the 4f electron and to provide charge neutrality, one electron was added to the conduction band. Their results give generally good agreement for the binding energies across the rare earth series. The calculated 4f binding energy for Ce is 1.9 eV. This is in very good agreement with the measured binding energy of the deeper feature. Since the calculated values are in the "completely screened" limit, there should be no 4f contribution at lower binding energies, which is contradictory with our experimental results. It should be pointed out that if one considers the errors in the calculations of Herbst et al., the binding energy may be as small as 0.4 eV. The uncertainty in their work has been treated as being much less since the binding energies found for the other rare earths agree very well with the values they calculate. If we make use of the uncertainty, we could identify the feature near the Fermi level as being the fully screened feature and the one at -2.0 eV as being the unscreened.
Recently Liu and Ho (66) have performed a many-body calculation on the photoexcitation of the 4f electron from cerium. They concluded that there were two final states, completely screened and unscreened. The excitation which leads to the unscreened f hole contributes to the intensity of the deeper feature. The fully screened mechanism introduces a second feature much closer to the Fermi energy. Upon transforming to α-Ce, the relative change in intensities of the two spectral features is accounted for by a slight decrease in the Coulomb repulsion between the 5d and the 4f electrons. This increases the matrix element for the screening mechanism while it decreases the unscreened one. The decreased Coulomb repulsion indicates a slight delocalization of the 4f level accompanying the phase transition, which is consistent with the interpretation of the partial yield spectra.

Several questions have been raised as to how the energies to examine the 4f character are chosen, and at what binding energy we should normalize the EDCs (67). The discussion of the photon energy dependence has been given earlier. The position in the valence band to use for normalization was chosen from the 30 to 115 eV curves, where the 4f contribution should be negligible. Since the EDCs at these photon energies peak at about -1.0 eV, and they are presumably contributions from only the s and d electrons, this position was chosen for the normalization procedure. Additionally, rather than compare EDCs at discrete photon energies, we can compare constant initial state spectra for different features in the valence band. This avoids the problems associated with the normalization procedure when subtracting two curves.
In Fig. 21 are two EDCs for CeF$_3$ taken with 120 and 113 eV photon energies. The curves have been normalized to the fluorine 2p emission. Notice that the features associated with the cerium ion are enhanced whereas the fluorine 2s level is only superimposed on a different background. For this case, the normalization procedure is straightforward, in that the fluorine 2p cross section should not change drastically from 113 to 120 eV and that the features in the EDC do not overlap. Figure 22 shows the CIS spectra for the cerium 4f and the fluorine 2p levels. Our assumptions of a constant 2p cross section are seen to be valid. The vertical scales are different for each curve.

The important thing to notice is that we can follow the enhancement of the 4f level as we scan the photon energy through the 4d core threshold. The corresponding CIS for the 2p level shows only a slight increase at 121 eV, probably due to the increased absorption depth at these energies. We see that instead of deciding on a normalization procedure, we can compare the CIS spectra of two features in an EDC and determine if they are due to the same level in the solid.

Figure 23 is a comparison of the partial yield of CeF$_3$ to the 4f CIS spectrum. In the fine structure, we see a one-to-one correspondence between the yield and the CIS spectra, but with a change in line shape and peak position. The difference arises from the two mechanisms involved in emitting the electron for either the partial yield or the CIS spectra. In the case of the yield, the number of electrons measured is only dependent on the excitation process. Therefore, it will have a maximum intensity at the energy of maximum absorption and the features
Figure 21. EDCs of CeF$_3$ at 120 (solid) and 113 eV (dashed). Notice the enhancement of the cerium related features.
Figure 22. Constant Initial State (CIS) spectra of the cerium 4f level and fluorine 2p level in CeF$_3$. The energy range spans the 4d core energy of cerium.
Figure 23. Comparison of the CIS spectra to the partial yield of CeF$_3$. 

\textbf{CeF$_3$}

- Partial Yield
- 4f - CIS
will be symmetric about that energy. The intensity in the CIS is
dependent not only on the absorption process, but also on the decay
process. This leads to an asymmetric line shape which has been described
by Fano (68). Due to the asymmetry, the maximum is not expected to occur
at the maximum of the absorption process.

The CIS shows large fluctuations in the intensity of the 4f feature.
These fluctuations are associated with a second process for emission of
the 4f electron, other than the direct excitation. Besides exciting
the 4f electron out of the solid, the incident photon can be absorbed
by the 4d electron leaving the solid in an intermediate excited state.
After the absorption process, we have a $4d^94f^2$ configuration and with
the 4d core hole present, Auger transitions can occur. Since the 4d and
4f wavefunctions overlap, we expect the 4f to be the electron most
likely to decay into the 4d core hole. Accompanying this decay, a
second electron is emitted from the solid. The energy of the emitted
electron is the same as it would be in direct excitation, since the
level from which the decay took place was originally produced by the
incident radiation. Since the electron is emitted from the solid with
the same kinetic energy for both processes, there is only one feature
observed in the EDC. The measured intensity is, therefore, a sum of
two processes: 1) direct excitation, and 2) an Auger-like transition
from the intermediate excited state. At these photon energies, the
cross section for 4f excitation is small, but because of the Auger
effect, the measured intensity has been enhanced.
Above 115 eV, we no longer see a one-to-one relation between the yield and the CIS spectra. The CIS spectrum consists of one sharp feature located at 121.6 eV. This feature is still associated with the Auger-like transitions but, because of the increased absorption, the enhancement is much greater than that observed in the fine structure. Above this energy, the excited states are above the vacuum level and can, therefore, leave the solid without having to take part in the Auger process. These electrons are said to autoionize and are emitted with very low kinetic energy. With the Auger process no longer enhancing the 4f emission, the intensity decays back to that associated with direct emission.

Figures 24 and 25 show the CIS spectra taken for the two features in the valence band of \( \gamma \)- and \( \alpha \)-Ce, respectively. The inset shows the fine structure, as measured by the yield and the two CIS spectra. As in the fluoride, the fine structure seen in the yield is reproduced in the CIS spectra. Also, the CIS curves are broadened from that observed in CeF\(_3\). Above 115 eV, we again see a single feature for both CIS curves but shifted slightly in energy.

The CIS curves for both features in the valence band of \( \gamma \)-Ce show essentially the same \( h\nu \) dependence with only a few differences. In the fine structure, we see that the peak positions are shifted slightly to lower energy and the minimum intensities between features is not as great for the feature near the Fermi level as that deeper in binding energy. Above 115 eV, the CIS curves are similar to that for CeF\(_3\) in that there is a single peak. For \( \gamma \)-Ce, the maximum intensity for the
Figure 24. Comparison of the CIS spectra of both 4f features in \(\gamma\)-Ce to the partial yield.
Figure 25. Comparison of the CIS spectra of both 4f features in α-Ce to the partial yield.
deeper feature in the EDC occurs at 121.9 eV, whereas the maximum intensity of the peak at the Fermi level occurs at 121.2 eV. The corresponding peak positions for α-Ce are 121.6 and 120.9 eV, respectively. The difference between the two CIS curves for one phase can be accounted for by taking into account the fact that the intensity at the Fermi level is a sum of the f as well as s and d emissions. From Zangwill and Soven (69), we see that the s and d maxima occur about 2eV lower in energy than that of the 4f level. When these are superimposed, the total will peak at an energy between the two. Therefore, if the s-d contribution could be subtracted from the intensity at the Fermi level, the two CIS curves should be identical.

Summary

The energy distribution curves show a very simple valence band spectrum. The energy positions of the 4f features are -2.0 and about -0.3 eV. It is possible that the feature near the Fermi level could be located at the Fermi level but, due to the finite resolution and the cut-off associated with the Fermi level, it appears at a deeper binding energy. The existence of the two features is explained in terms of the screening process in which there are two possible states: 1) the unscreened state, and 2) the screened state. The unscreened state will appear at a deeper binding energy than the screened. Upon transforming to the α phase, the intensity of the screened feature is increased while that of the unscreened feature decreases. The theoretical work by Liu and Ho shows that the change in the intensities can be accounted for by a small change in the Coulomb repulsion, making the screening process
more likely to occur. The CIS curves for these features show very similar \( h\nu \) dependence. The differences are accounted for by noticing that the intensity at the Fermi level is composed of emission from both the s-d valence band and the screened final state associated with the 4f level.
CONCLUSION

The results of the partial yield and the energy distribution curves show very little change in the 4f level on transforming from γ- to α-Ce. These changes have been discussed in terms of the delocalization of the 4f level. Since the changes in the spectra accompanying the phase transition have been observed to be small, the difference in the 4f level in both γ- and α-Ce is also shown to be small.

The fact that we see no dramatic changes in the 4f character between the two phases is evidence against the promotion model. We cannot distinguish between the remaining two models, the Mott transition or complete band model. The difficulty arises in determining when the 4f level becomes band like. In CeF₃, it was concluded that the 4f level is as nearly atomic in character as possible but that the 4f level has become delocalized in γ- and α-Ce. The question then raised is "at what point in the delocalization does the formation of bands begin to occur?"

Therefore, we have shown the inadequacy of the promotion model in describing the phase transition, but we have not been able to reconcile which of the remaining models does give an appropriate interpretation. Our results are consistent with previous position annihilation (24), Compton scattering (25), and muon spin rotation experiments (70). These all have indicated a constant, or nearly constant, 4f occupation in both the γ and α phases of cerium. The observation of the many-body state near the Fermi level may resolve the difficulty in reconciling the experimental results of photoemission and the low energy probes,
e.g., specific heat. The mechanism for this many-body state is not unique to cerium and further proof of its suitability can be found by examining other rare earth metals for the existence of a satellite structure. Finally, the fact that we were able to produce α phase samples is an important step in resolving the questions of the γ-α phase transition.
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