1990

Photoemission and inverse photoemission studies of CeSn3 and LaSn3

Sayong Hong
Iowa State University

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Photoemission and inverse photoemission studies of CeSn₃ and LaSn₃

Hong, Sayong, Ph.D.

Iowa State University, 1990
Photoemission and inverse photoemission studies
of CeSn$_3$ and LaSn$_3$

by

Sayong Hong

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Major: Solid State Physics

Approved:
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In Charge of Major Work
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For the Major Department
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For the Graduate College

Iowa State University
Ames, Iowa
1990

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CHAPTER 1. INTRODUCTION

Ce and its compounds exhibit interesting chemical and physical properties due to the Ce 4f electrons. Some lanthanide compounds with Pd, Sn, and In crystallize in the Cu₃Au structure. These compounds have been extensively studied because most of them are fairly easy to prepare by congruent solidification from the melt [1]. Sometimes they even can be prepared as single crystals. Moreover, the simple structure makes it easy to perform self-consistent band-calculations. Elemental Ce has two fcc phases [2] [3] [4]; the high-volume, local-magnetic-moment γ phase and the low volume, Pauli paramagnetic α phase. In general, the effective volume and magnetic character of Ce in intermetallic compounds can be characterized as being γ-Ce-like and α-Ce-like [5]. Ce intermetallic compounds, in which the volume of the Ce ion is similar to that of γ(α)-Ce, are called γ(α)-Ce-like. CeSn₃, which is a γ-Ce-like material [6], also displays a number of unusual properties that classify it as a mixed-valent metal. Its lattice constant at room temperature is intermediate between those expected for trivalent and tetravalent Ce [7]. The unusually large thermal expansion coefficient of CeSn₃ [7] [8] [9] [10] (nearly double that measured for LaSn₃ and PrSn₃ between 90 K and 300 K) implies a small additional continuous increase in the valence. The electronic specific heat [11] [12] [9] and thermal expansion are also anomalously large. The magnetic susceptibility follows a Curie-Weiss law at
high temperature with an effective moment near the trivalent value for Ce and a large negative paramagnetic Curie temperature of -195 K [7] [13]. The magnetic susceptibility in the 40-300 K range is approximately constant, and below 40 K, it increases very rapidly with decreasing temperature. Mössbauer measurements indicate no magnetic ordering down to 1.6 K [14]. Neutron scattering measurements of the induced magnetic form factor show that in the ground state, there is a nearly equal mixture of 4f and conduction states at the Fermi level, significantly different from that of just an atomic 4f electron on each Ce ion [15]. In CeSn₃ there is an unexplained increase in the d character of the Ce neutron scattering form factor with decreasing temperature below 40 K, and its form factor disagrees with the band structure calculations at the Fermi level. De Haas-van Alphen experiments [16] [17] show the presence of electrons with high effective masses at $E_F$ (masses ranging from 4.2 to 9.2) indicating the presence of strong hybridization between the conduction band and 4f states. LaSn₃ has recently attracted attention as a proper reference material for the study of the mixed valence state in CeSn₃. But it also has its own interesting properties. In LaSn₃, which also has the AuCu₃ crystal structure, the La nuclei form simple cubic sublattice and the Sn nuclei occupy each face-centered position of the simple cubic unit cell. The space group is identical to that of the La sublattice, i.e. $Pm\bar{3}m$: the reciprocal lattice is thus simple cubic [18]. The thermal behavior of the molar susceptibility of LaSn₃ shows a relatively weak dependence on temperature above 200 K [11] [12]. The heat capacity at constant volume data suggests that the Debye parameter ($\Theta_D$) is fairly constant at 205 ($\pm5$)K at high temperature, [7]. The coefficient $\gamma$ of the electronic specific heat is relatively large, suggesting a large density of states at the Fermi level. The specific heat $\gamma$ is 11.0
Table 1.1: Physical properties of $CeSn_3$ and $LaSn_3$

<table>
<thead>
<tr>
<th>Property</th>
<th>$CeSn_3$</th>
<th>$LaSn_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>$Pm3mAuCu_3$</td>
<td>$Pm3mAuCu_3$</td>
</tr>
<tr>
<td>Lattice parameter ($\text{Å}$)</td>
<td>4.72</td>
<td>4.77</td>
</tr>
<tr>
<td>electronic specific heat constant $\gamma$ ($mJ\text{mole}^{-1}K^{-2}$)</td>
<td>53</td>
<td>11</td>
</tr>
<tr>
<td>Work function (111) surface</td>
<td>3.7 eV</td>
<td>3.6 eV</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>Curie-Weiss</td>
<td>Pauli</td>
</tr>
</tbody>
</table>

$mJK^2\text{mole}^{-1}$ [7] [10]. The inverse bulk paramagnetic susceptibility of $LaSn_3$ does not follow a Curie-Weiss behavior, showing that there is no evidence for the existence of a magnetic moment localized on the La atoms. The neutron scattering data [19] show that the form factor of $LaSn_3$ is quite different from that of atomic La. Thus, the main contribution to the bulk magnetic susceptibility of $LaSn_3$ comes from Sn 5d states, which agrees with the band calculation but disagrees with the analysis of the NMR experiments [20] [21] [22]. While $CeSn_3$ shows no superconductivity down to 7 mK [23], $LaSn_3$ has a relatively high superconducting transition temperature (6.42 K).
G-S Model

Ce and many its compounds show double-peaked photoemission spectra, which are believed to arise from the 4f state. There are quite a few models which tried to explain the origin of this phenomenon. In 1983, Gunnarsson-Schönhammer [24] [25] [26] [27] [28] and Allen (1985) [29] proposed a simple method for calculating the valence photoemission, the 3d-4d x-ray absorption, and the bremsstrahlung isochromat spectra (BIS) of Ce and its compounds. In a Ce atom, the conduction-state wave functions, 5d and 6s, are extended and have substantial weight at the Wigner-Seitz radius [30]. The 4f wave functions, however, are localized, located mainly inside the 5s and 5p wave functions which belong to the Ce core. Because of the localized nature of the 4f orbitals, the overlap between 4f orbital and a conduction orbital on another site is very small, and the Coulomb interaction $U$ between two 4f electrons in the same site is large. Therefore, it is essential to include these interactions in the G-S model of Ce compounds. They assumed that the Coulomb interaction between the conduction electrons and 4f hole could be neglected. Some, however, suggested that this Coulomb interaction could be the main cause of the double peaked structure [15] [31] [32] [33] [34]. The starting point of the G-S model is the Anderson lattice Hamiltonian [35] [36]

$$ H = \sum_{\nu=1}^{N_f} [\int e_\nu \psi_\nu \psi_\nu + \sum_{\nu,\mu,\nu<\mu} n_\nu n_\mu, (1.1) $$

where $\mu$ is a combined index for the orbital and spin degeneracies, and $e$ and $\nu$ refer to a conduction state and an f state, respectively. The first two terms are the conduction states with energy $e$ and the f level with the energy $e_f$. The conduction states are
transformed into the same symmetry representation as the f-state for convenience. The third term leads to hopping between 4f and the conduction states and the last term represents the Coulomb interaction between the f electrons in the same site. This model is best discussed with the aid of Fig. 1.1. The hopping matrix element is defined as

$$\tilde{V}(\epsilon) \equiv \sqrt{N_f} V(\epsilon), \quad (1.2)$$

so that $\tilde{V}(\epsilon)$ is independent of the f-level degeneracy $N_f$. The singlet ground state is described by

$$|0\rangle = \prod_{\nu=1}^{N_f} \prod_{\epsilon \leq \epsilon_F} \psi_{\epsilon\nu}^\dagger \psi_{\nu} |\text{vacuum}\rangle, \quad (1.3)$$

with the empty f-level and filled conduction states below the Fermi energy $E_F$. In the G-S model, a simple elliptical density of states was chosen for the conduction states. The state $|0\rangle$ becomes the state (a) in Fig. 1.1 when one electron below the Fermi energy hops into the f-level:

$$|\epsilon\rangle = \frac{1}{\sqrt{N_f}} \sum_{\nu} \psi_{\epsilon\nu}^\dagger \psi_{\nu} |0\rangle. \quad (1.4)$$

The states (b) and (c) are

$$|\epsilon\epsilon'\rangle = \frac{1}{\sqrt{N_f(N_f-1)}} \sum_{\nu,\nu',\nu' \neq \nu''} \psi_{\epsilon\nu}^\dagger \psi_{\epsilon'\nu'} \psi_{\nu''}^\dagger \psi_{\nu''} \psi_{\nu''} |0\rangle \quad (1.5)$$

$$|\epsilon\epsilon\rangle = \frac{1}{\sqrt{N_f}} \sum_{\nu} \psi_{\epsilon\nu}^\dagger \psi_{\epsilon\nu} |0\rangle. \quad (1.6)$$

The matrix elements of the Hamiltonian are

$$\langle\epsilon | H | 0\rangle = \tilde{V}(\epsilon) \quad (1.7)$$
Figure 1.1: Schematic representation of the basis states.
Solid circles show electrons and open circles show holes. The hatched part indicates the filled conduction band and the horizontal line the f-level. The arrows show which states couple to each other. A solid line indicates the strength $V$ and a dashed line the strength $V/\sqrt{N_f}$.
\begin{align}
\langle \varepsilon | H | \varepsilon' \rangle &= \frac{N_f - 1}{N_f} \tilde{V}(\varepsilon') \delta(\varepsilon - \varepsilon') + \tilde{V}(\varepsilon) \delta(\varepsilon' - \varepsilon') \\
\langle \varepsilon | H | \varepsilon' \rangle &= \frac{\tilde{V}(E)}{\sqrt{N_f}} \delta(\varepsilon - \varepsilon').
\end{align}

Since the contributions to the total energy are reduced to the order of \( \frac{1}{N_f} \) as one goes to the lower row, and the large Coulomb interaction among the \( f \) electrons prohibits the system from accommodating more than two electrons in the same site, the number of basis sets can be limited in an actual calculation. In PES (Photo-Electron Spectroscopy), the situation is similar to Fig. 1.1, but it involves a hole in the initial states. The basis set, therefore, does not have the state \( \theta \) in Fig. 1.1. The photoemission can be described by

\[ \tau = \sum_{\kappa i} \tau_{\kappa i} \psi_{\kappa}^\dagger \psi_i \]  

where \( \tau_{\kappa i} \) is a dipole matrix operator between states \( | \kappa \rangle \) and \( | i \rangle \). According to the golden rule, the photoemission current is given by

\[ j(\varepsilon) \sim \sum_{\kappa} \sum_{n_l} | \langle E_n(N-1) | \psi_{\kappa} \tau | E_0(N) \rangle |^2 \times \delta(\varepsilon - \varepsilon_{\kappa}) \delta(\varepsilon + E_n(N-1) - \hbar \omega - E_0(N)), \]

where \( \hbar \omega \) is the energy of the photon.

This can be rewritten as

\[ j(\varepsilon) \sim \frac{1}{\pi} \sum_i \sum_{\kappa} | \tau_{\kappa i} |^2 \delta(\varepsilon - \varepsilon_{\kappa}) \text{Im} g_{ki}^<(\varepsilon - \hbar \omega - \varepsilon_{\kappa}), \]

where the Green's function

\[ g^<(z) = \langle E_0(N) | \psi_i^\dagger \frac{1}{z - E_0(N) + H} \psi_i | E_0(N) \rangle. \]
Thus

\[ j(\epsilon) \propto g_i^<(z), \]  

(1.14)

where

\[ z = \epsilon - \hbar \omega - \imath \theta, \]  

(1.15)

which is the kinetic energy of an emitted electron.

The advantage of the G-S model is that a single set of parameters (\( \tilde{V}(\epsilon), n_f \) and \( U \)) characterizing the electronic structure of the solid can give a reasonable description of both PES and BIS data for a given material [37] [38] [39] [40] [41] [42] [43].

Band Theory

There are two major approaches for treating the f electrons in the rare-earth metals and their compounds. The first one is to treat the f states as localized states and start from a model Hamiltonian such as the Anderson lattice model. The other one is to calculate a self-consistent band structure by using the local-density approximation. The most serious problem in calculating a band structure for 4f systems is how one treats the electron correlations.

One of the complications of photoemission is that the photoemission results reflect the final states rather than the initial state, and in some cases, the photoelectron will give rise to more than one final state. As a result of the sudden change in the central potential of an atom, an electron in a given orbital may go into an exited (electron shakeup) or continuum (electron shakeoff) state [45]. Therefore, the ground state from the band structure may not give the correct picture of the photoemission spectra.
The de Haas-Van Alphen effect has been observed for the coherent hybridized Bloch states in $\text{CeSn}_3$ [16] [44] [17]. It suggests that the 4f-states should be treated in a band picture rather than a localized electron picture. The Fermi surface of $\text{CeSn}_3$ was mapped and the observed de Haas-Van Alphen effect could be explained by the band calculation. The magnetic neutron scattering form factor on $\text{CeSn}_3$ was shown to be good agreement with the conventional band calculations, which suggests that 4f electrons in $\text{CeSn}_3$ are in Bloch states. On the other hand, band theory cannot give a correct picture of the XPS (X-ray Photoelectron Spectroscopy) data from Ce and its compounds because the theory indicates that the 4f-state should be very close to the Fermi energy, hybridized with other states, and not a pure 4f band. It fails to give correct values of the effective mass and the density of states for the Ce compounds at the Fermi energy. The 4f states were generally treated as Ce valence bands and the charge density was determined self consistently by a local density approximation. As a result, the 4f bands with large dispersion appeared at the Fermi energy.

Recently, a new method called "renormalized band theory" has been tried to improve the 4f electron treatment [46]. Strange and Newns calculated the $\text{CeSn}_3$ band structure from the LMTO (Linearized Muffin Tin Orbital) method. They recalculated the band structure by using a renormalization based on the infinite Anderson lattice model [47]. To achieve the one-electron band calculation, they replaced the Anderson Hamiltonian by the mean-field Hamiltonian. This calculation gave more realistic effective masses and density of states at the Fermi energy of $\text{CeSn}_3$. This model was further investigated by Hofmann and Keller [48].

The band calculations for both $\text{CeSn}_3$ and $\text{LaSn}_3$ were done by the Linearized
Augmented Plane Wave method (LAPW) [49][50] for comparison with the experimental data [51]. One electron potentials for both CeSn₃ and LaSn₃ were calculated in a relativistic approximation by Koelling. The band structures and densities of states are shown in Figures 1.2-1.5. The calculated band structures agree with the previous results [52][53][54][55], which show the mixed states of 4f and conduction states with considerable dispersion extending below the Fermi energy. Since the tin dominates the lower part of the valence band, CeSn₃ and LaSn₃ show almost identical structures below the Fermi energy.
Figure 1.2: Energy band structure of CeSn$_3$. The Fermi energy is located at 0.475 Ry (solid line)
Figure 1.3: Density of states of CeSn$_3$. The Fermi energy is located at 0.475 Ry
Figure 1.4: Energy band structure of LaSn$_3$. The Fermi energy is located at 0.468 Ry (solid line)
Figure 1.5: Density of states of \( \text{LaSn}_3 \). The Fermi energy is located at 0.468 Ry.
CHAPTER 2. THEORY OF PHOTOEMISSION AND INVERSE PHOTOEMISSION

In 1887, Hertz observed an electric discharge between two electrodes when one of the electrodes was illuminated with ultraviolet light. One year later, Hallwachs [56] reported the first observation of electron emission from a surface caused by electromagnetic radiation. This effect, however, was not understood until Einstein [57] presented the relation between the incident frequency and the photoelectron energy (light quanta) in 1905. X-rays, the first inverse photoelectric effect, were discovered by Röntgen [58] in 1895 and the detailed investigation of the x-ray bremsstrahlung spectrum was made by Duane and Hunt [59] in 1915. While the photoelectric effect has been developed into a powerful and widely used photoelectron spectroscopy since the 1960s, inverse photoelectron spectroscopy (IPES) was studied only by a few pioneers [60] [61] [62] until an experiment in the UV range was done by Dose [63] in 1977. But inverse photoelectron spectroscopy (IPES) is becoming a promising experimental tool due to the accessibility of the region between the Fermi level and the vacuum level which can not be reached by PES. When the x-ray radiation is emitted under high energy electron bombardment, the technique is referred to as BIS (Bremsstrahlung Isochromat Spectroscopy), when a low energy photon is emitted, it is called IPES. Though some other techniques, such as X-ray appearance poten-
tial spectroscopy and soft X-ray absorption spectroscopy can probe the region, IPES can give angle-resolved information besides the accessibility. These advantages over other techniques make IPES proper for investigating magnetic materials, semiconductor surfaces, and chemisorption.

Theory of Inverse Photoemission

Both inverse photoemission and photoemission can be explained by the same physics illustrated in Fig. 2.1. In fact, the theoretical equivalence has been emphasized by Pendry [64] [65]. So instead of discussing the theoretical aspects of both techniques, emphasis will be placed more on IPES. When an electron is emitted from a surface of a metal by the action of a photon its kinetic energy will be

\[ K.E. = h\nu - W, \]

where \( h\nu \) is the energy of the absorbed photon and \( W \) is the work required to remove the electron from the metal, which is needed to overcome the attractive fields of the atoms in the surface and losses due to internal collisions of electrons. Now when the electron suffers no internal collision, the kinetic energy will be a maximum. Hence

\[ K.E._{\text{max}} = h\nu - \Phi, \]

where \( \Phi \), a characteristic energy of the metal, called the work function, is the minimum energy needed by an electron to pass through the metal surface and escape from the attractive forces that normally bind the electron to the metal.
Inverse Photoemission

Electron in  

\[ e^- \]

Photon out  

\[ E_i \]

\[ \hbar \omega \]

\[ E_V \]

\[ E_f \]

\[ E_F \]

\[ \hbar \omega = E_i - E_f \]

Photoemission

Photon in  

\[ \hbar \omega \]

Electron out  

\[ e^- \]

\[ E_f \]

\[ E_V \]

\[ E_F \]

\[ E_i \]

\[ E_f = \hbar \omega - E_i - \phi \]

Figure 2.1: Comparison between PES and IPES
In quantum mechanics, the expression can be rewritten

\[ E_f = \hbar \omega - \Phi - E_i, \]  

(2.3)

where \( E_i \) is the initial energy state of the electron below the Fermi energy. \( E_f \) is the final energy state above the vacuum level. Now in inverse photoemission, the photon is emitted with energy \( \hbar \omega \) when an electron with energy \( E_i \) impinges on a solid and is de-excited. Then

\[ E_i = E_f + \hbar \omega, \]  

(2.4)

where \( E_i \) is the energy of the incident electron above the vacuum level. \( E_f \) is the energy of the final state of electron. In these processes, it was assumed that the photon was absorbed by one electron or one photon was emitted by one de-excited electron (one-electron approximation). Since both photoemission and inverse photoemission involve interaction between photons and electrons, the Hamiltonian \( H \) of an electron in the presence of an electromagnetic field is described in terms of the vector potential \( A \) and the scalar potential \( \Phi \).

\[ H = \frac{(p + eA/c)^2}{2m} + V(r) - e\Phi. \]  

(2.5)

Choosing the gauge such that the scalar potential is zero, Eq.(2.5) becomes

\[ H = \frac{p^2}{2m} + V(r) + \frac{e(A \cdot p + p \cdot A)}{2mc} + \frac{e^2}{2mc^2} |A|^2. \]  

(2.6)

By ignoring \( A^2 \), the interaction Hamiltonian is

\[ H' = \frac{p^2}{m} A \cdot p. \]  

(2.7)

\( \nabla \cdot A \) is chosen to be zero in the Coulomb gauge. Now replace the vector potential
by the field operator (i.e., second quantized form)

\[
A(x, t) = \frac{1}{(V_p^{1/2})} \sum_q \sum_\alpha c \frac{2\pi \hbar}{\omega} a_{q, \alpha}(t)e^{i\mathbf{q} \cdot \mathbf{x}} + a_{q, \alpha}^*(t)e^{i\mathbf{q} \cdot \mathbf{x}} \tag{2.8}
\]

where \( \hat{e}^{(\alpha)} \) is the linear polarization unit vector whose direction depends on the photon propagation direction of \( \mathbf{q} \) which is the photon wave vector. \( a_{q, \alpha}^* \) and \( a_{q, \alpha} \) are creation and destruction operators respectively for the state \( q, \alpha \). \( V_p \) is the normalization volume for the photon. According to Fermi's golden rule for time-dependent transitions, the transition rate for Eq.(2.7) and Eq.(2.8) becomes

\[
R = \frac{2\pi}{\hbar} |M_{f,i}|^2 \rho_p = \frac{2\pi}{\hbar} c^2 \frac{2\pi \hbar}{\omega} \frac{1}{V_p} <b|\hat{e} \cdot p|k>|^2 \rho_p, \tag{2.9}
\]

where \( \rho_p \), the photon density of states, is

\[
\rho_p = \frac{V_p \omega^2}{(2\pi)^3 \hbar c^3} d\Omega. \tag{2.10}
\]

\( b \) and \( k \) are the bound state (final state) and continuum state (initial state), respectively, and \( d\Omega \) is the solid angle of emission. Then the transition rate is

\[
R = \frac{\alpha}{2\pi} \frac{\omega}{m^2 c^2} |<b|\hat{e} \cdot p|k>|^2 d\Omega \tag{2.11}
\]

where \( \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \). Now the cross section is the transition rate divided by the incident electron flux, which is

\[
j = \frac{\hbar k}{m V_e}, \tag{2.12}
\]

\[
\left[ \frac{d\sigma}{d\Omega} \right]_{IP} = \frac{\alpha}{2\pi} \frac{\omega}{m^2 c^2} |<b|\hat{e} \cdot p|k>|^2. \tag{2.13}
\]

By analogy to inverse photoemission, the cross-section for the photoemission is

\[
\left[ \frac{d\sigma}{d\Omega} \right]_{PE} = \frac{\alpha}{2\pi} \frac{k}{m \hbar \omega} |<k|\hat{e} \cdot p|b>|^2. \tag{2.14}
\]
Table 2.1: Comparison between PES and IPES

<table>
<thead>
<tr>
<th></th>
<th>PES</th>
<th>IPES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Means of Excitation</td>
<td>electron</td>
<td>photon</td>
</tr>
<tr>
<td>Output</td>
<td>photon</td>
<td>electron</td>
</tr>
<tr>
<td>Accessible Range</td>
<td>—</td>
<td>above $E_v$</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>between $E_v$ and $E_F$</td>
</tr>
<tr>
<td>Yield</td>
<td>$\sim 1$ electron/10$^5$ photons</td>
<td>$\sim 1$ photon/ 10$^9$ electrons</td>
</tr>
</tbody>
</table>

The ratio between the two cross-sections is

$$
\left[ \frac{d\sigma}{d\Omega} \right]_{IPES} = \frac{\omega^2}{\omega^2 k^2} = \frac{q^2}{k^2} = \frac{1}{\lambda_{ph}} \left[ \frac{\lambda_{ph}}{\lambda_{ph}} \right]^2
$$

(2.15)

In the ultraviolet region, the ratio is about $10^{-5}$, which explains the dominance of photoemission applications over inverse photoemission. Both experimental photoemission and inverse photoemission spectra can be qualitatively interpreted by a three-step model [66] [67]. Though the one electron model gives a more complete and correct picture, the three-step model often gives better physical insight. The brief comparison between PES and IPES is illustrated in Table 1.1.

In the three-step model, inverse photoemission is treated as a sequence of the following steps:

1. Optical de-excitation of an electron: an incident electron couples with one of the unoccupied states $E_i$ above the vacuum level ($E_v$) and decays vertically into an empty final state $E_f$. It is assumed that this decay is a direct (i.e.,
21

$k$-conserving) transition within the band structure.

2. Transport of the photon to the surface

3. Escape of the photon through the surface into the vacuum.

In step one, there is a high probability that the incoming electron decays non-radiatively through inelastic electron-electron scattering which is the origin of the short inelastic penetration depth in a metal surface. Therefore, the yield function of emitted photons $I(E, \omega)$ is generally a sum of a primary contribution $I_p(E, \omega)$ from electrons without inelastic collisions prior to the radiative decay, and the background $I_b(E, \omega)$. In the three-step model, the primary distribution $I_p(E, \omega)$ is assumed to be described by

$$I_p(E, \omega) = D(\omega) \cdot T(E, \omega) \cdot P(E, \omega), \quad (2.16)$$

where $D(\omega)$ is an escape function, $T(E, \omega)$ is a transport function describing the propagation of the photon, and $P(E, \omega)$ is the bremsstrahlung distribution. By analogy with photoemission, $P(E, \omega)$ can be written in golden-rule form,

$$P(E, \omega) \propto \int_{\Omega} d^3k \ |< i \mid A \cdot p \mid f >|^2 \delta(E_i(k) - E_f(k) - \hbar \omega) \delta(E_i(k) - E), \quad (2.17)$$

where $p$ is the momentum operator and $A$ is the vector potential. $i$ and $j$ are band indices which denote initial and final state respectively, and $\Omega$ is the volume of integration in $k$-space determined by experimental conditions. The total emission per incident electron at energy $E$ is

$$P_{dir}(E, \omega) \propto \frac{\sum_{i,f} P}{\sum_{i} \int_{\Omega} d^3k \delta(E_i(k) - E)}, \quad (2.18)$$
which is the result of a sum over all possible final states and an average over initial states. One interesting point about Eq.(2.18) is the difference from the photoemission result. The numerator is the energy distribution of the joint density of states (EDJDOS), which is the same as the photoemission result. But the denominator is the density of initial states, which is absent in photoemission. It can be understood by the fact that the incident electron should couple into an initial state in order to contribute to inverse photoemission. The transport function was first approximated by Berglund and Spicer. By analogy to photoemission,

$$T(E, \omega) = 1 - \frac{\lambda_e(E)}{\lambda_{ph}(\omega)} \ln(1 + \frac{\lambda_e(E)}{\lambda_{ph}(\omega)})$$

(2.19)

where $\lambda_e(E)$ is the electronic mean free path. $\lambda_{ph}(\omega)$ is related to the absorption depth of the photon. Since $\lambda_{ph}(\omega)$ is much bigger than $\lambda_e(E)$ in the ultraviolet region, $T(E, \omega)$ is close to 1. Especially for a fixed photon energy (9.8 eV) both $D(\omega)$ and $T(E, \omega)$ can be regarded as constants. Therefore, the bremsstrahlung photon flux mainly depends on $P(E, \omega)$. 
CHAPTER 3. EXPERIMENTAL SETUP

Inverse Photoemission

Detectors

Grating monochromators [68] [69] offer a variable photon energy and better energy resolution, but these systems are often very expensive and complex, and suffer from low counting rate because of their small acceptance angle. The most widely used photon detector for IPE is the iodine-filled Geiger-Müller counter [70] [71]. The counter is placed close to the sample and collects a large solid angle of photons. The counter filling consists of helium gas and iodine vapor. $CaF_2$ is used as an entrance window. While the $CaF_2$ window cuts off light beyond 10.2 eV energy, the lower energy detection limit is given by the $I_2$ ionization cross-section. The product of these two components has a peak at about 9.7 eV with a full width at half maximum of about 0.8 eV. Three kinds of detectors were tried in our system, including the Geiger-Müller counter. The second one consists of an electron-multiplier with a $CaF_2$ entrance window [72]. The product of the $CaF_2$ optical transmission and CuBe cathode spectral photoemission yield gives a peak at 9.8 eV with a full width half maximum about 0.6 eV. The spectral characteristics are shown in Fig. 3.1.
Figure 3.1: Spectral sensitivity of the photon detector used in IPES. The detected photon energy is 9.8 ± 0.3 eV
The electron-multiplier (EM132, manufactured by Thorn EMI) is basically an electron-multiplier with a BeCu cathode, and gain of $1.5 \times 10^6$, which is comparable to that of the Geiger-Müller counter. This detector has several advantages over the Geiger-Müller counter, such as compact size, ease of operation, "no" dead time, and better vacuum compatibility. This detector was adopted for the system because it is compact and easy to operate. The last detector we tried was a LiF lens used as a monochromator. The motivation was to make a tunable photon detector without complexity in the monochromator detector [73]. The idea is very simple. LiF has a high transmitting cutoff (11.7 eV), which makes this material useful for UV optical elements. It also has strong chromatic aberration, which means that the incident photons have different refractive indices [74] according to their energy. Thus using a converging LiF lens with a movable pinhole, one can select a desired photon energy. The lens system was designed and simulated by using ray tracing techniques. To achieve good resolution, however, we need to have a big acceptance angle and a lens with long focal length, which eventually makes a whole detector too big for the system. This should have been considered before designing a chamber.

Electron Gun

Electron and ion optical systems often consist of a series of cylindrical tubes which have different potentials. These systems can be broken into two coaxial cylinders with radius R, separated by a gap S, which makes the basic electrostatic lens (Fig. 3.2). The whole system can be calculated by a superposition of such single lenses.
Figure 3.2: Schematic diagram of the basic electrostatic lens
There are two very simple methods to evaluate the electron optical properties of electrostatic cylinder lenses. One is using tabulated data on the focal properties and the other is ray tracing on computer by using the Gaussian approximation [75]. The theories of both methods are basically the same, but the latter method is more satisfying since the actual beam shape can be investigated. In the single gap lens, which has two coaxial tubes, the potential can be approximated as [76]

\[ \varphi(r, z) \approx V_1 + \frac{(V_2 - V_1)}{s} \left[ U_1(r, z + \frac{s}{2}) - U_1(r, z - \frac{s}{2}) \right], \quad (3.1) \]

where

\[ U_1 = z + \sum_{\mu} \frac{J_0(\mu r)}{\mu^2 J_1(\mu)} e^{-\mu z}, \quad (3.2) \]

for \( z > 0 \)

\[ U_1 = \sum_{\mu} \frac{J_0(\mu r)}{\mu^2 J_1(\mu)} e^{\mu z}, \quad (3.3) \]

for \( z > 0 \).

Then

\[ \frac{\partial \varphi}{\partial z} \approx \frac{(V_2 - V_1)}{s} \frac{\partial U_1(r, z + \frac{s}{2})}{\partial z} - \frac{\partial U_1(r, z - \frac{s}{2})}{\partial z}, \quad (3.4) \]

where

\[ U_1 = 1 - \sum_{\mu} \frac{J_0(\mu r)}{\mu J_1(\mu)} e^{-\mu z}, \quad (3.5) \]

for \( z < 0 \)

\[ U_1 = \sum_{\mu} \frac{J_0(\mu r)}{\mu J_1(\mu)} e^{\mu z}, \quad (3.6) \]

for \( z > 0 \).
where $J_0$ and $J_1$ are the Bessel functions. The values of

$$
\sum_{\mu} \frac{J_0(\mu r)}{\mu^2 J_1(\mu)} e^{-\mu z} \tag{3.7}
$$

and

$$
\sum_{\mu} \frac{J_0(\mu r)}{\mu J_1(\mu)} e^{-\mu z} \tag{3.8}
$$

can be tabulated for the calculation. Now by Gaussian approximation ($r \gg a$),

$$
\varphi(r, z) \approx \varphi(0, z) = \varphi(z). \tag{3.9}
$$

If we consider a small disk at the center of a tube, then by Gauss' theorem

$$
\int \mathbf{E} \cdot \hat{n} = 0, \tag{3.10}
$$

$$
E_r = -\frac{r}{2} \varphi'' = \frac{r}{2} \varphi'' = \frac{r}{2} \varphi''. \tag{3.11}
$$

The equation of motion can be described in terms of $f_r$ and $f_z$, which are

$$
f_r = m \frac{d^2 r}{dt^2} = -\frac{1}{2} er\varphi''(z) \tag{3.12}
$$

$$
f_z = m \frac{d^2 z}{dt^2} = -\frac{1}{2} er\varphi'(z), \tag{3.13}
$$

which can be rewritten

$$
f_z = \frac{1}{2} m (\frac{dz}{dt})^2 = e\varphi. \tag{3.14}
$$

After eliminating the time dependence, the equation of motion is

$$
\frac{d^2 r}{dz^2} + \frac{\varphi'}{2\varphi} \frac{dr}{dz} + \frac{\varphi''}{4\varphi} r = 0. \tag{3.15}
$$
Let $R = r\varphi^{1/4}$ then

$$R'' + TR = 0, \quad (3.16)$$

where

$$T = \frac{3}{16} \left(\frac{\varphi'}{\varphi}\right)^2. \quad (3.17)$$

The equation can be solved numerically by computer rather easily [77].

Since the yield is quite low ($2 \times 10^4 \text{photons/\mu A}$) for IPES, high current and small energy spread are required for the electron emitter. A tungsten filament is a common choice as an emitter, but it has very high operating temperature with low emission current (100 mA/cm$^2$ at 2000 °C). As a result, the energy spread is quite big ($\sim 0.5$ eV). Thoriated tungsten (tungsten with 1% of thorium oxide) is better than plain tungsten [78]. Its emission current is 1 and 5 A/cm$^2$ at 1600 and 1400 °C, respectively. A thoriated tungsten filament was used at the beginning in the system, but later replaced by a BaO cathode because it suffered from a short lifetime when it was operated at high temperature (at $\sim 2000$ °C) for large currents. The emitter used in the experiment was an osmium-coated BaO dispenser cathode (200-311-80-M made by Spectro-Mat) which is the improved version of the tungsten dispenser cathode to get a low work function. Its emission current is 8 A/cm$^2$ at 1050 °C. At that temperature, the energy spread is about 0.3 eV. Since it is electrically isolated from its heating unit, the voltage drop across the cathode can be avoided.

There are generally two kinds of electron guns used in IPES. One is an electrostatic lens system explained before, and the other is the Pierce gun [79] which can draw the highest current. But the target-to-cathode distance is too small (order of mm) for reliable sample movement [80]. The electron gun used in our system was designed and built according to the work by Erdman and Zipf [80]. The schematic layout is
shown in Fig. 3.3. The OFHC (oxygen-free, high-conductivity) copper was used for vacuum compatibility and sapphire balls were used for spacers as well as insulation between the copper cylinders. To get the optimized potentials for each cylinder, the electron gun was numerically simulated by the method mentioned above. In the real experiment, the voltages were optimized by measuring the beam currents and beam sizes by using a Ta wire coated with graphite as a target. We found that $V_1 = 20 \text{ V} - 30 \text{ V}$ and $V_3/V_0 = 6 - 8$ were optimum for the system, where $V_0$ was the kinetic energy of the electrons. The results of the computer simulation were different from the real values, which can be accounted for by the fact that the distance between the cathode and pinhole 1 was not accurately controlled and the electron trajectory was very sensitive to distance, which was expected in the ray-tracing.

Chamber

In surface science, ultra-high vacuum (UHV) is essential to keep the sample surface from contamination. The chamber was designed and built solely for the ARIPES (Angle-Resolved IPES). The chamber was pumped by a turbo-molecular pump (Leybold turbovac model 150), a $200 \text{ l/sec}$ ion pump (TLI model NP 200), and a titanium sublimator (getter pump). Very careful baking was needed to get good vacuum (low $10^{-10}$ to high $10^{-11}$) Torr. Thus, the whole chamber was wrapped with Thermolyne heating tapes, covered with Al foil, and baked at a temperature of $150^\circ C$. The turbopump and gate valves were kept under $100^\circ C$, and the electron gun was baked at $400^\circ C$ for filament maintenance. The main part of the chamber consists of the measurement level and the preparation level.
Figure 3.3: Schematic diagram of the electron gun assembly
Sample preparation such as sputtering, evaporation, and annealing, was carried out in the preparation level, which is 2" lower than the measurement level. Then the sample was moved to the measurement level for the LEED/AES (Model $11-020/11-500$) and IPES measurement. The LEED electron optics were used for AES. The detailed design and the cross-section of the measurement level are illustrated in Table 3.1 and Fig. 3.4, respectively.

Since the chamber was designed for IPES, magnetic shielding was required for the low energy electrons (as low as 5 eV) to prevent them from being perturbed by magnetic fields. Two $\mu$-metal cylinders, separated by 1/4 inch, were used for the magnetic shielding. The shielding material was CO-NETIC (0.04 inches thick) with a high permeability (up to $1.4 \times 10^5$). According to the calculation [81], a double cylindrical shield can give $\sim$ mgauss, but it gave 15 mgauss at the center of the chamber due to the large hole for the LEED optics. Since the LEED has its own magnetic shielding, the magnetic field is expected to be quite small ($\sim$ mgauss) after installing the LEED optics.

**Photoemission**

The light source of the photoemission experiments was from the synchrotron radiation from the Aladdin electron storage ring [82] located at the University of Wisconsin Synchrotron Radiation Center (SRC), Stoughton Wisconsin. The storage ring was usually operated at 800 MeV. The experiments were done on the Ames/Montana ERG/Seya beam line [83] [84].
Figure 3.4: Cross-sectional view of the IPES chamber at the measurement level
Table 3.1: Arrangement of the chamber

<table>
<thead>
<tr>
<th>Port</th>
<th>Flange</th>
<th>Tube</th>
<th>Position</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Z</td>
<td>φ</td>
<td>θ</td>
</tr>
<tr>
<td>A1</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>19&quot;</td>
<td>180° 90° extra</td>
</tr>
<tr>
<td>A1</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>19&quot;</td>
<td>270° 90°</td>
</tr>
<tr>
<td>B1</td>
<td>8&quot;</td>
<td>0.5&quot;</td>
<td>13&quot;</td>
<td>0° 90° LEED</td>
</tr>
<tr>
<td>B2</td>
<td>3.37&quot;</td>
<td>0.4&quot;</td>
<td>13&quot;</td>
<td>180° 90°</td>
</tr>
<tr>
<td>B3</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>13&quot;</td>
<td>120° 90° extra</td>
</tr>
<tr>
<td>B4</td>
<td>2.75&quot;</td>
<td>1.2&quot;</td>
<td>13&quot;</td>
<td>240° 90°</td>
</tr>
<tr>
<td>B5</td>
<td>3.37&quot;</td>
<td>3&quot;</td>
<td>13&quot;</td>
<td>285° 90° photon detector</td>
</tr>
<tr>
<td>B6</td>
<td>3.37&quot;</td>
<td>1.75&quot;</td>
<td>240°</td>
<td>45° window</td>
</tr>
<tr>
<td>C1</td>
<td>2.75&quot;</td>
<td>1.2&quot;</td>
<td>11&quot;</td>
<td>90° 90° thickness monitor</td>
</tr>
<tr>
<td>C2</td>
<td>2.75&quot;</td>
<td>7&quot;</td>
<td>11&quot;</td>
<td>130° 90° Ar gun</td>
</tr>
<tr>
<td>C3</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>11&quot;</td>
<td>230° 90° window</td>
</tr>
<tr>
<td>C4</td>
<td>2.75&quot;</td>
<td>1.75&quot;</td>
<td>270°</td>
<td>135° evaporator</td>
</tr>
<tr>
<td>D</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>7&quot;</td>
<td>240° 90° shutter</td>
</tr>
<tr>
<td>E</td>
<td>6&quot;</td>
<td>0.8&quot;</td>
<td>4&quot;</td>
<td>90° 90° turbo pump</td>
</tr>
<tr>
<td>F1</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>3&quot;</td>
<td>180° 180° up to air valve</td>
</tr>
<tr>
<td>F2</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>3&quot;</td>
<td>180° 0° roughing gauge</td>
</tr>
<tr>
<td>F3</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>3&quot;</td>
<td>180° 300° ion gauge</td>
</tr>
<tr>
<td>F4</td>
<td>2.75&quot;</td>
<td>0.5&quot;</td>
<td>3&quot;</td>
<td>180° 240° R.G.A.</td>
</tr>
</tbody>
</table>
Figure 3.5 shows the schematic layout of the system. The effective energy of the photons was 5 eV to 1 KeV. The measurements were made with the Seya monochromator (1800 1/mm grating), except the resonance photoemission whose high energy required the ERG. The spectral characteristics of the Seya are shown in Fig. 3.6. The resolution of the beam varies from 0.04 to 0.5 eV depending on the photon energy, slit width, the ruling density of the grating, and the grating radius. The VSW (Vacuum Science Workshop) hemispherical analyzer was used for collecting and analyzing the photoelectrons. Figure 3.7 shows the schematic layout for the measurement system. The analyzer was mounted on a goniometer which had two degrees of freedom for rotation. The analyzer has an angular acceptance of 2°. The energy resolution of the analyzer is about 1 % of the pass energy, which was 15 eV during most of the measurements. The slit width during the measurement was 200 μm and the energy spread from the grating was less than 40 meV for the range up to 30 eV. Thus the total resolution mainly depended on that of the analyzer, which was about 200 meV for the angle-resolved photoemission.
Figure 3.5: Schematic layout of the PES chamber. 1-4: entrance lens; 5,6: hemispherical deflectors; 7: channeltron
Figure 3.6: Spectral output of the Seya
Extended Range Grasshopper - Seya Namloka Monochromators

Figure 3.7: Schematic layout of the Ames/Montana state ERG/Seya combined monochromator beam line
CHAPTER 4. RESULTS AND DISCUSSION

Sample Preparation

Since Ce, La, and their compounds oxidize very easily in air, the samples were always kept in a vacuum desiccator. First, the samples were filed and electropolished in order to remove the heavy oxide layers in order to get Laue back-reflection patterns from the single crystals. In the electropolishing, an electrolyte of 5% perchloric acid in methanol was used in a dry ice and acetone bath. The current density was around 0.5 A/cm².

After obtaining the angles for the desired surfaces, the samples were spark-planed to get strain-free surfaces. Then the samples were re-electropolished and oriented according to the x-ray patterns to within 1°. A simple type of jig was used for both orienting and polishing the single crystals. The jig was designed and constructed according to the design by Chang [85]. To avoid moisture, which is the main cause of corrosion, absolute methanol (or ethanol) was used for the mechanical polish. When orienting the sample, the (100) and (110) directions were also checked because the samples could be rotated only about one axis in the IPE chamber, therefore, samples needed to be placed in the right position to get the desired directions. Just before putting them into the vacuum chamber, the samples were electropolished again.

The main initial impurities were oxygen, carbon, sulphur, and chlorine, the latter
coming from the electropolish. To obtain clean surfaces, repeated cycles of sputtering and heating were carried out because the main impurity, oxygen, is believed to diffuse from the bulk. Sulphur and chlorine were removed rather easily in the first a few cycles, but it took around 100 cycles to reduce the oxygen photoelectron peak at 6 eV to an acceptable range.

In the inverse photoemission chamber, the impurities were checked by Auger spectroscopy using LEED optics (retarding field analyzer). The samples were sputtered at 1 keV and heated until there was no trace of the oxygen peak. After obtaining clean surfaces, both samples were annealed at $600^\circ C$ for around 5 minutes. LEED was used to confirm the (111) surface structure. The (111) surface was chosen because the (111) surface in the $AuCu_3$ structure was expected to have the same surface stoichiometry as the bulk. In the $AuCu_3$ structure, (111) surfaces are favored energetically, since these have least dangling hybrid states.

The experiment to measure the surface stoichiometry for $CeSn_3$ was done in a separate chamber because both the inverse photoemission and photoemission chambers were not equipped with a CMA (Cylindrical Mirror Analyzer), which is the standard for AES. The 82 eV (for Ce) and 430 eV (for Sn) Auger peaks were measured (Physical Electronics Model 10-155 $\Phi$), to be compared with standard data [86] and normalized by the ratios of their densities and weights ($\sim 1.3$). The result was about $CeSn_{2.5}$. The surface structure was monitored by LEED. The surface stoichiometry and the LEED patterns stayed the same for annealing temperatures from $550^\circ C$ to $800^\circ C$.

The sputtering knocks out more tin atoms than cerium atoms because of their atomic mass difference, and annealing recovers the surface stoichiometry. One hour
of sputtering at 1.5 keV made the Ce:Sn ratio almost one to one on the surface. Therefore, it suggests that many short cycles of sputtering and annealing are better than heavy sputtering and annealing.

In CeSn₃ after achieving surface cleanliness, it took less than one hour in 2 × 10⁻¹⁰ Torr before the oxygen peak in PES grew noticeably and in LaSn₃, it took around half an hour at 2 × 10¹⁰ Torr.

Resonance Photoemission

For the rare-earths, the 4d-4f resonance has been used to isolate the 4f-derived features from the spectra. The excitation can be written as

\[ h\nu + 4d^{10}4f^n(5d6s)^3 \rightarrow 4d^{9}4f^{n+1}(5d6s)^3 \]

These transitions were characterized by the absorption spectra [87] [88]. After the excitation, the intermediate state can decay into a number of states, e.g.,

\[ 4d^{9}4f^{n+1}(5d6s)^3 \rightarrow 4d^{10}4f^{n-1}(5d6s)^3 + e^- \]
\[ 4d^{9}4f^{n+1}(5d6s)^3 \rightarrow 4d^{10}4f^n(5d6s)^2 + e^- \]

The CeSn₃ data shown in Fig. 4.1 generally agree with the previous results from polycrystalline CeSn₃ [89], which have two main peaks at 0.3 eV and 2.5 eV.
Figure 4.1: Resonance PES of CeSn$_3$ (111)
There is another kind of spectroscopy which can be used with continuum light source. It is called CIS (constant initial state) spectroscopy. In CIS, \( E - \hbar \omega = E_{\text{constant}} \) is achieved by making a synchronous scan of the photon energy and the kinetic energy of the photoemitted electrons. Thus a CIS spectrum provides the density of final states modulated by the electric dipole matrix element. The CIS spectra near resonance are shown in Fig. 4.2. The solid line represents the peak at a binding energy of 0.3 eV and the dotted line corresponds to the peak at 2.5 eV. These have been normalized so that the intensities appear to be the same, but on real scales, the intensity of the dotted line is 30% larger than that of the solid line at 122 eV. In Fig. 4.2, the CIS curve of the peak at 2.5 eV B.E. (binding energy) has a maximum at 122 eV while that of the peak near the Fermi energy is shifted around 0.7 eV to lower energy.

Lawrence et al. [90] had the same results for CeAl and CeSi₂ and proposed that the difference in peak energies was from the different cross-sections for 4f and 5d photoelectrons [90] [91]. Their assignment was that the peak at high binding energy was from the 4f emission and the peak near the Fermi energy was due to the 5d states. Their interpretation was that 5d and 4f emission cross-sections had maxima at slightly different energies.

A G-S model calculation for CeSn₃ was done to fit the resonance spectrum at a photon energy of 122 eV in Fig. 4.1 [92]. A single 4f level before hybridization at 2 eV binding energy fits the two-peak structure quite well.
Figure 4.2: CIS spectra of CeSn$_3$. The solid line represents the peak near the Fermi energy. The dashed line represents the peak at a binding energy of 2.5 eV.
The hopping term, $V$, in the calculation, however, is significantly different from the result of the fitting to core-level XPS (3d) by Fuggle et al. [38], which has $V = 0.14$. The use of such parameters for valence band photoemission gives a spectrum which has a very weak peak at near the Fermi energy. Figure 4.3 shows the calculated spectrum from the G-S model. In the G-S model, the two peak intensities can be adjusted by varying the hopping matrix element term $V$. The peak near the Fermi energy grows as we increase $V$ [26].

In Fig. 4.4, the valence band EDCs for $LaSn_3$ are exhibited for a photon energy near the 4d-4f resonance. The results are strikingly similar to those of $CeSn_3$. The spectra shown in Fig. 4.4 exhibit peak at 0.4 eV, 2.5 eV, 4.6 eV, and 5.8 eV. We assign the peaks at 4.6 eV and 5.8 eV to contamination (carbon 2p and oxygen 2p emission, respectively).

$La$ is more reactive toward oxygen than $Ce$, and the resonance peaks in $LaSn_3$ are smaller than those in $CeSn_3$ by almost one tenth. That is why the oxygen peak appears relatively large in the $LaSn_3$ spectra. The main difference between the spectra of $CeSn_3$ and $LaSn_3$ is that the peak at 2.5 eV is broader and weaker in $LaSn_3$.

Since $LaSn_3$ is not expected to have an f-electron in the ground state, the two-peak structure shown in Ce compounds is not supposed to occur in $LaSn_3$. 
Figure 4.3: G-S model calculation of photoemission EDC from CeSn$_3$. 

CeSn$_3$

$E_F = -2.0$ eV
$N = 1.0$
$B = 6$ eV
$V = 0.5$
$U = 5$ eV
$N_f = 14$
In the G-S model calculation, the peak near the Fermi energy can be fitted by placing the f-state at or a little above the Fermi energy, but the G-S model does not give a two-peak structure for \( LaSn_3 \). The d-f correlation model also predicts a one-peak structure near the Fermi energy for La compounds due to the unscreened 4f hole (which is the peak at the binding energy 2.5 eV in \( CeSn_3 \)) [93]. This theory predicts a two-peak structure for the Ce compounds [31] [32] [33] [34].

The CIS spectra of \( LaSn_3 \) for the peaks near the Fermi energy and a binding energy of 2.5 eV are shown in Fig. 4.5. The peak at 2.5 eV shows the same resonance as the peak near the Fermi energy at 117 eV. In Fig. 4.4, the peak has its maximum at photon energy about 112 eV, but since this peak is sitting on the large tail of the peak near the Fermi energy, it appears that it has a maximum at higher energy.

We propose that the peak near the Fermi energy is the contribution from the 4f level, and the peak at 2.5 eV is due to the density of states of the tin 5p states which has a maximum at 2.5 eV [55]. The resonance of the peak at higher binding energy, however, is hard to explain this way because the tin 5p cross-section has quite a different characteristic from the resonance spectrum shown in Fig. 4.5 and there is little Sn 5p-Ce 4f hybridization 2.5 eV below the Fermi energy.

There are other possible interpretations for the peak at 2.5 eV, e.g., a satellite or a surface shift. A surface-induced peak was seen in the cerium compound CeN at 1.2 eV which was identified by the fact that the peak depended on surface contamination [94] [95].
Figure 4.4: Resonance PES of LaSn$_3$ (111)
Figure 4.5: CIS spectra of $LaSn_3$. The solid line represents the peak near the Fermi energy. The dashed line represents the peak at a binding energy of 2.5 eV.
A surface effect was excluded for CeSn₃ because there was no contamination dependence in the peak. For the satellite picture, when the peak near the Fermi energy is regarded as the main peak, electron shake-up can produce a satellite peak at higher binding energy. But such a shake-up peak is expected to appear at an energy higher than 2.5 eV due to the large Coulomb interaction. In the 3d photoelectron spectra of LaSn₃, a satellite peak is observed on the lower binding side of the main peak [38]. This spectral splitting of about 4 eV can be attributed to two final states, well-screened and poorly screened states (4f¹ for the satellite peak and 4f⁰ for the main peak, respectively) [96] [97] [98]. In CeSn₃, which supposedly has the same effect if it is a satellite peak, such a peak is hard to identify due to the presence of the large peak at the same energy.

Work Function Measurement

The work function measurements from the (111) surfaces of both LaSn₃ and CeSn₃ were done during the photoemission experiments by a simple method. The samples were biased from ground by a battery so that the emitted electrons could have higher kinetic energy and a relatively low photon energy (~ 20 eV) was used to scan the full range. The kinetic energy is scanned until the counts drop to zero (the background). Figure 4.6 shows the spectrum from the LaSn₃ (111) surface.

Since the work function of the system is already accounted for in the Fermi energy of the spectrum, the work function of the sample is the difference between the width of the spectrum and the photon energy. We obtained 3.6 ±0.1 eV for the (111) surface of LaSn₃ and 3.7 ±0.1 eV for the CeSn₃.
Figure 4.6: Work function measurement of LaSn$_3$. $h\nu = 16$ eV. The sample was biased at -9.36 eV from the ground.
Angle Resolved Photoemission

Figure 4.7 shows the angle resolved photoemission data from the CeSn$_3$ (111) surface. The spectra should be called $\vec{k}$-resolved because they did not involve any rotation. The normal direction with varying photon energy was chosen because the method is easiest to analyze and the (111) surface does not have any symmetry direction for rotation away from the normal. $\vec{k}_\parallel$ is conserved in the photoemission process, whereas $\vec{k}_\perp$ is not conserved. Thus to determine the electron wavevector $\vec{k}$ is not easy. For using normal emission ARPES, occupied band dispersions are simply obtained by energy conservation ($E_k(\vec{k}) = E_f(\vec{k}) - \hbar \omega$), $\vec{k}_\parallel$ conservation ($\vec{k}_\parallel = 0$), and $\vec{k}_\perp = \vec{k}_\perp(E_f)$, where $E_f$ is approximately given by a free-electron dispersion. The full wave vector $\vec{K} = \vec{G} + \vec{k}$, where $\vec{k}$ reduced wavevector and $\vec{G}$ is a reciprocal lattice vector.

The effect of oxidation on the valence band spectra was tested by letting the sample sit in the vacuum chamber ($2 \times 10^{-10}$ Torr) without sputtering for several hours. The peak at B.E. = 6 eV grew very rapidly with time, which suggested that the main portion of the oxygen diffused from the bulk. The positions of other peaks, as well as their relative intensities, however, remained the same.

Figure 4.8 shows spectra from LaSn$_3$. Both spectra show peaks near the Fermi energy without dispersion and peaks at a binding energy around 1 eV with small dispersion. In the CeSn$_3$ spectra, the peak at B.E. = 2.5 eV, which appears in the resonance photoemission, is still present, even at low photon energy, with very little dispersion, even if its characteristics are quite different from the resonance spectra. But the same peaks (B.E. = 2.5 eV) in LaSn$_3$ are not present in the spectra. Instead, there are peaks with considerable dispersion between 2.5 and 3.5 eV. The LaSn$_3$
spectra also show peaks at a binding energy of about 2 eV, which are quite noticeable at photon energies $\geq 28$ eV.

The peaks marked with * and • are from the tin 4d and those with o and o are from Ce and La 5p, all four due to the second-order radiation from the grating, which is at twice the energy of the first order. Thus they should be ignored. Figure 4.9 shows core-level spectra for $LaSn_3$ and $CeSn_3$. The core level PES of $CeSn_3$ was taken at the beginning of the experiment when the sample had not been properly treated. Thus the spectrum shows broader peaks than that of $LaSn_3$ due to the oxygen contamination.

There are many puzzling questions about these two spectra. A semiempirical test for band emission in $\gamma$-Ce was done by Jensen and Wieliczka [99]. They concluded that the two-peak structure at a photon energy of 60 eV was from atomic-like f states and the similar structures obtained with 24 eV photons mostly followed one electron selection rules. The peaks near the Fermi energy, if we follow Jensen and Wieliczka's observation, are from the band structure which predicts significant dispersion. But no significant dispersion of the peak near the Fermi energy was observed in the present work.

The band calculations show that the band structures below the Fermi energy for both $CeSn_3$ and $LaSn_3$ are almost identical. At low photon energy (below 24 eV), the peak behaviors of both spectra look quite similar. Both peaks near the Fermi energy show maxima for about 17 eV photons and peak intensities are relatively strong.
Figure 4.7: $k$-resolved photoelectron spectra from the CeSn$_3$ (111) surface
Figure 4.8: $\mathbf{k}$-resolved photoclectron spectra from the $LaSn_3$ (111) surface
Figure 4.9: Core level PES of CeSn$_3$ (dashed line) and LaSn$_3$ (solid line)
In the high photon energy region (above 25 eV), whereas those from LaSn\textsubscript{3} are relatively weak, the peaks from CeSn\textsubscript{3} are as large as the peaks at 2.5 eV, which is different from the resonance spectra. This may reflect a final-states effect but the final states are expected to be similar for both materials. Angle-resolved valence band spectra from the (111) surface of CeSn\textsubscript{3} and LaSn\textsubscript{3} were taken to see the dispersion of the peak near the Fermi energy (Figures 4.10-4.12). The results were that this peak for both CeSn\textsubscript{3} and LaSn\textsubscript{3} did not disperse within 100 meV. But the spectra showed considerable dispersion in other peaks. These lead us two possible conclusions:

1. There is a very flat band just below the Fermi energy for CeSn\textsubscript{3} and LaSn\textsubscript{3}.

2. There is a final state effect which produces the peak even for a low photon energy.

Some of the occupied bands of LaSn\textsubscript{3} could be mapped from the angle resolved spectra. The \(E(\vec{k})\) points for the direct transitions were determined by treating the final states as free-electron-like with an inner potential \(V_0 = 2.6eV\) and an effective mass \(m^* = m_0\). The result is shown in Fig. 4.13, which agrees quite well with the calculated band structure, even though the fitted bands were mainly from the tin 5p states. The bands near the Fermi energy deviate significantly from the experimental spectra.
Figure 4.10: ARPES from the CeSn₃ (111) surface to the (110) direction. $h\nu = 25$ eV
Figure 4.11: ARPES from the CeSn (111) surface to the (100) direction. $h\nu = 25$ eV
Figure 4.12: ARPES from the La$_3$Sn$_4$ (111) surface to the (110) direction. $\hbar \omega = 16$ eV
Figure 4.13: Experimental $E(k)$ points of $LaSn_3$ compared with the calculated band structure. $\circ$ (from the dashed line in Fig. 4.8), $\triangle$ (from the solid line in Fig. 4.8)
Angle-Resolved Inverse Photoemission

The angle resolved inverse photoemission experiments for $LaSn_3$ and $CeSn_3$ were done in the separate system described in chapter 3. The sample preparation procedures were the same as those of the photoemission experiment. The base pressure in the vacuum chamber was $1 \times 10^{-10} Torr$ during the experiments.

The samples were rotated toward the (100) direction but $k_\parallel$ was not along a symmetry line. The spectra are shown in Figures 4.14 and 4.15 for $CeSn_3$ and $LaSn_3$, respectively. The spectra for $CeSn_3$ have little similarity to the BIS spectra [94]. The BIS spectra have two main peaks, one near the Fermi energy and the other at about 4 eV, both of which were interpreted as 4f related. It suggests that the 4f state contribution to the ARIPES spectra is very small. The photoionization cross-section for 4f electrons exhibits a delayed onset from the threshold due to the large value of the centrifugal barrier $\left(\frac{l(l+1)}{r^2}\right)$ [100] [101] [102]. Therefore, the probability for transitions, such as between 4f and 4d, at a low photon energy is expected to be small even if the joint density of states (JDOS) is large for the transition.

For $LaSn_3$, the spectra are also quite different from the BIS data for $La$, which had one big peak at about 5.3 eV. Both spectra show shoulders near the Fermi energy. These shoulders could be identified as peaks because the resolution of IPES is quite poor and the shoulders were consistent through the angles.

The calculated band structures of both materials are very similar except for 4f part but their spectra show significant differences. Both spectra show weak peaks at the normal direction, but as the angle gets bigger, they show distinct structures with little dispersion.
Figure 4.14: ARIPES from the $Cs\nu_3$ (111) surface with the $k_\parallel$ increasing from 0 toward the (100) direction
Figure 4.15: ARIPES from the LaSn₃ (111) surface with the k|| increasing from 0 toward the (100) direction
At large angles, the CeSn₃ spectra show a two-peak structure (2.5 eV and 6.5 eV) aside from the shoulder at the Fermi energy and indistinguishable peaks in between. The peak at 6.5 eV has a maximum intensity at 30°. The LaSn₃ spectra exhibit a three-peak structure (2.5 eV, 5 eV, and 6.5 eV at large angles. The peak at 5 eV grows as the angle gets bigger. Figure 4.16 shows the comparison between two spectra.

Since the band structures of both materials are very complex and the (111) surface does not have any symmetry for rotation from the normal direction, band mapping is rather difficult. Thus, all the possible direct transitions along the rotational direction ($\vec{k}_f = \vec{k}_i$ and both are parallel to the Λ) with 9.8 eV photon emission for both materials were calculated from the band structures in order to compare with the experimental spectra. Figures 4.17 and 4.18 show all the final states of the possible transitions for CeSn₃ and LaSn₃, which reflect the joint densities of states (J DOS). Due to the complexity of the band structures, a collection of all possible transitions are rather difficult to analyze. So, the dipole matrix elements were used to exclude the weaker transitions. Figures 4.19 and 4.20 show the direct transitions with the dipole matrix elements from the calculated band structures. The calculated spectra were broadened by the Lorentz function so that the results were comparable to those from the experimental data.

The calculation for CeSn₃ shows strong transitions to states without much dispersion near the Fermi level. The origin of these states is mainly the 4f state of Ce which is hybridized with conduction states, otherwise, the transitions would be very weak. But in the CeSn₃ spectra, these peaks are very weak if they can be identified as peaks.
Figure 4.16: Comparison between the ARIPES from $CeSn_3$ and $LaSn_3$. The solid lines indicates the spectra from $CeSn_3$ and The dashed lines the spectra from $LaSn_3$. 
Figure 4.17: All possible direct transitions with 9.8 eV emission from the calculated band structure of CeSn$_3$. 

Rotation Angle (degree) To (100) 

Energy Relative To $E_F$ (eV)
Figure 4.18: All possible direct transitions with 9.8 eV emission from the calculated band structure of LaSn₃.
Figure 4.19: 9.8 eV direct transitions with the dipole matrix elements from the calculated band structure of CeSn₃.
Figure 4.20: 9.8 eV direct transitions with the dipole matrix elements from the calculated band structure of LaSn$_3$. 
It suggests that the states just above the Fermi energy have very little hybridization with other states. The calculation for LaSn₃ also gives strong transitions near the Fermi energy with some dispersion (a few tenths of an eV). According to the band calculation, these states have considerable 4f character. The spectra from LaSn₃ show that the peaks near the Fermi energy are stronger than those of CeSn₃, but without noticeable dispersion.

Conclusion

For a properly treated CeSn₃ (111) surface, the stoichiometry was close to that of the bulk and 3-fold symmetric LEED patterns from both CeSn₃ and LaSn₃ (111) surfaces were observed.

The two-peak structure from the resonance PES of CeSn₃ was fitted by the G-S model by placing the single 4f-level at 2.0 eV below the Fermi energy before hybridization. In the resonance PES of LaSn₃, a two-peak structure was unexpectedly also observed. The higher binding energy peak was assigned to tin p states even though other interpretations were possible.

ARPES from CeSn₃ showed quite different spectra from resonance PES spectra. But the peak near the Fermi energy from both CeSn₃ and LaSn₃ was observed persistently without noticeable dispersion. Since the G-S model for PES was developed on the basis on the sudden approximation, the applicability of this model to the low energy PES is in doubt. Band theory, also, cannot explain the peak near the Fermi energy. In LaSn₃, the experimental $E(k)$ points from the band mapping agreed well with the calculated band structure. The fitted bands were, however, mainly from the tin p states, and the bands near the Fermi energy were quite different from the
experimental spectra.

In ARIPES, the spectra of both $\text{CeSn}_3$ and $\text{LaSn}_3$ were totally different from the BIS spectra. In $\text{CeSn}_3$, the states just above the Fermi energy had mainly 4f character and mixing with other states (conduction bands) was quite small, contrary to the band calculation. In $\text{LaSn}_3$, the band calculation predicted the existence of considerable 4f character in the state just above the Fermi energy even if the main 4f state was located about 3 eV above the Fermi energy. The spectra from $\text{LaSn}_3$ showed the peak near the Fermi energy but the dispersion expected from the band calculation was not observed.


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