APPLICATION OF SOFT X-RAY APPEARANCE POTENTIAL SPECTROSCOPY
TO LIGHT LANTHANIDES, 4d TRANSITION METALS, AND INSULATORS

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Ph.D. Thesis Submitted to Iowa State University

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Application of soft x-ray appearance potential spectroscopy
to light lanthanides, 4d transition metals, and insulators

by

Richard James Smith

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Application of soft x-ray appearance potential spectroscopy
to light lanthanides, 4d transition metals, and insulators

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Evaporated films of La, Ce, Yb, Y, Ag-Mn(5%), KCl, MnF_2 , CsCl and LaF_3 were studied using the soft x-ray appearance potential spectroscopy (SXAPS) technique. Studies were also made of bulk polycrystalline samples of Y, Zr, Nb, and Mo. The results are discussed in terms of existing SXAPS theories. Several similarities between soft x-ray absorption (SXA) data and the SXAPS results are discussed, and it is shown that the SXA data can aid in the interpretation of SXAPS spectra when using the well-known self-convolution model. In this approximation the absorption coefficient, $\alpha(E)$, is substituted for the density of states, $N(E-E_c) \rightarrow \alpha(E)$. For more localized excitations, a convolution of $\alpha(E)$ with bremsstrahlung isochromat data, based on Wendin's two density of states formalism is used to predict SXAPS results.

For Y, the $M_{4,5}$ and $M_{3,2}$ core excitations have similar intensities and line shapes. The importance of the transition matrix elements is discussed, and the spectra suggest that the Y 4d band maximum is 4 eV above excitation threshold. The bulk samples of Y, Zr, Nb, and Mo give $M_{4,5}$ spectra which decrease in intensity with increasing Z. The $Mn L_{2,3}$ excitations in Ag-Mn(5%) were about 1.5 eV above the corresponding metallic Mn excitations and may result from excitations to the Mn local magnetic

moment. For the rare earth metals, the spectra are interpreted in terms of the multiplet splitting which results from final-state interactions of the type $4d^{10}4f^N \rightarrow 4d^94f^{N+1}$ as for the SXA data. The presence of the additional scattered incident electron in SXAPS tends to shift "subthreshold" multiplets to higher energies by an amount, ΔE , which depends on the inner shell vacancy as well as the position of the $4f$ states, while the broad band above threshold is well described by $d\sigma/dE$. The principle difference between the La and Ce spectra is the presence of additional structure for La beyond that predicted by SXA. This is attributed to final-state interactions involving the incident electron. A Ce^{4+} film was also investigated and observed to have La-like spectral features. The average ΔE values (eV) for these metals were: 5.1 ($N_{4,5}$) and 4.4 ($M_{4,5}$) for La, 2.1 ($N_{4,5}$) and 1.8 ($M_{4,5}$) for Ce^{3+} , and 2.9 ($N_{4,5}$) for Ce^{4+} . For Yb, only oxidized films were obtained and these exhibited a weak $d \rightarrow f$ excitation in agreement with SXA and EEL data. The optically forbidden $3d_{3/2} \rightarrow 4f_{7/2}$ transition was also observed. For the insulators studied, charging was not a problem but the thin films were very susceptible to electron beam damage. The K $L_{2,3}$ (KCl), Mn $L_{2,3}$ (MnF_2), Cs $N_{4,5}$ and $M_{4,5}$ (CsCl), La $N_{4,5}$ and $M_{4,5}$ (LaF_3) transitions were studied and agree very well with the SXA data. The Cs $N_{4,5}$ spectra had a broad peak due to the $d \rightarrow f$ delayed transitions. The LaF_3 results resembled the metallic La spectra with the exception of secondary structure which is attributed to the fluorine environment.

CHAPTER I. INTRODUCTION

Soft x-ray appearance potential spectroscopy (SXAPS) has become fashionable during the past five years because it is one of the simplest core-level spectroscopies available. Using SXAPS, one obtains information about the binding energy of atomic-like core levels in a solid or, from another point of view, the core-level spectra can be used to identify contaminants on a solid surface. By studying the SXAPS line shape, for a given core excitation, one also obtains information about the empty density of states above the Fermi level, E_F , of a solid. However, at the present time, the electronic processes characteristic to SXAPS are not sufficiently understood to interpret the spectra reliably.

We initially chose SXAPS as a means of studying evaporated La films with the hope of locating the position of the 4f states above E_F . The results we obtained were unexpected in light of our understanding of SXAPS at that time. The present study was a consequence of those early La results and had a two-fold purpose. First, we chose to study several materials which could shed light on the nature of the electronic transitions involved in SXAPS. We also collected results from other core-level spectroscopies, such as soft x-ray absorption (SXA), Auger electron spectroscopy (AES), and x-ray photoemission spectroscopy (XPS), and began a systematic study of these results to correlate observed structures in these methods with SXAPS data. As a result, we found that our data were quite closely related to the

absorption coefficient measured by SXA. With this knowledge we were able to extract additional information from our results and thus answer some of our original questions about La and the other materials studied.

A second goal of this work was to see if SXAPS could be applied successfully to insulators, since most of the earlier studies had been for metals only. We chose the insulating compounds MnF_2 , KCl , CsCl , and LaF_3 because each had special spectral characteristics to which the sensitivity of SXAPS was unknown. For example, we wondered how excitons and the band gap would manifest themselves in SXAPS, and to what extent charging would be a problem.

In Chapter II we discuss the electronic processes involved in SXAPS. The one-electron theory often used for SXAPS is developed and the relationship between several different core-level spectroscopies is discussed. In Chapter III we discuss the experimental apparatus used for these studies, and the related problems of sample preparation, experimental broadening, and energy calibration. Chapter IV contains the results of this study for several transition metals, rare earth metals, and insulators. Additional theoretical arguments are developed there to explain our results.

CHAPTER II. THEORY

Soft x-ray appearance potential spectroscopy has been developed as a means of studying the electronic configuration and composition of solid surfaces. Briefly, one measures the derivative of the total x-ray fluorescence yield of a sample, induced by electron bombardment of the surface. The theory most often cited in the literature to describe SXAPS line shapes was originally suggested by Dev and Brinkman (1) and further developed by Houston and Park (2). The one-electron theory seemed to work quite well for 3d transition metals (3) and some of the simple metals (4,5). As the technique became more popular, and the types of materials studied increased, discrepancies began to appear and it soon became evident that a better theory was needed. Failures of this theory were observed for the rare earths (6-11), light elements (12,13), and the 4d transition metals (14,15). A recent review article (16) gives a thorough development of the one-electron theory and an extensive summary of its successes and failures. The following discussion draws from this article as well as the reviews by Tracy (15) and Nagel (17).

In soft x-ray appearance potential spectroscopy, an electron beam is used to excite the atomic core levels in a sample. The excited states decay, emitting x-rays of different energies characteristic to the excited core level. In addition, the incoming electron can be scattered elastically, or radiatively decay to an empty state with the emission of bremsstrahlung. Inelastic collisions may occur and characteristic collective oscillations (plasmons) can be excited. The x-rays emitted

as a result of these mechanisms span the energy interval whose upper limit is the incident electron energy. The x-rays then strike a photocathode. A few of the excited electrons in the photocathode escape into the vacuum and are collected. This photocurrent is a measure, then, of the total x-ray yield due to electron excitation of the sample core levels.

An abrupt change in the total number of x-rays occurs when the incoming electron has just enough energy to raise a new core-level electron to an empty state at the Fermi level, E_F , of the material. These new x-rays correspond to the decay of upper-level states to the newly created core hole. The increase in the total x-ray yield at this point is usually quite small, typically less than one per cent. Differentiation of the total yield curve enhances this change and results in the spectrum of SXAPS.

The interactions of the incident electron beam with the electrons of a solid fall into two categories; interaction with the valence electrons, and core-level interactions. The first category dominates at low beam energies since there are no core levels to excite. The electron may be scattered elastically or lose energy to the valence electrons by inelastic collisions, causing the ejection of secondary electrons. Also in this category are the plasmon excitations and bremsstrahlung, which dominates at higher energies, and results from the decay to empty states near E_F .

At high enough incident energies, the core-level electron can be excited. The decay of this excited state is usually accomplished either by the direct transition of a conduction band electron to the created

vacancy with the emission of a characteristic x-ray, or by the energetically more favorable Auger process, a subgroup of which are the Coster-Kronig-type transitions (15,18). Fig. 1 shows a flow chart for these decay mechanisms. In SXAPS the change in the total number of photoelectrons produced by x-rays is measured as the energy of the incident electron is scanned across the threshold for a particular core-level excitation. We must know the energy dependence of each channel, then, to predict the SXAPS results.

So far, it has been implied that the various de-excitation channels are mutually exclusive. This assumption becomes less valid as the electron energy is increased above a particular core-level excitation threshold. At threshold all the energy may be used, for example, to excite a core electron to E_F with the eventual emission of a characteristic photon in the decay process. Above the threshold energy, the incident electron may suffer inelastic collisions and still have sufficient energy to excite the core level. Thus, at an energy, $\hbar\omega_p$, above threshold, where ω_p is the plasma frequency, a new threshold may appear due to a change in the total yield of x-rays as the core-level excitation threshold is crossed once again by those electrons which have first excited a plasmon. Other processes interconnecting the channels can be imagined. For example, Houston and Park (12) have suggested that the sensitivity of SXAPS to light elements, which have a high probability for Auger de-excitation, may be due in part to electrons which radiatively decay to the conduction band. This would generate a synchronous bremsstrahlung signal, since the creation of the Auger electron is modulated by the appearance of the

Figure 1. Available de-excitation channels for an electron-excited solid

initial core hole. Another interchannel relaxation mode is the radiative Auger decay (19-21). In this case, an Auger electron and a photon are emitted simultaneously, and the kinetic energy of the electron is less than that of a true Auger electron by an amount equal to the photon energy. In such a case the x-ray spectrum may exhibit successive photon bands (19) or merely asymmetries in the low energy side of x-ray lines. These bumps in the x-ray yield could give rise to structure in SXAPS although the integrated intensity of such bands is typically less than one per cent of that due to the main line (21). Furthermore, this effect decreases with increasing atomic number, Z , due to the decreasing Auger electron yield, and it is surface sensitive (20). Due to the low yields from this mode of decay, it will be neglected in the following discussion, but it should not be forgotten, particularly for low Z materials (21).

Since only photons contribute to the SXAPS signal, at the threshold for core-level excitation only the bremsstrahlung and characteristic x-ray channels will be considered. Above threshold the other channels cannot be eliminated with confidence, as just discussed. For thick targets, and in the energy range of 0 to 2.5 MeV, the average energy loss due to bremsstrahlung can be described empirically by (22)

$$\Delta E_B \approx 7 \times 10^{-10} Z E^2, \quad (1)$$

where Z is the atomic number, E is the incident electron energy and the units of E and ΔE_B are eV. As shown in Fig. 1, the fractional energy losses through the various channels are characterized by the

parameters α , β , and δ . Thus for the bremsstrahlung channel, we have

$$\delta = \frac{\Delta E_B}{E} \approx 7 \times 10^{-10} ZE. \quad (2)$$

Below the core-level excitation threshold, E_t , α is zero and the result for δ is as written. Above this threshold, α is non-zero and the energy dissipated through the bremsstrahlung channel is $(1 - \alpha)\delta$. For the lower channel, α defines the number of core holes created. If ω_i is the fraction of these holes which decay with characteristic photon energy E_i , the fractional energy loss through this channel is just

$$\beta = (\sum_i E_i \omega_i) / E_t. \quad (3)$$

The total fluorescence yield is defined as

$$\omega = \sum_i \omega_i. \quad (4)$$

Defining $\bar{E}$ as the average photon energy emitted due to the recombination of the core hole with energy E_t , we have

$$\bar{E} = (\sum_i E_i \omega_i) / \omega, \quad (5)$$

so that

$$\beta = \omega \bar{E} / E_t. \quad (6)$$

Looking again at Fig. 1, we see that the total x-ray yield, Y , defined as the total fraction of energy converted to photons at the threshold, E_t , is

$$\begin{aligned}
 Y &= (1 - \alpha) \delta + \alpha \beta \\
 &= \delta + \alpha(\beta - \delta).
 \end{aligned}
 \tag{7}$$

Since α is zero below E_t , and positive above E_t , Y will have a positive change in slope if $\beta > \delta$, that is, if the creation of the core hole results in a net increase of the total x-ray yield. Using the above values of β and δ , this condition is

$$\omega \bar{E}/E_t > 7 \times 10^{-10} ZE$$

or

$$\bar{E}/E_t > 7 \times 10^{-10} (ZE/\omega). \tag{8}$$

$\bar{E}$, the average photon energy for a given core-hole de-excitation, can only be approximated, although it is necessarily less than E_t . Values for ω are available to some extent (23). Thus only a rough estimate of the potential SXAPS signal for a given core state can be made. The dependence on $1/\omega$ on the right hand side is significant. Tracy (15) has commented on the decreased sensitivity of SXAPS to 4d transition elements when compared to 3d materials. For Cr, ω_{2p} is an order of magnitude larger than ω_{3p} for Pd. The weaker Pd signals might be explained by the above inequality since the right hand side would be increased by an order of magnitude for Pd.

According to the above development, near threshold the magnitude of the SXAPS signal will be determined by the fractional probability α , which is (16)

$$\alpha(E) = \int_{E_t}^E dE' \int_0^\infty dx \sigma(E'-E)N(x)f(E'-E, x), \quad (9)$$

where $\sigma(E'-E)$ is the total excitation cross section for the core level whose binding energy is E_t , $N(x)$ is the atomic density distribution function, and $f(E'-E, x)$ is the electron energy distribution as a function of penetration depth, x , into the sample. Since the mean free path for inelastic electron collisions may be less than $10^{\circ} \text{ \AA}$ (24), absorption effects can be neglected, that is, the electron will in general, experience an inelastic collision long before absorption effects have significantly altered the electron energy distribution. Thus we can use the distribution

$$f(E'-E) \propto \int_0^\infty f(E'-E, x)dx, \quad (10)$$

which includes only the effects due to discrete energy losses, such as plasmon excitations. These losses will be included later and for now we write

$$f(E'-E) = \delta(E'-E_t).$$

The inclusion of discrete losses will merely involve an additional convolution integral with $f(E'-E)$ at the end. With these assumptions then, we have (16)

$$\alpha(E) = \lambda_{ee} N \sigma(E_t - E), \quad (11)$$

where λ_{ee} is the electron mean-free-path for inelastic electron collisions and N is the total density distribution of scattering centers.

For convenience, we define the zero of energy at the Fermi level, define the incident electron energy as E_0 , and let the excited core level be at $-E_c$, as shown in the energy-level diagram of Fig. 2.

The total excitation cross section, $\sigma(E)$, is now calculated using first order perturbation theory. The excitation rate depends on the transition matrix element

$$M = \int d\tau \bar{\alpha}_i(H)\alpha_f, \quad (12)$$

where $\bar{\alpha}_i$ and α_f are the total, many-body wavefunctions of the crystal and extra electron in the initial and final states respectively. H is the Coulomb interaction Hamiltonian (25). Several simplifying assumptions are now made. We assume that the incident electron interacts only with the core electron, so that the only non-zero portions of M are the one-electron matrix elements of the Coulomb interaction. The transition rate is then $W(E_1 \rightarrow E_2) \cdot N(E_2)$, where $W(E_1 \rightarrow E_2) \approx |M(E_1 \rightarrow E_2)|^2$ and represents the squared transition matrix element for state E_1 going to state E_2 , and $N(E_2)$ is the density of final states with energy E_2 . Thus we have (15)

$$\sigma(E) \approx$$

$$\int_0^{E_0} \phi(E' + E_c) dE' \int_0^{E_0 + E'} W(E' \rightarrow \epsilon_1) W(E_0 \rightarrow \epsilon_2) N(\epsilon_1) N(\epsilon_2) \delta(E' + E_0 - \epsilon_1 - \epsilon_2) d\epsilon_1 d\epsilon_2. \quad (13)$$

Here $\phi(E' + E_c)$ represents the core-level line shape, determined by the core-hole lifetime. It is usually assumed to be a Lorentzian centered at $-E_c$. If it is assumed to be narrow, we can take it as a delta function

Figure 2. Schematic energy level diagram for core-level excitation including discrete energy losses prior to excitation

times a population factor, $N_c \delta(E' + E_c)$. The other delta function in the above equation restricts the transitions to those which conserve energy such that

$$E_0 + E' = \epsilon_1 + \epsilon_2. \quad (14)$$

This corresponds to the transitions labeled AA' in Fig. 2 where ϵ_1 and ϵ_2 are also shown. We are still excluding discrete energy losses prior to the core excitation.

Now we make an approximation for the combined transition, or scattering matrix element which, in first-order perturbation theory is

$$M' = \langle 1, 2 | \frac{e^2}{k|\vec{r}_1 - \vec{r}_2|} | 3, 4 \rangle - \langle 1, 2 | \frac{e^2}{k|\vec{r}_1 - \vec{r}_2|} | 4, 3 \rangle, \quad (15)$$

where 1 and 2 refer to the incident particle and core electron, while 3 and 4 refer to the final two-electron state. The second matrix element is necessary to allow for the exchange of the indistinguishable particles in the final state. We note that the potential, $e^2/k|\vec{r}_1 - \vec{r}_2|$, where k is the dielectric constant for the medium, can be expanded in terms of spherical harmonics (26) and therefore contains all values of angular momentum. Thus no strong selection rules apply here as they do for optical excitations. Next, it is assumed that $|M'|^2$ is a slowly varying function of energy so that it can be removed from the integrals. We now have

$$\begin{aligned} G(E) &= \int_0^{E_0} N_c \delta(E' + E_c) dE' \int_0^{E_0 + E'} |M'|^2 N(\epsilon_1) N(\epsilon_2) \delta(\epsilon_1 + \epsilon_2 - E' - E_0) d\epsilon_1 d\epsilon_2 \\ &= N_c \frac{2\pi}{h} |M'|^2 \int_0^{E_0 - E_c} N(E_0 - E_c - \epsilon_2) N(\epsilon_2) d\epsilon_2. \end{aligned} \quad (16)$$

The matrix element has also been averaged in $\bar{k}$ - space and is appropriately normalized (5). We thus have the simple result that the total interaction cross section is proportional to the self-convolution of the empty density of states, and from Eqs. (16), (11) and (7) we have for the total x-ray yield

$$Y_{\text{total}}(E) = \delta(E) + A(E) \int_0^{E_0 - E_c} N(E_0 - E_c - \epsilon_2) N(\epsilon_2) d\epsilon_2. \quad (17)$$

$\delta(E)$ has approximately a linear E-dependence from Eq. (2). Neglecting the energy dependence of $A(E)$, the differential yield is (27)

$$dY(E)/dE_0 = \text{constant} + A \int_0^{E_0 - E_c} N(\epsilon_2) \frac{\partial}{\partial E_0} N(E_0 - E_c - \epsilon_2) d\epsilon_2 + AN(0)N(E_0 - E_c). \quad (18)$$

Recall that all our assumptions made this expression good only near threshold. Differentiation reduces the bremsstrahlung to a constant background and gives a signal, at threshold, proportional to the square of the density of states at the Fermi level. The integral term will give structure away from threshold, but in light of the approximations already made, the model is only valid near threshold.

The agreement of this model with SXAPS data for the 3d transition metals (3) and for some of the simple metals (4,5) is remarkable considering the extensive approximations made. Even for Ca, where the density of states peaks somewhat above E_F , a derivative of the self-convolution of $N(E)$ does resemble the L_3 spectrum (28). For most of these materials, however, the agreement breaks down as one moves above threshold. In some of the lighter elements such as carbon or boron, new features appear in the spectrum due to the excitation of collective

modes (12,13), and finally, for Ba (6) and the rare earths (7, 8, 9, 28) the above model fails completely. The spectra for the rare earths La, Ce and Yb are presented in Chapter IV of this work, as well as some typical carbon results.

A more realistic model can be achieved if we relax the assumptions regarding the ionization cross section matrix element, and include the effects of discrete losses. The matrix element, $|M'|^2$, may rise somewhat above threshold (17), giving more weight to the structure away from threshold. Returning to Eq. (10) we can include the effect of discrete losses by a convolution in the above model with a distribution function $f(\epsilon)$ which smears the energy distribution of the incident beam. This is indicated in Fig. 2. The incident electron in transition B first loses energy ϵ , due to scattering from the valence band, and can still excite the core electron to E_F , transition B', if $(E_0 - \epsilon) - E_c = \epsilon_2$. Thus the total x-ray yield involves the convolution integral over the energy losses, ϵ ,

$$Y(E)_{\text{total}} =$$

$$\delta(E) + A \int_0^{E_0 - E_c} d\epsilon_2 N(\epsilon_2) \int_0^{E_0 - E_c - \epsilon_2} f(\epsilon) |M'(E_0 - \epsilon)|^2 N(E_0 - E_c - \epsilon - \epsilon_2) d\epsilon. \quad (19)$$

The SXAPS signal, dY/dE_0 , becomes quite complex, losing the simple relationship to the density of states obtained previously.

Nagel (17) has pointed out the similarity of SXAPS and the technique of characteristic isochromat spectroscopy (CI). In the latter the intensity of a particular characteristic x-ray line is measured as the electron

beam energy is swept past the core-excitation threshold. The results, under the same approximations used above, yield Eqs. (17) and (19) without the bremsstrahlung term so that an SXAPS spectrum is simply the derivative of a CI spectrum. The agreement for the Ni L_3 line is quite good (17), and the two techniques should be compared, when the data are available for both.

Other sources of data for testing and interpreting SXAPS results are the bremsstrahlung isochromat (BI) and short wavelength limit (SWL) techniques. As described by Nagel (17), with the BI technique the x-ray intensity is measured for a fixed photon energy, usually away from any characteristic lines, as the electron beam energy is swept past this fixed energy. In the SWL technique, the electron beam energy is fixed and the x-ray intensity is measured at the high-energy threshold. Neglecting discrete losses and using the one-electron picture again, Nagel shows that both techniques have intensity distributions that directly measure the empty density of states (17)

$$I(E_0, \hbar\omega) \sim N(E_0 - \hbar\omega).$$

Thus both SWL and BI techniques can provide useful input for the interpretation of SXAPS data. A very important difference exists, however. In SXAPS the created core hole may alter the distribution of empty states near E_F if the core wavefunction greatly overlaps with the conduction band wavefunctions. In SWL and BI the core hole does not exist and the density of empty states may be more characteristic of the N-particle neutral atom with the addition of an extra electron at E_F , that is,

an $N+1$ particle density of states. This difference must be remembered when the data are compared and will prove useful in our data analysis.

Up to this point, the one-electron theory has been used to develop a model for SXAPS processes. The result assumes constant transition matrix elements, infinite core-hole lifetime, one-electron energy bands, and neglects the effects of discrete energy losses prior to core excitation. The result is repeated here

$$I_{\text{SXAPS}} = \frac{dY_{\text{total}}}{dE_0} = \frac{dY_{\text{brem}}}{dE_0} + A \frac{d}{dE_0} \int_0^{E_0-E_c} N(E_0-E_c-\epsilon)N(\epsilon)d\epsilon, \quad (20)$$

where the subscript on ϵ_2 has been dropped, $A(E)$ was assumed constant, and Y_{brem} is identically $Y(E)$. Eq. (20) is the starting point for much of the data interpretation, and often will be referred to as the one-electron theory.

Using the one-electron theory, it has been pointed out that SXAPS, CI, SWL and BI spectra all have something in common in that they depend on the density of unoccupied states above E_F . In addition, the first two make use of the core level as a window. Intercomparison of the results aids in the interpretation of SXAPS line shapes. Another useful piece of information can be gained from the soft x-ray absorption (SXA) spectra. This is particularly valuable since the absorption coefficient can usually be found in the literature. The absorption coefficient, α , is defined as (29)

$$\alpha(\hbar\omega) = \frac{2k\omega}{c}, \quad (21)$$

where k is the imaginary part of the complex index of refraction,

$\tilde{N} = n + ik$, ω is the photon frequency, and c is the speed of light.

α , as defined here, is the fraction of energy absorbed in passing through unit thickness of the material. In terms of the total interaction cross section for photon absorption, $\sigma(\hbar\omega)$, this is (30)

$$\alpha(\hbar\omega) = \rho \frac{N_0}{A} \sigma(\hbar\omega), \quad (22)$$

where ρ is the density of the material with atomic number A , and N_0 is Avogadro's number. $\sigma(\hbar\omega)$ can be calculated using first-order perturbation theory. The result can be found in most texts on quantum mechanics, and, for a single transition from initial state $|s\rangle$ to final state $|k\rangle$, is (31)

$$\sigma(\hbar\omega) = 4\pi\alpha_0\omega_{ks} |\langle k|\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}|s\rangle|^2 \delta(\omega - \omega_{ks}). \quad (23)$$

Here, the delta function conserves energy, $\hbar\omega_{ks} = E_k - E_s$, α_0 is the fine-structure constant, and the matrix element results from the standard dipole approximation. In addition, it has been assumed that only the two one-electron states, $|k\rangle$ and $|s\rangle$, are involved in the interaction. Defining the transition oscillator strength as (31)

$$f_{ks} = \frac{2m}{\hbar^2} \hbar\omega_{ks} |\langle k|r|s\rangle|^2, \quad (24)$$

and doing a sum on the polarization direction, $\hat{\mathbf{e}}$, gives

$$\sigma(E) = C f_{ks} \delta(E - E_{ks}), \quad (25)$$

where C is a constant. If we now consider the transitions from the initial state $|s\rangle$ to all possible final states $|k\rangle$ we have

$$\sigma(E) = C \sum_{k > k_F} f_{ks} \delta(E - E_{ks}), \quad (26)$$

where $\sum_{k > k_F}$ means that we sum over available discrete states and integrate over the empty bands. As in the one-electron SXAPS model, we now assume that the oscillator strength is not a strong function of energy and can be removed from the sum, so that

$$\sigma(E) \propto \sum_{k > k_F} \delta(E - E_k + E_s). \quad (27)$$

The right hand side is just the one-electron density of available final states, i.e. the density of unoccupied states as defined by (32)

$$N(\omega) = \sum_i \delta(\omega - \omega_i). \quad (28)$$

We then have for the absorption coefficient

$$\alpha(E) \propto \sigma(E) \propto N(E + E_s). \quad (29)$$

To be consistent with the energy level scheme shown in Fig. 2, for an incident electron energy E_c , the transition to the Fermi level, $E = 0$, originates from the core level $E_s = -E_c$. Thus we have the useful result that

$$\alpha(E) \propto N(E - E_c). \quad (30)$$

Putting this result into the self-convolution model, Eq. (20), gives

$$\frac{dY_{\text{total}}}{dE_0} = \frac{dY_{\text{brem}}}{dE_0} + A' \frac{d}{dE_0} \int_0^{E_0 - E_c} \alpha(E_0 - \epsilon) \alpha(E_c + \epsilon) d\epsilon. \quad (31)$$

Thus, using the data from SXA experiments for $\alpha(E)$, an SXAPS spectrum can be calculated and compared to the actual spectrum. This should be quite helpful in the interpretation of the excitation schemes involved

in SXAPS. However, a note of caution is necessary in such a comparison. First, the excited state in SXA contains only the excited core electron while in SXAPS an additional electron is present which may make Eq. (30) a bad approximation. Second, the absorption coefficient has been derived in the dipole approximation and dipole selection rules apply. Consequently, photon excitation of s-symmetry core levels will reflect the p-symmetry density of states (33). Core levels of p-symmetry will reflect the s- and d-partial density of states. As pointed out earlier, in SXAPS the electron excitation process permits transitions of all symmetries since angular momentum is easily conserved. Hence the two techniques may reflect different densities of states. The relative contribution from the different partial densities of states is determined through the energy-dependent oscillator strengths which have here been assumed constant. Thus the success or failure of the one-electron model, as well as of the prescription with $N(E)$ replaced by $\alpha(E)$, will ultimately depend on the validity of the approximation for the transition matrix elements.

At the beginning of this chapter, it was pointed out that the theory of SXAPS has not been sufficiently developed to reliably interpret the spectrum of an arbitrary material in terms of its electronic configuration. The one-electron model developed above works well for some simple metals and the 3d transition metals, but fails to describe the results for many other materials. Many of the materials studied in this work do not fit the model and some modifications of this theory become necessary. A discussion of this is postponed until the data are presented, since a better understanding can be obtained then.

CHAPTER III. EXPERIMENTAL CONSIDERATIONS

The technique of soft x-ray appearance potential spectroscopy (SXAPS) is relatively simple compared to other electron and x-ray core-level spectroscopies. The vacuum system and associated instrumentation, as discussed below, need not be elaborate. It is, perhaps, the simplicity of SXAPS that makes the technique very attractive as a tool for identification of unknown elements on a solid surface.

In this chapter the vacuum system constructed for our work is described in detail. The instrumentation is then discussed, including a consideration of noise, resolution, and calibration. Finally we treat the problem of sample preparation and other related topics.

Vacuum System

The original motivation for constructing the spectrometer was to study the La core excitations with the hope of locating the position of the empty 4f states relative to the Fermi level, E_F . This question had not been answered by other spectroscopy methods and is of interest, particularly in the area of superconductivity (34,35). Consequently, the vacuum system was designed with only the essential items for such a measurement, resulting in a compact, relatively inexpensive spectrometer.

The vacuum shell consists of two $1\frac{1}{2}$ in. stainless steel crosses and one tee, providing a total of seven access ports. As shown in Fig. 3, a 20 liter/second differential ion pump, nude ion gauge, and bakable valve occupy three ports. A stainless steel pipe leads from this valve to an auxiliary 5 liter/second ion pump which is used during the initial

Figure 3. Schematic diagram of the spectrometer used in this work

pumpdown, and afterwards, to maintain a low pressure in this line during bakeout of the main shell. This smaller pump keeps the line at a pressure of 10^{-7} Torr which protects the gold-foil seal in the bakable valve from oxidation at the higher temperatures during bakeout. At the end of this line there is a liquid-nitrogen cooled sorption pump and another valve for roughing the system during the initial pumpdown.

A fourth arm on the main shell houses the evaporator. In most cases a tungsten wire basket was used to hold the evaporant, although some materials, for example the MnF_2 powder, required other types of boats. A mask was installed above the basket to confine the evaporant to the substrate surface and to limit contamination of the rest of the system. Some contamination problems were still encountered, especially with Yb. This will be discussed in Chapter IV. Directly opposite the evaporation port is the spectrometer detector, the construction of which will be discussed below. With this arrangement a 180° rotation of the target holder moves the substrate from the evaporation position into place for a measurement. The rotation is accomplished with a magnetically-coupled rotary feed through. A pin, installed on the rotor shaft, insures proper alignment of the substrate with respect to the evaporation mask and detector. Many such special precautions were necessary since we had no viewing ports on the system.

The final port provides the high voltage connection for the target. A piece of boron nitride (grade HP) (36) electrically isolates the target from the stainless rotor shaft. This material was chosen since it machines easily and does not have to be fired as do many lava materials.

Boron nitride was also used in the construction of the detector.

Two types of sample holders were used in this work. Both were machined from stainless steel. The first was a disk, $1/8$ in. thick by $3/4$ in. diameter, which was used as a substrate for evaporated films of all materials. In a few cases, where crystals of different materials were to be studied, a four-sided mount was used. This target had four faces, $3/4$ in. by 1 in., and fit over the end of the boron nitride extension. The samples were then fastened to each face with Al masks. This target required a special rotary stop to insure proper alignment with the detector since there was no viewing window. A collar was designed for the rotary shaft, with four small radial holes around its circumference. A soft-iron pin was machined and positioned in the vacuum shell to fall into a hole in the collar when a face of the sample holder was properly aligned. The iron pin was lifted out of the hole by means of an external magnet. This target was used only when several externally prepared samples were to be studied, since only one evaporator existed in the system. The primary disadvantage of this target assembly was the soft-iron pin which had a relatively high vapor pressure, giving base pressures of only 1×10^{-8} Torr. In future work with this target assembly, it would perhaps be useful to gold-plate the iron pin to reduce this source of gas. With the other target holder, base pressures of 8×10^{-11} Torr were achieved. In the work with La and Ce, experimental runs could be made in the 10^{-10} Torr region. Other materials were studied in the low 10^{-9} Torr range.

The final element of the system to be discussed here is the detector. This compact device was based on the design of Musket and Taatjes (37). The detector has cylindrical geometry and is mounted on a four-pin, medium-current feed through (Ultek No. 281-2650). The pins were shortened to accomodate the detector with an overall flange-to-sample distance of 12.6 cm. As shown in Fig. 4, the photocathode is a cylindrical can of Ta, 1 in. in diameter by $2\frac{1}{2}$ in. long, with one side slightly flattened to give a D-shaped cross section. Ta was used because it has a fairly high photoelectric cross section and can be easily formed into the desired shape. Tracy (15) has reported on the influence of photocathode material in the SXAPS spectrum, but in this work, no strong Ta features were ever detected. The open end of the Ta can faces the sample and is covered by an 80 per cent transparent woven tungsten grid. Tungsten was chosen after attempts with photoengraved Au and Ni screens failed. With a grid-to-filament distance of only 0.7 cm, the Au and Ni screens were destroyed due to the high operating temperatures of the tungsten wire filament.

The stainless steel collector pin is mounted along the photocathode axis. To provide electrical shielding from the nearby ion gauge and filament leads, the copper feed through rod was fitted with a coaxial glass sleeve and a stainless steel tube which was in contact with the flange. The leads for the electron filament are $1/8$ in. copper rods, shaped to pass along the flat side of the photocathode. The boron nitride baseplate and ring insure electrical isolation of the filament leads from the photocathode and grid. The baseplate provides rigidity for the detector assembly and the front ring is used for attaching the grid to the assembly with electrical contact to the photocathode. The

Figure 4. Schematic diagram of the x-ray detector used in this work

electron filament is suspended from the two over-hanging copper electrodes and is typically a 0.020 in. tungsten wire, bent in a V-shape, with the apex centered on the grid. To localize the electron emission, the tip of the wire was chemically etched to approximately half the wire diameter. Tungsten was used since its work function is well known (38) and quite reproducible in vacuum.

With this detector geometry the filament-to-sample distance is about 0.3 cm, and the filament-to-grid distance is 0.7 cm. The solid angle subtended by the grid, as seen from the center of the sample, is then 0.73π sr. The loss of solid angle due to the flat side of the grid is small since the total solid angle for a full circular cross section at 1 cm distance is 0.75π sr, or about three per cent greater. Other detector geometries have been used (3, 5, 10) in SXAPS. In particular the cylindrical geometry of Nilsson and Kanski (5) may have some advantages over that of this work. Decreasing the sample-to-grid distance, with our geometry, to 0.5 cm would increase the collection angle to about 1.25π sr. However, this would also require a smaller sample diameter to clear the chamber walls during rotation, reducing, in effect, the x-ray flux. It would also place the hot electron emitter dangerously close to the grid. It was felt that the present geometry provided a good compromise. Another point to consider in determining the best geometry is the angular distribution of the emitted x-rays. No study was made of this effect with the present apparatus. It is known (39) that self-absorption by the sample becomes more important as the take-off angle is increased, since the mean escape path is effectively increased. In SXAPS this may still be a

negligible effect since the penetration depth of the unscattered electron beam is only a few atomic layers to begin with.

The system as described above required about two days to reach vacuums in the low 10^{-9} Torr range. The most efficient pumping method consisted of initial roughing, followed by a short period of pumping with the sorption pump. The ion pumps usually started after a few hours with the shell at 250° C. The system was then pumped for another day at 250 to 300° C. In most cases this was sufficient to reach a pressure in the 10^{-9} Torr range. No titanium sublimators were used to assist in the pumping although the rare earths studied seemed to getter quite well, and the best vacuums obtained during the work with La and Ce were below 1×10^{-10} Torr.

Instrumentation

Electronics

The circuit used for these measurements is shown in Fig. 5. It is basically the same as that of Park and Houston (16) with the exception of the detection circuit. The electrons leaving the filament, F, are attracted to the sample, S, at high voltage, creating x-rays and secondary electrons upon impact. The electron current is returned to the filament through an ammeter and a potentiometer in parallel with the filament. The ammeter measures the total current, consisting of the true beam current and a much smaller current drawn by the high-impedance digital voltmeter. The correction for this latter portion is easily made to arrive at the true emission current. This entire circuit is biased about 40 V, ($= V_B$), above ground to prevent electron current to the grounded photo-

Figure 5. Block diagram for the spectrometer instrumentation.

cathode. The high voltage supply is resistance programmable and the output voltage can be swept through the region of interest by a variable speed, motor-driven potentiometer circuit. The digital voltmeter is positioned as shown in Fig. 5 to read the actual filament-to-sample accelerating potential. There are no corrections necessary then for voltage drops across the transformer windings or ammeter. An output from the digital voltmeter provides the x-drive for an x-y chart recorder.

To insure that the electrons are returned to the filament at the same potential with which they were emitted, the reversing switch, S1, is used in conjunction with the filament potentiometer. With this standard configuration two scans are made across a relatively sharp feature, like the Cr L_3 excitation, one for each direction of the d.c. heating current. Successive pairs of scans are then made, and the potentiometer is adjusted until the scans for each direction of heating current overlap exactly. The voltage drop across the filament and connecting leads was typically less than two V. The actual drop across the filament could not be measured. The success of this method depends on the sharpness of the feature being used, which depends on the magnitude of potential modulation and the reproducibility of the heating current when reversed. The zero crossing in the derivative of the Cr L_3 structure was usually used since Cr peaks from the stainless steel target holder were always present before sample evaporation. In practice, it was found that the filament and its leads were sufficiently symmetric with respect to the emitting portion of the filament to eliminate the potentiometer completely, and to allow the use of one-half of the potential measured

across the filament at the return point, as a correction to the digital voltmeter reading.

The final consideration in this portion of the circuit is the introduction of the potential modulation. An isolation transformer was used to superimpose an a.c. voltage on the d.c. accelerating potential. A frequency of 1.5 kHz was used in this work. At lower frequencies the signal-to-noise ratio was somewhat worse, and at higher frequencies the response of the lock-in amplifier was reduced due to the large source impedance ($R=1 \times 10^6 \Omega$). The amplitude of the modulation was varied from 0.2 to 2.0 volts peak-to-peak (V_{pp}), depending on the resolution required and the strength of the detected signal. The modulation amplitude was always measured at the high voltage vacuum feed through connection.

The detection of the electron-excited x-ray fluorescence in SXAPS has seen several modifications in the past two years. The circuit used in this work is by far the simplest, and most likely the least sensitive, although it proved adequate for most of the materials studied. Its primary advantages are of course its reliability, simplicity of construction, and lack of tedious fine tuning. The Ta photocathode, P, and tungsten grid, G, are at ground potential. This prevents the thermionic electrons from reaching the positively biased collector, C. X-rays from the target pass through the mesh and strike the photocathode, producing photoelectrons which are then collected by the positively biased pin. The collected photocurrent is returned to the photocathode through a metal-film resistor, producing a synchronous voltage to be measured by

the lock-in amplifier. No filtering or preamplification prior to that of the synchronous detector was used. The output of the lock-in amplifier is recorded on the y-axis of an x-y recorder as the sample potential is swept through the region of interest. The 600 V bias of the collector, V_C , is well into the saturation region of this simple photodiode. A 300 V bias was satisfactory for most purposes, however the 600 V battery introduced no detectable increase in noise and increased the signal strength by about ten per cent. At an emission current of about two mA our root-mean-square (rms) signals were from one to $30 \mu\text{V}$ with the $10^6 \Omega$ load. The major disadvantage of this scheme was the necessity of working at such low voltage levels where extraneous pick-up, despite shielding, and microphonics, due to the cables and the detector itself, could cause problems. With no external preamplification the sensitivity was often limited by the lock-in amplifier rather than by the inherent noise as discussed below.

Variations of this simple detection scheme are abundant. Houston and Park (2) have used a resonant LC tank circuit as a preamplifier and have also used an electron multiplier to measure the photocurrent. Tracy (15) used an operational amplifier with a gain of 10^7 prior to synchronous detection. Baun et al. (40, 41) have used various thin foil filters with an electron multiplier, and later, a cesium-iodide photocathode (42), to measure both a synchronous signal and a d.c. signal which was then numerically differentiated. Pocker (43) has combined the advantages of an operational preamp with those of the resonant tank filter in a doubly resonant current-to-voltage preamp which should be

useful for SXAPS. Andersson et al. (44) have eliminated the need for large emission currents by using a liquid-nitrogen cooled silicon surface-barrier diode to detect the emitted photon flux. They report that it behaves as an ideal detector in that the signal-to-noise ratio is limited only by the shot noise produced by the photon flux. The main advantage of such a detector is the ability to work with lower emission currents and thereby reduce the disorder and desorption caused by larger electron beam currents as discussed below.

Noise

Three types of noise cause distortion with the detection scheme used here. They are: first, the photon flux and thermal noise which are inherent to the diode and resistor respectively; second, stray pick-up and microphonics of the cable and detector; and third, instability of the various circuit components. Each of these is discussed separately.

The load resistor is a source of noise itself due to the random motion of electrons from one end to the other. This thermal (Nyquist) noise can be expressed as (45)

$$\langle \Delta v^2 \rangle = 4kTR,$$

where $\langle \Delta v^2 \rangle$ is the mean-square voltage per unit cycle of bandwidth, k is Boltzmann's constant, and T is the absolute temperature of the resistor with resistance R . The bandwidth of the Ithaco 353 lock-in amplifier with a one second time constant, τ , and 12 db/octave rolloff is approximately $1/8\tau$ or 0.125 Hz (46). The noise figure of the 353, with

a source impedance of $10^6 \Omega$ at a frequency of 1.5 kHz, is nearly unity, so it introduces negligible self-noise. The rms thermal noise is then 4.3×10^{-8} V or 1.2×10^{-7} V_{pp}. Since we are concerned with photocurrent here it is more meaningful to work with rms noise current which is then 4.3×10^{-14} A or 1.2×10^{-13} A_{pp}.

The 1/f noise (current noise) is given by (45)

$$\langle \Delta v^2 \rangle = (KI_{d.c.}^2)/f,$$

where $\langle \Delta v^2 \rangle$ has the same meaning as above, f is the frequency of modulation, K is a constant determined by the geometry and construction of the resistor, and $I_{d.c.}$ is the d.c. photocurrent. Such noise is large in composition type resistors due to the intergranular contacts but is absent in metals and thus of no concern with a metal-film or wire-wound resistor.

Shot noise arises due to the photon flux in the photodiode. It is a measure of the random emission of electrons from the cathode material. The mean-square shot noise increases with the photocurrent and is given by (45)

$$\langle \Delta i^2 \rangle = 2eI_{d.c.},$$

where $\langle \Delta i^2 \rangle$ is the mean-square current per unit cycle of bandwidth and e is the electronic charge. In the derivation of this expression it is assumed that each emitted electron reaches the collector independently of all the other electrons, that is, it neglects space-charge limitations. The collector bias voltage used in this work is well beyond the space-

charge region. For typical data in our work, the total d.c. signals at the larger accelerating potentials were about 6 mV across $10^6 \Omega$ or 6×10^{-9} A. This gives an rms current due to shot noise of 1.6×10^{-14} A or approximately 4.4×10^{-14} A_{pp}. The total rms noise, then, for a resistor of $10^6 \Omega$ is 0.6×10^{-13} A or 1.64×10^{-13} A_{pp}. This becomes significant when compared to that portion of the synchronous current due to core-level radiative de-excitation, which may represent in some cases only one part in 10^3 of the total photocurrent, or about 10^{-12} A. The rms noise voltage from above is about 6×10^{-8} V. Peak-to-peak signal levels were 30 μ V for some of the strongest transitions and noise was not a problem there. At the other extreme, some of the weakest transitions reported here, for example the fluorine 1s excitation, had signal-to-noise ratios on the order of two or three. Uncertainties due to noise will be pointed out in Chapter IV when appropriate.

It is important to note that increasing the resistance, R, increases the signal strength linearly, as long as the lock-in response is unaffected, but increases the thermal noise only as the square root of R. Furthermore, the shot noise increases as $(I_{d.c.})^{\frac{1}{2}}$ whereas the signal strength is linear in $I_{d.c.}$. Hence, large resistors and large emission currents are desirable. The disadvantage of higher emission currents, as mentioned before, is sample damage.

With some of the insulating materials studied in this work, e.g. LaF_3 , the d.c. photocurrents were about an order of magnitude larger than just discussed. However, to avoid film damage with the insulators, the

emission currents were held below one mA in general. The d.c. photocurrent was then of the same magnitude as that used in the calculations above, and thus the same noise figures apply to that work as well.

The second category of distortion to be discussed is stray pick-up. To minimize this effect, short cables were used, ground-loops were avoided and special shielding was designed for the SXAPS feed through. Inside the vacuum, the collector lead was shielded as discussed earlier. Outside the vacuum the load resistor and battery were placed close to the vacuum flange to provide a signal voltage as soon as possible. The two Cu electrodes going to the detector were shielded at the flange to avoid pick-up from the neighboring two electrodes which passed the filament heating current.

Another potential source of pick-up is the stray capacitance between the grounded photocathode and the sample, on which there is an a.c. voltage present. Eastman (47) observed such an effect when the potential of the photodiode itself was modulated in a photoemission experiment. He corrected for it with a null-technique using a bridge circuit. The diode bias in our experiment is fixed and the capacitance of interest is between sample and photocathode, not between photocathode and collector. If such pick-up is present it should give rise to a constant synchronous background, the magnitude of which depends on the product of the electrode capacitance, modulation frequency, and modulation amplitude. No such frequency or amplitude dependent background was encountered in this work.

The final consideration in this category is noise due to microphonics, that is, noise voltages generated by movement of electrodes or cables due to vibration. In addition, movement of the photocathode might cause intensity fluctuations, depending on the photon flux and the sensitivity of different regions of the photocathode. To minimize microphonics in the photodiode, the boron nitride insulators were designed with an outer diameter just slightly smaller than the vacuum walls, providing some support for the structure. By using short cables and avoiding external disturbances where possible, the vibration problem was minimized. Despite all precautions taken, the combination of stray pick-up and microphonics probably accounted for some of the noise observed in this work. In some of the worst cases the rms noise was about $0.1 \mu\text{V}$, approximately half of which is accounted for by the thermal and shot noise figures obtained earlier.

The last category of distortion to be discussed is that due to instability of the circuit components, primarily in the electron beam circuit. The detection circuit was not a problem since the only bias used here was provided by a battery. The load resistance and lock-in amplifier were also quite stable. However, variations in either electron current from the filament to the target, or in the amplitude of potential modulation would cause problems since the synchronous signal depends almost linearly on both. The observed fluctuations were usually on the order of one part in 20, and when they occurred, were random and infrequent. Such large instabilities were not due to the oscillator and in most cases they could be correlated with an observed change in the

emission current. A constant current supply provided the filament heating current of approximately 12 A with a rated stability of about one part in 100 (48). The larger fluctuations were then most likely due to non-uniform emission of the filament itself, or changes in the effective filament impedance as seen by the heater supply. Since the fluctuations were random and infrequent, any doubt about possible structure in a spectrum was removed by repeating the scan. No further regulation was tried although control circuits have been constructed for use in other SXAPS work (5, 9, 10, 15). The principle advantage of an emission control circuit is in the removal of space-charge effects. For the lower accelerating potentials, the build-up of space charge reduces the beam current and therefore the signal strength. With the geometry used here this occurred primarily below 100 eV. A regulation circuit raises the filament temperature in this region to keep the filament-to-target current constant. Most of the signals of interest to us were above 100 eV. In addition, a first-order correction for the variation of emission current can be made, as discussed in Chapter IV, and this was done when the structure was believed to be influenced by the variation in emission current.

Resolution

A very attractive feature of SXAPS is the resolution obtained for relatively minor effort when compared to other core-level spectroscopies. The final resolution achieved depends on several parameters which will be discussed below, but typically is between 0.5 and 1.0 eV. For the sake of comparison, XPS measurements are often resolution-limited by the

monochromaticity of the exciting radiation. The Mg and Al K_{α} lines used have natural widths of about one eV (16). The dispersion of the electrostatic analyzer may reduce the resolving power even more. With a retarding potential analyzer, a resolution of one eV was obtained by Suzuki et al. (49) for the Au 4f line. Park and Houston (50) have reviewed the different core-level excitation techniques and conclude that SXAPS resolution is competitive with the others. For methods such as Auger spectroscopy, ionization spectroscopy and characteristic isochromat spectroscopy, electron beams are used to excite the core levels and the resolution is ultimately limited by the spread in energy of the exciting beam as in SXAPS.

A limiting factor in SXAPS resolution is the thermal spread in energy of the electron beam. This depends on the operating temperature of the electron filament, which in our case is estimated to be about 2800 K. The electrons escaping from the metal filament are represented by the high energy tail of the Fermi-Dirac distribution function which, at these temperatures, is roughly described using a Maxwellian velocity distribution. Using this distribution function, one can calculate the average kinetic energy per electron crossing a surface outside the emitter. The result is just $2kT$ per electron (51) which, in our case, is about 0.5 eV. This average thermal kinetic energy is used in the calibration of our raw data as discussed below. The same value is used by Nilsson et al. (52) while Park and Houston (3) use instead just kT for this energy correction. To get an estimate of the spread in energies of the incident electrons, we can use the same distribution function as above to calculate the mean-

square energy per electron leaving the emitter. The result is just $6(kT)^2$. Using one standard deviation as a rough estimate of the monochromaticity of the electron beam, we obtain a value of 0.34 eV for the root-mean-square thermal energy broadening.

Resolution can be further limited by the potential drop along the emitting portion of the filament, which could not be measured directly in this work since the hot portion of the filament was inside the vacuum. However, an absolute upper limit can be measured at the filament feed through. For most of the work reported here this limit was about 1.3 eV. The broadening contribution due to this potential drop can be decreased by using an indirectly heated cathode or using material of lower work function (7). This can lead to new problems, however, since cold cathodes may need to be flashed after exposure to air and this can result in contamination of the nearby sample (10). Another alternative is to use an a.c. heating current with the detector gated to measure only at the zero-crossing point of the applied heater voltage.

A third source of broadening in SXAPS is that due to potential modulation (53). This technique of taking derivatives is also used in Auger and photoemission work and, although its use can suppress annoying background (54), it introduces broadening by the fact that the measured signal at a given energy is actually a weighted average of the true signal over a spread of energies determined by the amplitude of modulation. The exact form of this dynamic broadening has been derived for sinewave modulation by Houston (55) and only the results will be presented here.

The total x-ray fluorescence yield, $Y(E)$, is the true function to be measured. The potential modulation is of the form

$$E(t) = E + e \cos \omega t,$$

and a Taylor expansion of $Y(E(t))$ gives

$$\begin{aligned} Y(E(t)) &= Y(E) + (e^2/4) Y^{[2]}(E) + \dots \\ &+ (eY^{[1]}(E) + (e^3/8) Y^{[3]}(E) + \dots) \cos \omega t \\ &+ ((e^2/4) Y^{[2]}(E) + \dots) \cos 2\omega t + \dots, \end{aligned}$$

where $Y^{[n]}(E)$ indicates the n th derivative of Y evaluated at E . We see that the n th-harmonic term of the series contains the n th derivative as well as higher order derivatives. For small modulation amplitudes, e , one usually neglects the higher order derivatives and equates the n th harmonic to $Y^{[n]}$, scaled by the modulation amplitude. The error in this method is made somewhat worse by the fact that the synchronous detector used here, when set to measure the first-harmonic signal, $Y(\omega)$, actually measures

$$Y = Y(\omega) + (1/3)Y(3\omega) + (1/5)Y(5\omega) + \dots$$

The first truncation error is avoided by the exact formalism for dynamic broadening (53). Here, the measured n th harmonic, H_n , is related to the true n th derivative, $Y^{[n]}$, by

$$H_n = t_n * Y^{[n]}.$$

The asterisk indicates a convolution product (56), and t_n is the dynamic instrument response function. For the first two harmonics this function

is given by (55)

$$t_1 = 2/\pi (1-(E'/e)^2)^{\frac{1}{2}}$$

$$t_2 = (e/3) 2/\pi (1-(E'/e)^2)^{3/2},$$

and t_n is defined to be zero outside the interval $E - e \leq E' \leq E + e$. The problem of higher harmonics being measured by the amplifier is still present and the appropriate t_n would broaden these as well. For the small values of e used here we neglect this distortion.

With the above formalism we could deconvolve our measured signal to get at the unbroadened, true derivatives. Houston and Park (53) have demonstrated the effect of potential modulation on a Lorentzian peak in terms of the parameter, e/Δ , where Δ is the half-width at half-maximum for the input function. The dynamic broadening for $e/\Delta \lesssim 0.5$ is small. In addition, we have calculated the broadening for the derivative of a Lorentzian peak, since this more closely resembles the SXAPS peaks. The results are shown in Fig. 6. We have normalized the peaks to unity and show the unbroadened curve as a solid line. The dashed curves represent $e/\Delta = 0.25, 0.5, 1, 2.5$, and 5 , reading from the solid curve out. Here also we see that only slight broadening is introduced for $e/\Delta \lesssim 0.5$.

Deep core states may have natural widths of about 0.2 eV while higher-lying states may be a few eV in width. The proper modulation level then depends on the core state being studied. For most of our work a one V_{pp} modulation was used ($e = 0.5$ eV) so we would obtain essentially unbroadened results for $\Delta \gtrsim 1$ eV. Some structures in the

Figure 6. Dynamic broadening of the first-harmonic signal due to the potential modulation technique

rare earth spectra have natural widths much less than this, and there we used $0.5 V_{pp}$ to give true peaks for $\Delta \gtrsim 0.5$ eV. However, due to the thermal energy broadening, and the potential drop along the filament wire, as discussed earlier, our resolution is limited to something greater than 0.5 eV and further reduction of the modulation amplitude would be of little value.

The final consideration for resolution is the ratio of scanning speed to lock-in amplifier time constant, τ . The Ithaco 353, when operated at 12 db/octave rolloff, requires 3.4τ seconds to achieve 90% of the input signal (46). The scanning speed should then be set such that the energy interval corresponding to the desired resolution is scanned in a time, $t \gtrsim 4\tau$. Since the best resolution achievable here is about one eV, a speed of $0.25/\tau$ V/sec. is required. For a given signal strength the signal-to-noise ratio will determine an acceptable τ and this in turn determines the maximum scanning speed for optimum response.

Energy calibration

With any core-level spectroscopy the problem of absolute calibration of the initial- or final-state particle energy is always present. For example, in photoemission work, the calibration may be referenced to the Au N_6 and N_7 lines which are assumed to be well known (57). When electrostatic analyzers are used, their work functions must be measured, and use of accepted standard lines in a spectrum helps to accomplish this.

In SXAPS the detector work function does not enter into the calibration, but the filament work function does. Fig. 7 is a schematic diagram

Figure 7. Schematic energy level diagram for the standard electrode configuration at the threshold for electronic core-level excitation

of the energy levels involved at the electronic excitation threshold of a core level. The incident electron energy relative to the target Fermi level, $E_{F,T}$ is given by

$$E = eV + e\phi_f + 2kT.$$

Here V is the applied potential, e is the electronic charge, ϕ_f is the filament work function, and the contribution $2kT$, discussed earlier, is the average kinetic energy imparted to each electron due to thermal motion at temperature T in the filament. No correction is required for the detector work function, ϕ_c . Furthermore, the potential modulation as introduced here, does not add to the energy of the electron since the superimposed oscillations are symmetrically positive and negative about the applied d.c. potential. This would not be the case if the modulation potential were clamped to be strictly positive going with respect to the applied potential. The modulation amplitude can have an affect on the data analysis when trying to determine excitation threshold energies, since, as shown in Fig. 6, the modulation causes broadening of the true signal and shifts to lower energy the threshold of a peak in the spectrum. The controversy over determination of binding energy by SXAPS is not settled (3,58) and will be discussed in connection with the data analysis, since the main issue there is one of line shape interpretation.

The digital voltmeter (DVM) used to read the applied accelerating potentials, V , was a three and one-half digit meter capable of reading 160 per cent of full scale. Thus from 0 to 160.0 V, the absolute uncertainty would be ± 0.05 V, and from 160 to 1600 V the uncertainty would

be ± 0.5 V. The DVM calibration was checked against a standard voltage supply and it was confirmed that when the right-most digit switched by one unit, the relative uncertainty in the voltage at that point was at worst, 10 per cent of that unit change. In recording the spectra, tic marks were made manually precisely when the meter digit changed so that from 0 to 160.0 V our absolute uncertainty in V is ± 0.01 V and from 160 to 1600 V our absolute uncertainty is about ± 0.1 V. These values are less than our resolution limit and thus do not contribute significant additional error.

The x-axis of the x-y recorder was driven by an output from the DVM. During the recording of each spectrum, tic marks were made manually at selected DVM readings. Thus the recorder calibration was not a source of error. Also, the recorder had a slightly non-linear gain amounting to one part in 300. To avoid additional error, the DVM readings were marked at closely spaced intervals and these marks were used to calibrate the energy axis of the spectrum.

Sample Preparation

Surface preparation is crucial to SXAPS since the technique is surface sensitive, as are most spectroscopies using medium-energy electrons. The penetration depth for an electron of energy less than one keV has been determined by observing the escape depth of photoelectrons using thin film overcoatings (24, 59). A good estimate for λ_{ee} at one keV electron energy is $10 \text{ \AA}$, or a few atomic layers for many materials. Thus, surface preparation becomes important.

With only a few exceptions, evaporated films were used in our work. The exceptions were some early design work in which a polycrystalline Cr sample was used, and a later attempt to compare the 4d transition metals Y, Zr, Nb, and Mo using polished bulk samples, cut with no preferred orientation. The source materials were usually checked for purity before insertion into the vacuum.

The system had no special facilities for surface preparation other than electron beam heating. There was no thermocouple to measure sample temperatures during electron beam heating or during experimental runs and only an estimate of sample temperature could be made. It was felt that the temperatures achieved were not sufficient to effectively clean a bulk specimen prepared outside the vacuum so few bulk samples were studied. With evaporated films the amount of contamination was determined by the vacuum pressure and source purity, both of which could be controlled to some extent. In the case of the more reactive materials studied, oxidation affects were still present at pressures in the 10^{-9} Torr range and were observed as changes in line shapes.

No facilities were available for measuring film thickness or rate of evaporation. The peaks due to Cr in the stainless steel substrate were usually used as a measure of successful evaporation. Once the peaks had disappeared due to a thin film overcoat, the power level for evaporation was determined. From that point on, successively higher evaporation currents were used as the source material was depleted. Since the penetration depth in SXAPS is only a few monolayers, and because the evaporation system was quite crude, it can be safely assumed that many atomic

layers were deposited with each evaporation and consequently, that new material was being studied with each evaporation.

A final point to consider here is the effect of the electron beam on the surface being studied. Park et al. (60) reported that the electron beam heating could be used to anneal a substrate and commented (16) on the extreme importance of the surface condition in SXAPS. On the other hand, using combined Auger and LEED studies, Florio and Robertson (61) have shown that the electron beam can seriously alter the surface being studied. Using a focused electron beam of 500 V and one μA for Auger studies, they found that up to 80 per cent of an adsorbed Cl layer on Si can be removed in about one hour. LEED studies of the affected area showed no recognizable pattern whereas moving to a new spot on the sample gave an ordered (1 x 1) chlorine structure. They further concluded that roughly one atom for every 10^4 electrons was desorbed. Similarly, Tracy and Palmberg (62) have reported that the electron-beam dissociative desorption of CO on (100) Pd, ejecting oxygen and leaving C, frustrated attempts to study CO coverages on the surface. They also observed thermal diffusion of C and S to the surface as a result of heating. Lambert and Comrie (63) studied the impact effects of a 1500 eV focused electron beam for CO coverage on (111) Pt. They concluded that the desorption rate was much faster than the dissociation rate and that most of the ad-layer disruption was due to relatively slow backscattered electrons rather than to the fast primary beam.

To try to eliminate the electron beam effects of thermal diffusion, dissociation, disorder, and desorption, the obvious approach is to reduce

the electron current and use a defocused beam. Defocusing in the above-discussed cases reduced the problems significantly and permitted more reliable Auger spectra. Less destruction in SXAPS, using beam currents of several microamps, has been achieved by building more sensitive detectors (42, 44). Andersson et al. (44) have reported SXAPS results for chemisorption of O on Ni. They observed a change in the oxygen feature upon increasing exposure to O which is interpreted as a transition from chemisorbed O on Ni to nickel oxide.

In this work, emission currents of a few mA were used for most metallic samples. For many of the insulators, reproducible spectra were obtained only for beam currents below one mA and it was felt that higher emission currents were destroying the films. For CsCl and LaF_3 some effects attributed to larger beam currents were observed and will be discussed in the data analysis.

CHAPTER IV. RESULTS AND DISCUSSION

The materials studied in this work can be grouped into three classes. They are: the transition metals, Cr, Y, Zr, Nb, and Mo; the rare earths, La, Ce, and Yb; and the insulators MnF_2 , CsCl , KCl , and LaF_3 . Some work was also performed on the alloy Ag + Mn (5%) and will be discussed with the transition metals. Since each of these materials requires special consideration in the analysis, their spectra will be discussed individually.

Transition Metals

The 3d transition metals have received the most attention of all materials studied by SXAPS. The reason for this is quite probably that these materials give relatively strong SXAPS signals. Park and Houston (3) have studied the series from Sc ($Z = 21$) to Ni ($Z = 28$), demonstrating the change in line shape as the 3d band is gradually filled. The effects of oxidation on Ti, Cr, Fe, and Ni have been reported (2, 60, 64-66). A comparison of the surface and bulk core-electron binding energies has been made for Ti, Cr, and Ni using SXAPS and photon-excited AES (67), and for Fe and Ni using SXAPS and XPS (58). The L_3/L_2 intensity ratio for Cr has been studied using SXAPS and Auger-electron APS (68). Studies have also been made on the transition metal alloys TiNi (69), and NiCu (70). Musket (71) has compared the sensitivities of SXAPS and AES to several of these materials as well as to S, C, and O. Tracy (14, 15) has studied the sensitivity of SXAPS to 3d and 4d transition metals and concludes that very little information about the conduction band density of states can be obtained from insulators, semiconductors, and 4d transition metals.

To this argument Park and Houston (72) responded with results for Nb and Si, although the Si results were not sufficiently resolved to compare with the predictions of the convolution model (73).

In Table 1 we summarize the existing SXAPS literature for the elements Ca ($Z = 20$) through As ($Z = 33$) for future reference. The number at the top of each column gives the reference number and an "X" indicates which materials were studied. In several cases the spectra were not actually shown and only references to the work exist. A similar table for the 4d elements would be nearly blank and this prompted our interest in these materials. Nb and Mo spectra have been reported, but only using second-harmonic detection and large modulation potentials (72). Pd was shown to give quite weak first-harmonic signals (15).

In this section we discuss our Cr results primarily to demonstrate the success of the one-electron theory for 3d transition metals. We then present our results for Y, Zr, Nb, and Mo and relate our observations to the problem of decreased SXAPS sensitivity to 4d transition metals.

Chromium

In Fig. 8 we show the Cr $L_{3,2}$ spectra of Houston and Park (64) for clean and oxidized Cr. The polycrystalline samples in that work were sputter-cleaned in situ and annealed using electron beam heating. Fig. 9 shows a Cr $L_{3,2}$ spectrum obtained from the stainless steel substrate used in our work and the Cr oxide spectrum of Fig. 8. The agreement of the two curves is nearly exact, both in energy and line shapes. We expect the Cr spectrum from our substrate to represent a compound of Cr, presumably

Table 1. Summary of SXAPS studies for the elements Ca ($Z = 20$) through As ($Z = 33$).

reference number	2	3	14	15	28	44	58	60	64	65	66	67	68	69	70	71
element																
Ca					X											
Sc		X														
Ti		X	X	X					X	X		X		X		
V		X														
Cr	X	X	X					X	X			X	X			X
Mn		X			X			X								
Fe		X	X	X			X	X			X					X
Co		X														
Ni		X	X		X	X	X	X	X			X		X	X	X
Cu			X	X											X	
Zn																
Ga			X													
Ge		(see ref. 16)														
As			X

Figure 8. SXAPS spectra for the $L_{3,2}$ excitations of Cr (ref. 64)

Figure 9. A comparison of our results for the $L_{3,2}$ excitations of Cr in stainless steel with the spectrum for oxidized Cr (ref. 64)

Cr_2O_3 (60), although such good agreement in the line shape between our data from stainless steel, and that from oxidized polycrystalline Cr, is probably coincidental, since changes in the Cr L_3/L_2 peak-height ratio were observed when stainless steel was heat treated (60). In our work also, the L_3/L_2 peak-height ratio varied from 1.1 to 1.3 for the Cr spectra obtained prior to sample evaporation for each cycle. The same substrate was used repeatedly and was chemically etched prior to loading. However, for every cycle the zero crossing of the Cr L_3 peak was at the same energy, 580.0 eV, so that after some time, a scan of this line was often used to confirm the proper calibration of the instrument.

It should be mentioned here that all the initial chart recorder energy scales have been shifted to correct for the filament work function (4.5 eV) and the thermal spread of the incident electrons ($2kT \approx 0.5$ eV). Thus a total of 5.0 eV have been added to all the energy scales of recorded data. A value of $2kT$ was also used to correct the original data of ref. 64 presented here in Figs. 8, 9, and 10.

Having established the agreement of our data with those of Houston and Park for the oxide of Cr, we now look at their Cr results in terms of the one-electron theory. Fig. 10 shows the results (64) for clean Cr along with the calculated spectra, using the absorption coefficient data of Fischer (74) and our Eq. (20) for the one-electron model. We have neglected the bremsstrahlung term in this calculation. Also shown in the figure is the derivative of the absorption coefficient. The latter has been convoluted with a gaussian of one eV half-width to represent SXAPS

Figure 10. A comparison of the L_{3,2} excitations for Cr (ref. 64) with the one-electron theory and $d\alpha/dE$ (ref. 74)

broadening. This broadening removes some fine structure in the main peaks, which, in the unbroadened derivative, is about 0.5 to 1.0 eV in width.

From Fig. 10 we see that both curves predict the observed splitting of the L_3 and L_2 peaks, but neither one gives the correct position of the peaks. The convolution model gives a peak-height ratio of 0.88 compared to the value of about unity for SXAPS. The dip between the peaks is quite shallow in the convolution model. The derivative of the absorption coefficient on the other hand gives the observed negative peaks but predicts a peak-height ratio of about 1.9, in fair agreement with the expected ratio based on the statistical weighting of $2j + 1$ for each level. For $2p_{3/2}$ and $2p_{1/2}$ this ratio is 2. Houston and Park (68) have commented on the departure from this value for the SXAPS intensity ratios. They observed the statistical value of 2 for the peak-height ratio when detecting the Auger electron current from the electron bombarded sample, and a ratio of nearly unity for the x-ray fluorescence (SAXPS) of the clean material. They concluded that the excitation of these levels follows the statistical $2j + 1$ weighting, but that the $2p_{1/2}$ hole is twice as likely to decay radiatively as is the $2p_{3/2}$ hole. This could also explain the different intensity ratios for SXAPS and $d\alpha/dE$ in Fig. 10

Consider now the function shown in Fig. 11, which represents a model density of states in Cr. We have a sharply peaked function, representing a narrow band of empty d states, on top of a broad, increasing function which represents the s-p conduction band. We have ignored the filled d states, which would appear as a second sharp feature below E_F , since they are not involved in the convolution. Fig. 11 also shows the self-convol-

Figure 11. Demonstration of the expected SXAPS line shape for a model density of states, using the one-electron theory

ution of the empty part of this model density of states and the derivative of the convolution as described by the one-electron theory. We expect this line shape for the SXAPS spectrum of a core-level excitation in a transition metal with a half-filled d band. We see that the width of the positive derivative peak resembles the width of the empty density of states. The line shape is asymmetric, having reduced negative intensity due to the contribution of the conduction band. Finally, the zero level, or background, is higher after the main feature due to the conduction band contribution. Some of these features are present in the spectra of Figs. 8, 9, and 10.

Comparing the two curves of Fig. 8, we see first, that the L_3/L_2 peak-height ratio changes from unity for the clean material to about 1.25 for the oxide. Also, the line shape for the oxide spectrum appears more symmetric, having larger negative peaks. The L_3 width at half-maximum increases from 2.5 eV for the clean Cr to about 3.3 eV for the oxide. Finally, the L_3 peak is shifted about 1.7 eV to higher binding energy in the oxide while the corresponding L_2 shift is about 1.2 eV. Since SXAPS is sensitive only to the surface atomic layers we expect that these changes can be explained in terms of changes in the chemical environment due to oxidation.

Upon forming the oxide, Cr_2O_3 , the Cr ion becomes trivalent, giving up three electrons. This transfer of charge to the oxygen ions means that the inner Cr core levels experience reduced outer screening and their wavefunctions are contracted somewhat. There is a corresponding increase

in the binding energy and this chemical shift may be slightly greater for the $2p_{3/2}$ (L_3) than for the $2p_{1/2}$ (L_2) core electrons since the latter are partially screened by the former. This difference could explain the unequal chemical shifts of the two core levels and, at the same time, means that the overlap of the two features increases which would cause an increase in the L_3/L_2 peak-height ratio as is observed. In forming the oxide, the local density of states will also be changed. We expect the number of d-symmetry states above E_F to increase, and a band gap is formed which, depending on the localized nature of the d orbitals, will reduce the amount of s-d mixing. The increased d-symmetry above E_F could be responsible for the increased width of the oxide spectrum in Fig. 8, while a reduction of the conduction-band mixing could explain the more symmetric negative peaks as discussed earlier in connection with Fig. 11. The introduction of a band gap may also cause an apparent chemical shift to larger binding energies as explained later in our discussion of insulators.

We turn now to a discussion of the various model calculations shown in Fig. 10. The substitution of the absorption coefficient for the true density of states could be the cause of the reduced negative peak in the convolution result of Fig. 10. The features of SXA are of about the same width as the SXAPS features using the threshold-to-zero-crossing distance. Yet the SXAPS spectrum has a negative peak which implies that, in the convolution model, the function involved must be somewhat more narrow than α . As mentioned earlier, SXA measures the s and d partial density of states. For the data used here (74) the resolution was about 0.8 eV, comparable to

the SXAPS data, although no correction was made to remove instrumental broadening. It is possible then that the density of states measured in SXAPS is in fact narrower than that measured by SXA or, in other words, SXAPS may be measuring only the d-like density of states. This strongly conflicts with the notions of the one-electron model, since electron scattering should not adhere to such strict selection rules. This discrepancy between theory and experiment is not yet understood.

Turning now to the peak positions of the various models, we see in Fig. 10 that the SXAPS peaks lie between the other two and somewhat closer to the $d\alpha/dE$ peaks. Part of this may again be attributed to broadening of the curves since a broadened SXA curve may shift the $d\alpha/dE$ peak to lower energy. At the same time, however, removal of potential-modulation broadening will shift the SXAPS curve to higher energy. The data of Figs. 8, 9, and 10 were recorded with 1.0 V_{pp} which is probably less than the d band width, and consequently quite reliable data are obtained based on the calculations of Fig. 6. The models, in spite of their shortcomings, give peaks within 1.5 eV of the observed peaks, which is perhaps the strongest argument in their favor.

We must remember in addition that SXA is a probe of the bulk material whereas SXAPS probes the surface. Houston et al. (67) have suggested that due to reduced coordination at a surface, the binding energy of a surface core level may be shifted about one eV to lower energy. Andersson et al. (44) have expressed concern about the accuracy of this theory based on their studies of O chemisorption on Ni. Perhaps the problem is merely one of

determining what part of the SXAPS line shape gives the core binding energy. Webb and Williams (58) have compared XPS results with SXAPS data for Fe and Ni. In XPS, the core-level line shape is measured, the peak of which determines the binding energy. We have so far assumed that the core line shape is represented by a delta function so the SXAPS binding energy will correspond to the threshold of our structure. This is often (3) determined by the intersection of a straight-line-approximation to the slope with the base line. Such determinations are consistently lower than the XPS values. On the other hand, if the increase of the density of states is very sharp at E_F , simulating a step function, the derivative of the core line shape will be measured and the SXAPS zero-crossing will determine the core binding energy. The correct binding energy will of course be somewhere between these two extremes. Webb and Williams (58) suggest that the core-state line shape is involved in SXAPS since the derivative of XPS data agrees quite well with SXAPS data for Fe and Ni in the threshold region. Since SXA is also a bulk probe, it should, according to the reduced-coordination theory, yield binding energies slightly larger than those measured in SXAPS. It also will include core line shape broadening. These arguments favor the convolution-model spectrum more than the $d\alpha/dE$ curve since the former has a higher threshold.

In summary, the SXAPS data of the Cr $L_{3,2}$ region can be qualitatively predicted using either the self-convolution model with the absorption coefficient, or the derivative, $d\alpha/dE$, of the absorption coefficient. The peak positions are in fair agreement, however, the line shapes are not well predicted by either model. The selection rules and bulk sensitivity in-

herent to SXA seem to play a secondary role when predicting the SXAPS spectra for Cr. It is quite likely that the models used here would be just as successful for all the 3d transition metals since the SXAPS spectra for these materials are quite similar.

Yttrium

Yttrium, the first of the 4d transition metals, was studied for several reasons. First, the soft x-ray absorption data for Y are somewhat limited, and it was felt that, in light of the possible connection between SXA and SXAPS, a study of Y films in ultrahigh vacuum would be useful. Second, in connection with the SXAPS results for La, to be discussed later, a study of Y would provide an interesting comparison since the outer electronic configuration of Y is similar to that of La with the exception of the low-lying 4f states in La. Finally, previous SXAPS work on the 4d transition metals, as discussed earlier, has met with limited success due to low signal strengths relative to those of 3d metals. This is not predicted by the one-electron theory as developed earlier since both 4d and 3d metals have large densities of unfilled states at E_F , which should lead to comparable signal strengths.

The Y data were obtained primarily from films evaporated at a pressure of $\lesssim 10^{-7}$ Torr using a W basket. The spectra were recorded within 15 minutes after evaporation at a pressure of about 6×10^{-9} Torr. Fig. 12 shows the $M_{3,2}$ region corresponding to excitation of the $3p_{3/2}$ and $3p_{1/2}$ core states, and Fig. 13 shows the $M_{4,5}$ spectrum corresponding to the $3d_{5/2}$ and $3d_{3/2}$ excitations. The $M_{3,2}$ spectrum was obtained with a modulation

Figure 12. SXAFS results for the Y M_{3,2} excitations

Figure 13. SXAPS results for the Y M_{4,5} excitations

voltage of $1.0 V_{pp}$ and an emission current density of $0.35 \times 10^{-3} \text{ A/cm}^2$, while the $M_{4,5}$ spectrum was obtained with $0.5 V_{pp}$ and $0.7 \times 10^{-3} \text{ A/cm}^2$. Thus, since the signals scale approximately with the emission current and the modulation voltage, the two spectra have about equal intensity. This is unexpected if the selection rules for dipole transitions were to apply, since the empty density of states is predominantly d-like. It indicates that the $3d \rightarrow 4d$ transition has about the same strength as the $3p \rightarrow 4d$ transition. Both transitions are much weaker however than the $2p \rightarrow 3d$ transitions of the 3d transition metals. Since the 3d and 4d elements of each periodic group have similar densities of empty states at E_F , the difference in measured intensities must represent a matrix element effect, not considered by the models of Chapter II. This will be discussed in more detail below.

In Figs. 12 and 13 the vertical arrows mark the atomic core-level binding energies (75). The vertical dashed lines mark our observed thresholds. In Fig. 12 the observed thresholds are at 296.0 and 307.0 eV for $3p_{3/2}$ and $3p_{1/2}$ respectively. In the $M_{4,5}$ spectrum a sharp threshold is observed at about 157.5 eV, in agreement with the $3d_{5/2}$ atomic binding energy. The shoulder at 161.5 eV is followed by a strong peak at 165.2 eV. One might associate this latter peak with the $3d_{3/2}$ excitation; however the evidence is strongly against such an interpretation. First, the XPS data (57) do not resolve the 3d splitting although the resolution there ($\sim 2.7 \text{ eV}$) is somewhat worse than ours ($\sim 1.0 \text{ eV}$). Second, the spin-orbit splitting based on these two thresholds would be 4.0 eV, much larger

than the tabulated value of 2.2 eV (75). Finally, and perhaps most important, as shown in Fig. 14, the shoulders in both the M_3 and $M_{4,5}$ spectra nearly coincide when the data are plotted as a function of energy above the threshold, E_T . All of this suggests that the peak at 165.2 eV may correspond to a density-of-states feature a few eV above E_F .

In a study of the alkaline-earth metals, Ca and Sr, Kanski (28) observed a line shape similar to our $M_{4,5}$ spectrum for the $M_{3,2}$ Ca and $M_{4,5}$ Sr core excitations. Using the one-electron theory, he points out that this extra peak above threshold can be attributed to transitions into the empty d bands above E_F . The top curve in Fig. 14 shows the $M_{4,5}$ spectrum of Sr measured by Kanski. The spin-orbit splitting is resolved, giving rise to the two step-like features. The main peak occurs about 6 eV above threshold. Exposure to oxygen produced no changes in these results and no aging effects were observed.

For Y the situation is not as clearly defined. As shown in Fig. 14, the $M_{4,5}$ spectrum has only a hint of structure at the proper spin-orbit interval and, considering the noise level as indicated by the vertical bar, the weak structure at 160 eV cannot be taken too seriously. The main peak is about 7.7 eV above threshold. It is not clear why we do not resolve the spin-orbit splitting for Y (~ 2.2 eV) while the Sr splitting (~ 1.9 eV) is well resolved. It does not appear to be due to instrumental limitations, since sharper features were observed for aged Y films as discussed below. One possible explanation is that the combination of final-state interactions together with the extra 4d electron in Y is sufficient to smear out the two thresholds.

Figure 14. Comparison of the above-threshold line shapes for the Y $M_{4,5}$ and $M_{3,2}$ excitations, and the Sr $M_{4,5}$ excitations (ref. 28)

To better understand the observed Y line shapes we return to the self-convolution model. In Fig. 15 we show a model density of states similar to that used for Cr, but with the empty d band peak about 3 eV above E_F , and we ignore completely the splitting of this d band for simplicity. We see that the derivative of the self-convolution (solid curve) now contains a weak peak at the position of the density of states maximum, followed by a stronger peak at higher energy. The first peak corresponds physically to the case when one electron is added to the localized d states while the stronger peak corresponds to both the excited core electron and the incident electron occupying d states.

With this model in mind, we return to the spectra of Fig. 14 and consider the M_3 excitation which is free of overlapping structure. Apart from the absence of a large negative peak, this line shape, using the self-convolution model, indicates a density of states maximum about 4 eV above E_F . This gives rise to the shoulder at 4 eV, followed by the maximum at 6.5 eV above threshold. The $M_{4,5}$ spectrum is more difficult to interpret due to the presence of overlapping core excitations, but it suggests that the d band maximum is shifted slightly to higher energy. This shift probably results from final-state interactions between the core hole and the 4d excited states. The created core hole alters the d band density of states because the effective nuclear charge is increased. Since the 3p electrons screen the 4d states more effectively than do the 3d electrons, the created 3p core hole results in a more positive effective nuclear charge, causing greater contraction of the 4d wavefunctions. Optical

Figure 15. Demonstration of the expected SXAPS line shape using a model density of states for Y

transmission measurements on thin Y films show a normal absorption band at 5.6 eV (76) which may be due to the empty d states above E_F . It is not known whether the absence of a core hole in the optical excitations is sufficient to explain this 1.5 eV shift to higher energy.

Characteristic energy loss measurements also have shown a peak at 4.0 eV which is interpreted as due to a surface plasmon (77). A bulk plasmon in Y is observed at 12.4 eV. Plasmon excitations have been observed by SXAPS for the K excitations of some light elements such as C and B (12, 13) and possibly for the $L_{3,2}$ excitations of Be, Mg, and Al (4, 5, 28). Very little has been said about the evidence of plasma excitations in heavier elements however. When a plasmon is excited by the incoming electron in SXAPS, we expect secondary structure at integral multiples of the plasma energy above the main peak. A surface plasma excitation of 4 eV could be responsible for the observed peak in Y or could at least cause an enhancement of this peak structure if it is due to the d band density-of-states maximum.

Returning to Figs. 12 and 13, we observe a noticeable difference in the agreement of the observed thresholds with the measured atomic core binding energies (vertical arrows). The $M_{4,5}$ values are in good agreement but the observed $M_{3,2}$ thresholds are about 4 eV too low. As discussed earlier for Cr, it is not unusual to observe lower thresholds in SXAPS. Here, however, the difference of 4 eV is much larger than the typical one eV observed for the 3d transition metals and often associated with a surface chemical shift. Based on the arguments of Webb and Williams (58),

the core line shape could be contributing more in the case of the $M_{3,2}$ spectrum. On the other hand, the similarity of the line shapes in Fig. 14 suggests that the core contribution is the same in both cases.

The study of these structures was somewhat hindered by two unrelated problems. In the $M_{3,2}$ region, the carbon K spectrum was observed to interfere considerably in the initial evaporations. Presumably the carbon diffused to the surface from the stainless steel substrate and to a lesser extent originated by deposition from the hot W filament. After several evaporations and prolonged heating of the substrate by electron bombardment this became less of a problem. Carbon is still evident in Fig. 12 in the form of a step at 283.5 eV. To demonstrate the problem here, the $M_{3,2}$ Y spectrum is repeated in Fig. 16 with a carbon K spectrum obtained from the back side of the substrate. The complex carbon spectrum has been studied quite thoroughly from both experimental (12, 13) and theoretical (78-80) standpoints. The important thing to note here is that it overlaps completely the region of interest for Y 3p excitations. Thus we cannot absolutely rule out a carbon contribution to the $M_{3,2}$ spectrum although the similarity of the line shapes in Fig. 14 suggests that the carbon only contributes the step at 283.5 eV in the $M_{3,2}$ spectrum.

The second problem encountered with the Y study was the changing background in the $M_{4,5}$ region. As shown in the complete spectrum of Fig. 17 and the expanded portion, Fig. 18, a broad feature around 135 eV made a determination of the true $M_{4,5}$ line shape more difficult. In addition, the rise at about 180 eV is not accounted for by Y transitions. The shape of

Figure 16. Comparison of a typical carbon spectrum with the $M_{3,2}$ spectrum of Y

Figure 17. SXAPS results for Y from 0 to 700 eV

Figure 18. Expanded low energy region of SXAPS results for Y

these features was somewhat dependent on the emission current density and perhaps may be due to space-charge effects. The sharp break at 157.5 eV was always observed at the same energy for freshly evaporated films however, and the line shape on this changing background always showed the shoulder discussed above. The slope of the background above 170 eV was dependent on the current density.

As mentioned in the experimental discussion of Chapter III, the electron beam can have damaging effects on the sample. A single film was exposed to a current density of about $0.7 \times 10^{-3} \text{ A/cm}^2$ for nearly a full day. The results are shown in Fig. 19. The M_3 structure is now clearly resolved into two peaks. The threshold has not shifted much, but is considerably sharper. In addition, a small bump appears at 305.5 eV. The M_2 features repeat this sequence at the correct spin-orbit splitting, 12.2 eV, with the notable exception that the M_2 peak is not resolved as a doublet. Similarly, the $M_{4,5}$ spectrum shows additional structure. It is not worthwhile to attempt an explanation of these features since the condition of the film could not be observed. Presumably, a combination of oxidation and electron beam damage are responsible for these changes since a fresh evaporation of Y restored the spectra to those shown in Figs. 12 and 13.

Finally we return to the discussion of signal intensity. Tracy (15) has commented on the low signal intensity of 4d metals compared to the 3d metals. In a study of the series Ca, Sr, and Ba, Kanski (28) could not obtain reliable 3p spectra for Sr, while Ca 2p excitations gave good

Figure 19. Effects of electron-beam damage on an Y film

signals. In addition he reported that the Sr 3d excitations gave better signals than the 3p excitations, in agreement with our observations for Y. We have observed that the La 3d and 4d core excitations give intensities much larger than those for the transition metals. In the latter case the explanation is found in the large oscillator strength for $d \rightarrow f$ transitions, resulting from significant overlap of the 4d and 4f wavefunctions. This will be discussed in connection with the La data.

Fig. 20 shows the radial portion of the Y and Sc one-electron wavefunctions (81), calculated for the neutral atoms, for the core states relevant to this discussion. The SXAPS matrix elements will involve transitions from core levels to conduction band states. To represent such states by atomic functions is certainly in error but an important point can be made. The overlap integral for the 2p and 3d wavefunctions of Sc, indicated in Fig. 20, is an order of magnitude larger than that for the 3p and 4d wavefunctions of Y due to the extra nodal surfaces of the latter. The difference in overlap should result in significantly different matrix elements which consequently modulate the amplitude predicted by the one-electron theory.

Low intensities are characteristic of the entire 4d series as indicated in Fig. 21. The $M_{4,5}$ spectra of Y, Zr, Nb, and Mo were measured using polished polycrystals and a four-sided sample mount. The Y polycrystal gave even weaker signals than did the Y films studied earlier. In addition, no comparison could be made for the $M_{3,2}$ region since the carbon signals were quite dominant as a result of the prior mechanical polishing.

Figure 20. One-electron wavefunctions for some atomic core levels of Sc and Y

Figure 21. Comparison of the $M_{4,5}$ spectra for bulk samples of Y, Zr, Nb, and Mo

The weak intensity of the 4d elements can also be explained using the fluorescence yield rather than the wavefunction overlap as a parameter. As pointed out by Tracy (15), the fluorescence yield, ω_{3p} , of the 4d metals is somewhat lower than ω_{2p} for the 3d metals. From Eq. (8) we see that a decrease in ω_{nl} means, for constant δ , a smaller change in the slope at threshold and thus smaller signals for SXAPS.

A study of the x-rays produced by the decay of the 3d core hole for 4d transition metals showed (82) that relative to the Mg K_{α} x-ray intensities, the 4d metals had $M\beta$ (M_5N_3) intensities of 30(Y), 35(Zr), 25(Nb), and 15(Mo) per cent. Also the intensity ratio of the $M\beta$ x-ray line to the bremsstrahlung continuum at 4.5 keV excitation energy was determined to be 120(Y), 95(Zr), 90(Nb), and 95(Mo). These data support the variation in intensity found for the SXAPS results of Fig. 21, which show a decreasing intensity as we go from Y to Mo. Such a tendency is also explained, of course, by the decreasing empty density of states above E_F .

In Table 2 the excitation threshold values observed for the Y films are presented and compared to the binding energies of ref. 75. It is not implied here that these thresholds represent the true binding energies of the core levels, but rather that the onset of transitions to E_F occurs at this energy. The true binding energy may be somewhat higher, depending on the relative contribution of the core line shape.

In summary, the similarity of the line shapes in Fig. 14 suggests for Y a density-of-states peak about 4 eV above E_F , or a characteristic loss feature of this energy, or possibly both. The 4d elements also have an

Table 2. Summary of SXAPS results for Y

	$M_{4,5}$	M_3	M_2
Threshold ^a	157.5 ^b	296.0	307.7
Shoulder ^a	161.5	299.5	-
Peak ^a	165.2	302.5	314.0
ref. 75	157.4 159.6	300.3	312.4
ref. 57	158.5	301.0	312.8

^aThe values for each feature were obtained from the spectra shown in Figs. 12 and 13.

^bAll energies listed are in eV.

$M_{3,2}$ intensity somewhat weaker than the $L_{3,2}$ transitions of the 3d transition metals. The 3p and 3d core levels of Y yield approximately the same intensity signals. These last two effects are probably due to intensity modulation by the transition matrix elements rather than to density-of-states effects.

Ag-Mn alloy

Much of the present work was intended to test the usefulness of SXAPS on materials other than pure metals. Alloys of transition metals have been studied previously (69, 70) and some recent work (83) has been done on the

transition-metal dichalcogenides, TiSe_2 , TiS_2 , and VSe_2 . We were interested in the dilute Ag-Mn alloy to see if SXAPS would reveal the presence of the Mn local magnetic moment.

An alloy of Ag + five per cent Mn was evaporated from a W basket onto the stainless steel substrate. A thick film was deposited initially to insure that the Mn atoms being probed were those of the alloy rather than those in the stainless steel. The absence of Cr peaks after evaporation was used as a measure of good coverage.

When Mn appears as a dilute impurity in Ag, the 3d electrons tend to align with their spins parallel. The spin-up and spin-down states are split in energy. A theory for the formation of such split, localized d states has been described by Anderson (84) and Wolff (85). For the case of Mn in Ag, the splitting is sufficiently large to pull half of the d states completely below E_F with the remaining states somewhat above E_F . The states are somewhat broadened due to their interaction with the noble metal conduction band continuum, but retain their local nature. Hence they are referred to as virtual bound states.

In terms of the one-electron theory of SXAPS then, the local density of states near a Mn atom in the Ag matrix, will have a peak in the density of empty states somewhat above E_F . The SXAPS line shape should then consist of a small positive peak at the threshold for excitation to the Fermi level, followed by a larger positive and then negative peak as the energy of the excited electron passes through the virtual bound states above E_F . If we assume that the virtual states are very localized, only excitations

of the Mn core states will have this line shape. However, if there is considerable overlap with neighboring Ag atoms, the excited Ag core electrons may also probe the virtual bound states.

The films were evaporated using a prepared bulk sample of five per cent Mn in Ag. We had no means of verifying the composition of the evaporated films. It was evident that Mn was present, after the heavy evaporation, while all traces of Cr were gone. Even with the presence of Mn, we cannot be certain that a dilute alloy was formed and it is possible that some clustering occurred. The films were exposed to electron beam heating as well as to radiative heating due to the W filament, so that some diffusion was conceivable. The evaporated films studied by Myers et al. (86) showed evidence of local moments so we assume that our evaporation scheme was capable of providing useful alloys.

The results are shown in Fig. 22. The solid line is the $L_{3,2}$ excitation of Mn and the dashed curve shows the results of Park and Houston (3) for pure Mn films. No Ag core-level excitations were detectable and only the Mn $L_{3,2}$ excitations gave reliable spectra. The intensity of these levels also was quite low, being somewhat weaker than the Mn lines of stainless steel which has roughly the same Mn concentration. The spectrum shown here was recorded in a vacuum of 10^{-9} Torr with 2 V_{pp} modulation, which probably broadened the true signal slightly, a current density of 1.6×10^{-3} A/cm², and a three second time constant at 12 db/octave. The increase in signal intensity over the background represents 0.4×10^{-6} V across a $10^6 \Omega$ load. The curve has been normalized in the figure to have

2

Figure 22. SXAPS results for the Mn $L_{3,2}$ excitations of dilute Mn in Ag

approximately the background levels of the dashed curve, providing a somewhat artificial estimate of the intensity of the dilute Mn as opposed to the pure metal. The most noticeable difference in the figure is a shift of 1.5 eV to higher energy for the alloy spectrum. The thresholds were determined here by the intersection of a straight base line and the average slope, extrapolated to the base line. The ratio of L_3 to L_2 peak intensity is 1.39 for the pure metal and 1.13 for the alloy, where peak intensity is measured for both L_3 and L_2 from the L_3 base line. It appears that the L_2 peak is sitting on a higher background for the alloy, and a correction for this is made by approximating an L_2 base line at half of the difference between the L_3 base line and the final background level. Doing this gives L_3/L_2 ratios of 1.6 for the alloy and the metal. The minimum after each peak appears shallower for the alloy. Also, although the peak separation is the same for both spectra, the threshold for L_2 appears to be better resolved for the alloy. These differences in line shape may be explained by the convolution model if the contribution from the conduction band density of states is greater for the alloy. This is expected based on a free electron-like conduction band, since, for the alloy, the virtual states above E_F would sit on a larger conduction band. The better resolution at the L_2 threshold could be explained if the threshold for excitation to E_F were providing a shoulder at the pure metal threshold. Such a step is not observed for the L_3 structure in this case.

Looking at other measurements of the dilute Ag-Mn system provides some input for our interpretation. The reflection and transmission of

thin evaporated films (86) show two small bumps below the Ag d band threshold which occurs at about 4 eV. These two features correspond to transitions from the occupied Mn d states to E_F and to transitions from E_F to the empty virtual states. One peak, at 3 eV, is relatively stationary for concentrations up to 15 per cent Mn. The other peak moves from 1.6 to 2.0 eV for five to 15 per cent Mn. Steel and Treherne (87) observed just the opposite direction of motion with increasing concentration for the low energy feature using an ellipsometric method on bulk specimens rather than films. The total splitting is thus on the order of five eV. Photoemission measurements are sensitive to the occupied Mn d states below E_F but cannot probe the upper states due to the limitations imposed by the alloy work function. A peak is observed (88, 89) at 3.0 eV below E_F . It has a 2 eV width at half-maximum and seems to contribute to the distribution curves over a range of 3.5 eV (90). Consequently the remaining peak in the optical data, centered near 2 eV, must represent the transitions from E_F to the virtual states. Since it was not possible to determine the composition of our alloy after evaporation, nor was it possible for the films studied optically (86), we cannot look for better agreement.

A final consideration increases the complexity of the analysis. We have assumed that only the 3d states of Mn are affected and that the binding energy of the Mn 2p core levels was that of the metal. This is obviously a bad assumption in light of the earlier discussion of chemical shifts, be they due to oxidation or reduced surface coordination. Furthermore, the effect of the noble metal host on the core levels cannot be

ruled out. All or some of these effects could account completely for the 1.5 eV shift of the threshold. It thus appears that better sensitivity is needed for this system so that the step at the threshold for excitation to E_F can be observed, if it exists. The position of the d-states peak with respect to this threshold is a more meaningful SXAPS parameter than the overall shift of the line shape. It is for this reason that we feel the Ag-Mn results are inconclusive.

Rare Earths

As mentioned earlier, our initial motivation for constructing the appearance potential spectrometer was to study La metal in the hope of locating the position of the empty 4f levels relative to the Fermi energy. The rare earths are unique in that the 4f levels being filled are quite well shielded from the chemical environment by the electrons in the $n = 5$ and $n = 6$ shells (91). Consequently, the entire row is characterized for the most part by common physical and chemical properties, one of which is their rapid formation of an oxide. To a surface sensitive technique, such as SXAPS, this is of major importance. Consequently, vacuum pressures in the low 10^{-10} Torr range are required to maintain oxide-free surfaces. In general, only photoemission systems have been capable of achieving such vacuums since most other techniques require monochrometers or x-ray sources which tend to limit operating pressures to the 10^{-8} Torr range or higher. The possibility of oxidation must then be considered for most of the available metallic rare earth data. Furthermore, since ultrahigh vacuums require that the system be baked, considerable problems can arise with the more

volatile rare earths such as Yb and Tm (92), which may sublime at normal bakeout temperatures below 10^{-7} Torr. Thus a compromise between low vacuum pressures and preservation of the evaporant must be reached. Such was the case for the Yb results presented here.

Appearance potential spectra have been obtained for several of the rare earths and we summarize these studies in Table 3. The numbers in each column give the reference. We make the distinction here between materials studied in pure metallic form and those studied as impurities in an alloy. We have also indicated the materials studied in our work. It is apparent that the elements of Table 3 consist primarily of the light lanthanides. This is not unexpected since the heavy lanthanides give weaker signals due to the filling of the 4f states. In addition, the resolution of SXAPS is not sufficient to reveal all the fine structure which results for the intermediate lanthanide 4d core excitations. It will be seen, however, that even the gross features have not been sufficiently well interpreted.

Lanthanum

We studied the SXAPS of La from 0 to 1400 eV. The films were evaporated from a W basket onto a stainless steel substrate with the pressure during evaporation below 1×10^{-8} Torr. Typically, the pressure dropped into the mid- 10^{-10} Torr range immediately after evaporation and all runs reported here as clean La were recorded within 15 minutes after evaporation. The spectra were reproducible for several hours after evaporation. The evaporant was electropolished just prior to loading in the system. An

Table 3. Summary of SXAPS studies of the rare earths

reference number	7	8	9	11	16	28	41	42	this work
element									
La		X ^a O ^b	X	X	O				X
Ce		O							X
Pr		O				X			
Nd		O			O				
Pm									
Sm	X				O	X	X	X	
Eu									
Gd			X		O				
Tb									
Dy									
Ho									
Er					O	X			
Tm									
Yb									X
Lu									

^aX = pure metal material studied.

^bO = alloy material studied.

earlier analysis of the La by a spark source mass spectrometer revealed that the highest impurity levels were due to Pr (15 ppm) and Gd (10 ppm).

In Fig. 23 we show the first-harmonic spectrum of La from 0 to 1400 eV, recorded with an emission current density of $2.8 \times 10^{-3} \text{ A/cm}^2$ at 1200 V, 0.75 V_{pp} modulation potential, and a one second time constant. The low energy region is characterized by a sloping background, due for the most

Figure 23. SXAPS results for La from 0 to 1400 eV

part to space-charge limited electron beam currents. For example, at 130 eV the current density was $1 \times 10^{-3} \text{ A/cm}^2$, down by a factor of three from the saturation value at 1400 V. Consequently the true spectrum in this space-charge region is somewhat distorted. A correction for this will be made later and, for the time being, it is sufficient to note that the peak positions are not shifted by this correction. In Fig. 23, the vertical arrows indicate the approximate atomic binding energies of the La, oxygen, and carbon core levels (75). It will be noted that very little carbon is present and no oxygen was detected with this sensitivity, even though the film was nearly two hours old and the pressure, due to electron beam heating, had risen to 1×10^{-9} Torr by the end of this 35 minute scan.

The relative intensity of the various core-level excitations is striking. The strongest signals are obtained for the transitions involving d-symmetry core states at 100 eV ($4d \rightarrow 4f$; $N_{4,5}$) and 830 eV ($3d \rightarrow 4f$; $M_{4,5}$), where we assume that the density of empty states is predominantly f-like. The next strongest excitations are the $N_{3,2}$ and $M_{3,2}$ which involve p-symmetry core states, and finally the N_1 and M_1 excitations which involve s-symmetry core states. Harte et al. (8) interpret this as evidence for a dipole selection rule in La and the other rare earths. This is somewhat disturbing since the incident electron is represented by a plane wave which contains all values of angular momentum and thus can satisfy conservation of angular momentum for all core excitations. As used so far, the one-electron theory of Eq. (20) cannot explain this intensity variation since the convolution integral involves only the density of empty states which, neglecting final-state effects, is the same for each

core-level excitation. Returning to Eq. (16) however, we see two aspects of this theory which could account for the intensity variation. First, the core-state population factor, N_c , gives the ground-state occupation number for each core level. This decreases from 10, for the d-symmetry core states, to 6, for the p-symmetry core states, and 2 for the s-symmetry core states. Also, the matrix element, $|M'|^2$ is expected to decrease in magnitude as we go from d- to s-symmetry initial states since the overlap of the core-electron wavefunction with the 4f wave functions (81, 93) is largest for 4d core states, and somewhat less for p- and s-symmetry core states. Of course, the actual matrix elements are only roughly predicted by this trend, but the Coulomb interaction term will enhance the strongly overlapping portions most because it is largest when $\bar{r}_1 \approx \bar{r}_2$, as seen from Eq. (15). Furthermore, the relative intensity of the $M_{4,5}$ and $N_{4,5}$ excitation is deceptive in Fig. 23 for two reasons. First, proper emission current normalization will enhance the $N_{4,5}$ region. Second, the spectrum represents a derivative of the total x-ray fluorescence yield. The total yield is more relevant for discussing transition strengths since there, the integrated intensity represents the total yield for a particular core-level excitation. If a particular core yield has an abrupt onset, the spectrum of Fig. 23 would show large peaks corresponding to large derivatives and not necessarily larger transition strengths. At any rate, Fig. 23, by itself, is not sufficient evidence for a dipole selection rule. We now turn to a discussion of the various core-level excitations beginning with the $N_{4,5}$ region.

N_{4,5} region In Fig. 24 we show the N_{4,5} region of the full La spectrum. The conditions were the same as those of Fig. 23 except that a 300 ms time constant was used to permit faster scanning. The clean film was ten minutes old at a pressure of 5×10^{-10} Torr at the conclusion of this run and its spectrum is shown as the solid curve. The dashed curve was obtained under similar conditions at somewhat higher pressures from an earlier evaporation. The vertical dash marks the atomic N_{4,5} binding energy (75) and the arrows pointing down show the positions of XPS peaks (57), corresponding to E_F relative to the 4d_{5/2} and 4d_{3/2} core states (94). The arrows pointing up indicate the observed peaks in the SXA of La (94-98). Spectra from our first films gave results like the dashed curve. However, after several evaporations were performed from the same La source, the spectra began to change. The minimum at 123 eV gradually filled in, eventually yielding the results of the upper solid curve with the new peak, labeled D in Fig. 24. In addition, the lower peaks were shifted to slightly lower energy and developed into the doublets labeled AA' and BB'. At the same time the spectra of contaminants diminished so that no oxygen and negligible carbon were detected.

We believe that the evaporant was the source of the contaminated material rather than simple oxidation after deposition. To test this idea, a new piece of La, prepared more recently, was used. The initial evaporation again resulted in spectra like the dashed curve of Fig. 24. However after only two evaporations, the upper curve results were obtained. The material first used had been exposed to air several times over a period of months. Although the sample was electropolished to provide a metallic

Figure 24. SXAPS results for the La $N_{4,5}$ region. The contaminated film results are from an earlier evaporation

luster, the bulk could have been quite contaminated. The fresh La sample, on the other hand, was presumably less contaminated. In presenting our data, we have no way of knowing that the contaminated films were primarily oxide and in fact, La quite readily forms hydroxides (99). Consequently, whether we refer to the material as oxide or contaminated, we mean simply not a pure metal.

In Fig. 24 note that the initial structure of peaks AA' and part of BB' lie below the XPS-determined threshold energies for $4d_{5/2}$ and $4d_{3/2}$ respectively. Also, most of the integrated intensity lies well above E_F . In Fig. 25 we show again the $N_{4,5}$ results for clean La (solid curve), the absorption coefficient, α , using the data of Rabe (95) (dot-dash curve), the derivative of α (dotted curve), and the derivative of the self-convolution of α (dashed curve). The latter should resemble the SXAPS spectrum as described by the one-electron model used earlier. The failure of this model is evident in Fig. 25 since none of the main features of the $N_{4,5}$ region are satisfactorily predicted. We have previously reported this discrepancy (100) and the discussion here will expand on that report.

We note that $d\alpha/dE$ peaks in good agreement with the main peak C. The low energy structure in $d\alpha/dE$ is, however, about five eV below the corresponding peaks in the SXAPS curve. Also, there seems to be corresponding structure in $d\alpha/dE$ for peak E, shifted to slightly higher energies.

To a large extent we can explain for La the breakdown of the self convolution model and the partial resemblance of the $d\alpha/dE$ curve. For most of the rare earths (94-98, 101) the SXA data show several small, very sharp lines below the expected $4d$ excitation threshold, and a very broad band,

Figure 25. Comparison of SXAPS model calculations for the La $N_{4,5}$ region

some 10 to 20 eV wide, above threshold. These results have been interpreted (91, 102-104) as being due to a dipole transition of the type $4d^{10}4f^N \rightarrow 4d^94f^{N+1}$. Several arguments (91) support this assignment. The one-electron wave function for the lowest energy 4f orbital of La (93) is bound inside the centrifugal potential barrier and greatly overlaps the 4d wave function. Since the higher energy f orbitals are not bound by this barrier, most of the absorption strength from the 4d shell will go into transitions to the 4f shell. Second, because of the large overlap of the 4d and 4f wave functions, the exchange interaction between the 4d core vacancy and the $4f^{N+1}$ configuration is strong. This interaction splits the final state configuration into a multiplet spread over 20 eV. Some of the levels are pushed below the ionization threshold while others are pushed far above it. Most of the d to f oscillator strength goes into the latter terms of the configuration which then autoionize to the configuration $4d^94f^N\epsilon f$, where ϵf is a continuum state. The strength of the broad peak above threshold is observed to decrease as the 4f shell fills from La (Z=57) to Lu (Z=71) (97). This is explained by the exclusion principle for the available f states. A sum rule, relating the line strength to the number of 4f vacancies has also been derived (91). The number of levels pushed below threshold increases to a maximum when the 4f shell is about half filled. These states are responsible for the sharp lines observed in SXA, many of which are too closely spaced to be resolved by SXAPS as will be seen in our Ce results. Calculations based on these arguments have been made using an L-S coupling scheme for the tri-positive ions (102-105). The agreement with SXA for solids is remarkably good. This is perhaps not

unexpected however since the relevant transitions are somewhat shielded from their environment by the centrifugal potential barrier and the outer shells. Furthermore, studies of the rare earth compounds reveal very similar SXA spectra (106), and in fact, the LaF_3 SXAPS spectra discussed in this work will be seen to resemble the La metal results.

We mention here for later reference that the same interpretation has been applied to the $M_{4,5}$ transitions of La (107). Here, however, the overlap between the 3d core vacancy and the 4f subshell is less and hence the exchange interaction weaker. The spin-orbit splitting in this case still dominates and the individual terms cluster about the two split levels.

Returning now to the one-electron SXAPS model, we see that an interpretation in terms of atomic-like transitions, including exchange interaction, rather than in terms of continuous interband transitions invalidates the assumptions on which the model is based. Matrix element effects cannot be neglected and the approximation $\alpha(E) \sim N(E-E_c)$ is no longer valid. It has been suggested (104, 108) that a similar interpretation be applied to the SXA data of transition metals for the $3p \rightarrow 3d$ transitions. Only in the case of Ca have these transitions been measured by SXAPS (28). In that case, the $M_{3,2}$ spectra were considerably broader than the $L_{3,2}$ spectra. The success of the self-convolution model for the $2p \rightarrow 3d$ transitions also indicates the secondary role of localized effects for the 2p core states in these metals.

We now consider the success of the absorption coefficient derivative in predicting the SXAPS spectra. For high incident electron energies ($\sim$ few keV) the inelastic scattering probability for electrons in a solid

target is often described using a dielectric description of the solid (109). Here, the electron energy loss spectrum is related to the dielectric constant of the material via the loss function, $\text{Im}(-1/\tilde{\epsilon}(\bar{q}, \omega))$, where $\hbar\bar{q}$ is the momentum transferred to the solid, and $\hbar\omega$ is the energy loss, ΔE . The energy loss probability for a single scattering event is given by (109)

$$P(\Delta E, \Theta) d\Delta E d\Omega = (e/(\pi\hbar v))^2 \text{Im}(-1/\tilde{\epsilon}(\bar{q}, \omega)) D/(\Theta^2 + \Theta_E^2) d\Delta E d\Theta.$$

Here, D is the thickness of the thin target, and v is the velocity of the incident electron which is then scattered by an angle Θ into the solid angle $d\Omega$. The parameter Θ_E is just $\Delta E/mv^2$. The complex dielectric constant is $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ so we have

$$\text{Im}(-1/\tilde{\epsilon}) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2).$$

For small scattering angles, Θ , we consider the limit of small $\bar{q}$ and relate $\tilde{\epsilon}$ to the optical dielectric constant,

$$\tilde{\epsilon}(0, \omega) = (n + ik)^2 \approx \lim_{q \rightarrow 0^+} \tilde{\epsilon}(\bar{q}, \omega).$$

In regions of strong absorption we may have $n \approx k$ while away from any strong absorption edges we have (110) $k \ll n$ so that $\epsilon_2 \ll \epsilon_1 \approx n^2$ and

$$\text{Im}(1/\tilde{\epsilon}(0, \omega)) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2) \approx 2k/n^3 = c/(n^3\omega) \propto (\hbar\omega),$$

and

$$\lim_{q \rightarrow 0^+} P(\Delta E, \Theta) \approx 1/(n\Delta E)^3 \propto (\Delta E).$$

With these assumptions we have the result that the probability for electron energy loss due to inelastic scattering is proportional to the absorption coefficient. The SXAPS technique measures the derivative of this probability and thus $d\alpha/dE$.

This development has many weak points which need to be mentioned. Principally, we have neglected the presence of the incident electron which is part of the final-state configuration in SXAPS, but leaves the solid in the energy loss measurements. We have also neglected final-state interactions although these will be partially included through $\alpha(E)$. These problems will be discussed below. There are also problems with the approximations for $\tilde{\epsilon}(\vec{q}, \omega)$. First, this description will break down at low energies when large angle scattering becomes important and the assumption of $q \rightarrow 0$ breaks down (25). Also, at low energies we may have strong absorption so that the assumption $k \ll n$ breaks down. At higher energies this is not usually the case though since

$$k = (\hbar c)/2(\hbar \omega) \alpha \lesssim 10^{-5}/10^2 \cdot 10^6 \sim 0.1$$

The assumption for $q \rightarrow 0^+$ is only appropriate for direct interband transitions and breaks down when indirect transitions are involved.

Despite all of these approximations, the agreement between optically determined loss functions and the results of energy loss measurements is quite good (109), even far above threshold excitation. A direct comparison of α with energy loss measurements is, however, not as reliable due to the variation of n and k in regions of strong absorption. As a reminder of this weakness we have retained the dependence on n in the above develop-

ment. By way of example, Trebbia and Colliex (111) have studied the electron energy losses in the range of 120 to 190 eV and small scattering angles for several of the rare earths. The results agree qualitatively with the SXA measurements (96, 97, 101) and the atomic oscillator strength calculations (102). We thus have reason to expect qualitative agreement between SXAPS and $d\alpha/dE$.

We are still faced, however, with the presence of the extra electron in SXAPS which is not present in the final-state configuration of either SXA or energy loss measurements. We consider the following picture. Let the initial state of the system consist of the N-particle crystal ground state and the state of the extra, or incident electron. Based on our earlier discussion of the localized nature of the $4d \rightarrow 4f$ excitations in rare earths, we assume that the final state of the system consists of the excited N-particle system, that is, a single excited ion in the crystal, plus the state of the extra electron far from that ion and not interacting with it. Thus the extra electron goes into an N+1-particle state on a different ion. We would then measure the derivative of the "electron-excited" absorption coefficient in SXAPS.

Returning to Fig. 25 we note several similarities between SXAPS and the dotted curve, $d\alpha/dE$. Both curves show the broad band present above threshold and peaking at 115 eV. The SXA data have two sharp peaks below threshold at 97.2 and 101.7 eV (95). The SXAPS data have a threshold at 97.2 eV, and the two peaks, A' and B', occur with the same relative splitting although they are at somewhat higher energy. The secondary splitting, AA' and BB' is not explained by SXA results.

The difference between SXA and SXAPS must reflect the presence of the extra electron in the $N+1$ -particle state, where we still assume a non-interacting scheme. Wendin (112) has developed this two density of states model to explain the SXAPS results of Ba (28, 52). In that case the $N+1$ -particle $4f$ states are some 10 eV above E_F . Liefeld et al. (113) have observed a single peak about 5.5 eV above E_F in the continuum isochromat and short wavelength limit (SWL) spectra of La. They attribute this to a preferential scattering into $4f$ states above E_F . As suggested by Kanski (28) we use these spectra as an approximation to the $N+1$ -particle density of states. Then, when a particular term of the $\text{La}^{3+} 4d^9 4f$ configuration is excited with fixed energy, E_p , the scattered non-interacting projectile electron scans through the $N+1$ -particle density of states as E is increased. When its energy, $E - E_p$, is sufficient to penetrate the centrifugal barrier of the empty $4f$ states on the neighboring ion, there will be an increase in the total yield due to the preferential scattering into these states. Based on the isochromat measurements (113), this would occur about 5 eV above E_F .

In Fig. 25 we observe a step at 97.2 eV which we interpret as the excitation threshold E_p for the 3P_1 state (103) in agreement with SXA (95). This is followed by the pair of structures A and A' at 101.4 ($\Delta E = 4.2$ eV) and 102.7 ($\Delta E = 5.5$ eV). One or both of these may correspond to the preferential scattering into $4f$ states just mentioned. The threshold for the 3D_1 term at 101.3 eV is obscured by peaks AA' but the peaks BB' occur at 105.5 ($\Delta E = 4.1$ eV) and 106.9 ($\Delta E = 5.6$ eV) eV respectively. The symmetry of AA' and BB' seems to rule out the possibility that A corresponds to E_p for the 3D_1 term, although a 3D_1 threshold in this region, similar to the one

at 97.2 eV, may be responsible for the reduced resolution of A and A'.

These results are summarized in Table 4.

In the contaminated film spectrum of Fig. 24, the two low energy peaks are observed without splitting. The threshold has shifted to higher energy, 98.3 eV, and two peaks occur at 102.9 eV ($\Delta E = 4.7$ eV) and 107.6 eV. The main peak, C, is considerably sharper in this case. Nilsson et al. (52) attribute a similar narrowing for the case of Ba to the loss of outer charges to oxygen atoms. For La_2O_3 , charge from the 6s and 5d shells is lost so that the conduction band screening of the 4d vacancy is reduced. The 4d and 4f orbitals see a stronger potential and shift inward. This corresponds to an increase in binding energy but at the same time the 4f states are moved closer to the continuum at E_F . Thus the increasing energy shift of the $N_{4,5}$ threshold is more than that of the 1P_1 resonance position, which then appears sharper. We see in Fig. 24 that the minimum following peak B occurs about 1 eV higher for the oxide while the main peak C appears not to have shifted at all. The loss of transition strength above C reflects the loss of conduction band channels for the autoionization of the 1P_1 resonance.

As a test of the above, non-interacting picture we show in Fig. 26 the convolution of α with the SWL spectrum using the data of Rabe (95) and Liefeld et al. (113) respectively. As expected, the two low energy peaks are reproduced without the fine structure. The surprising result is the shift of the main peak into agreement with our peak D rather than peak C. It becomes apparent that the non-interacting model works well only below threshold. Since the main peak, C, is predicted by $d\alpha/dE$, we arrive

Table 4. Summary of results for the La $N_{4,5}$ spectrum

SXA ^a peaks (eV)	$d\alpha/dE^a$ peaks (eV)	SXAPS peaks (eV)	ΔE^b	
			SXA	$d\alpha/dE$
97.2	97.0	97.2 ^c	0	0.2
		A 101.4	4.2	4.4
		A' 102.7		
101.3	101.0	-	-	-
		B 105.5	4.2	4.5
		B' 106.9	5.6	5.9
117.5	115.2	C 115.0	-2.5	-0.2
		D 120.5	3.0	5.3
	132.5	E 127.3	-	-5.2

^aUsing the data from ref. 95.

^bThe ΔE values are the differences between the SXAPS values and the SXA and $d\alpha/dE$ values respectively.

^cThis is a threshold value. All the other SXAPS values are peak positions.

at the following picture for the non-interacting scheme. Below threshold, the bound state terms of the configuration have fixed energy, E_b , and the scattered electron carries off the excess energy $E-E_b$, scanning the $N+1$ -particle density of states. Above threshold, the transition strength is almost exclusively in the 1P_1 resonance. The excess energy is carried off, not by the scattered incident electron, but by the excited core electron, as in SXA, in the excitation to the $4d^9 4f$ configuration which then auto-

Figure 26. Comparison of the La $N_{4,5}$ SXAPS spectrum with the two density of states model calculation

ionizes to the $4d^9 4f$ configuration. This virtual, non-energy-conserving process is characteristic of the autoionization process (114). The peak D could then be a replica of the main peak, C, resulting from the 1P_1 resonance. On the other hand, no replica similar to peak D is found in the Ce $N_{4,5}$ spectra. This will be discussed later. Other explanations have also been offered for the La $N_{4,5}$ structure (9).

To complete the picture we must also consider the case when the projectile electron interacts with the excited ion configuration. The two density of states model is no longer appropriate and we must consider the final-state configuration $4d^9 4f^2$. Chamberlain and Baun (7) interpret the $M_{4,5}$ Sm SXAPS using an interacting picture which is more appropriate to excitation of the 3d shell and will be discussed with the La $M_{4,5}$ results.

The configuration $4d^9 4f^2$ is what we expect for the excited tri-positive Ce ion in the non-interacting scheme. However, the Ce SXA shows much more structure below threshold than is observed for La. The atomic calculations (102, 104) for Ce also predict this additional fine structure. Wendin (112) showed that the addition of an extra 4f electron to a neutral Ba atom in the $4d^9 4f$ configuration caused the maximum in the 3d-4f radial overlap to shift downward approximately 2 eV toward the threshold. This may be a less appropriate consideration when the exchange interaction is stronger, namely in the 4d region. On the other hand, for La the nuclear charge is one less than for Ce so that even with the exchange interaction the number of multiplet terms pulled below threshold could be reduced. We suggest that the splitting AA' and BB' may be explained by the interacting scheme, and our Ce results will show even stronger evidence for this interpretation. The

splitting does not appear to be due to a mixture of pure metal and oxide since the splitting appears simultaneously with the filling in of the high energy minimum of Fig. 24. Also, the relative intensity of the two components is always the same, and the peaks for the oxide are shifted to about 0.5 eV higher energy. If Wendin's scheme is applied to La we would expect to obtain a spectral shift of 1.4 eV to lower energy for the negative La ion in the configuration $4d^9 4f^2$. Peaks A and B would correspond then to the interacting case while A' and B' belong to the non-interacting case.

In Chapter III it was stated that the geometry during evaporation was such that some contamination of the photocathode could occur. This effect was later reduced by using a more restrictive mask which allowed deposition only in the center of the substrate. Then the substrate completely prevented direct access by the evaporant into the detector. However, during the La runs shown here, this was not the case. To confirm that the extra peaks A and B were not due to self-absorption effects by La on the photocathode, the entire system was disassembled and chemically etched clean. A new photocathode was constructed and freshly prepared La was electropolished and loaded immediately into the system. The first evaporation yielded spectra identical to the contaminated spectrum of Fig. 24. For the second evaporation, asymmetry was evident already on the low side of A' and B'. For the third evaporation, the peaks A and E were clearly resolved from A' and B' and the high energy region had filled in as the main peak C broadened. We are thus confident that self-absorption due to detector contamination cannot be the cause of the observed splitting.

It was mentioned earlier that the $N_{4,5}$ spectra were somewhat distorted due to the non-constant emission current in the space-charge region. It seems a good approximation to say that the total yield, Y , is related to the total photocurrent, S , by

$$Y(E) = S(E)/I_{em}(E),$$

where I_{em} is the emission current at a given energy. In the experiment we measure dS/dE and $I(E)$. Now we have

$$dY/dE = \frac{1}{I_{em}} (dS/dE) - \frac{S}{I_{em}^2} (dI_{em}/dE).$$

By fitting a curve to the emission current readings and integrating the measured spectrum (dS/dE) to obtain $S(E)$, we can compute a corrected spectrum. An uncertainty in this method is the constant of integration for $S(E)$ which would represent an additional term to be subtracted. We have assumed this constant to be zero here. In Fig. 27 we show the measured spectrum for clean La (dashed line) and the current-normalized spectrum (solid line) using the above equation. As expected, the main effect is to give additional weight to the low energy region where the original current was smaller. We note that the high energy region still remains positive, due to the background emission of bremsstrahlung. Also, none of the major peak positions have been shifted. In this curve, the emission current changed from 2 mA at 95 eV to 3.4 mA at 140 eV. No such correction is necessary for the $M_{4,5}$ spectrum which, at 800 eV, is well beyond the space-charge region.

Finally, for the $N_{4,5}$ region, we present, in Table 5, a summary of existing data for the La $N_{4,5}$ region. The references are listed across the

Figure 27. Comparison of the measured La N_{4,5} spectrum with the emission-current normalized spectrum

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Table 5. Summary of some existing data for the La 4d core excitations.
All data represent peak positions (eV) unless otherwise noted.

Experiment Reference	ATOMIC 75	XPS 57, 94	XPS 115	EMIS ^a 116	SXA 94, 98	SXA 96, 97	SXA 95
Spectral designation							
N ₅ O ₃				78.5			
N ₄ O ₃				80.0			
N ₄ O ₂				81.2			
satellite				90.0			
3P ₁				97.3	97.4	97.3	97.2
3D ₁				101.7	101.8	101.6	101.7
4d _{5/2}	98.9	102.8	103.7				
[3P ₁]*							
? ^b					103.7	103.7	104
4d _{3/2}	98.9	105.5	106.6				
[3F ₁]*							
1P ₁				115	118	117	117.5
[1F ₁]*							
?					124.5		
?				127			
?							
?					135	137	133
?				143			
?				159			

^aSoft x-ray emission.

^bUnidentified peaks.

^cT = Threshold.

Theory 102	Theory 103	Theory 104	Theory 105	APS 11	APS 9	APS our work	APS our work (oxide)
97.2	^{96.9} 97.2	97.1	98.4	96 (T) ^c	97.5 (T)	97.2 (T)	98.2 (T)
101.3	^{101.1} 101.3	101.3	103.8				
				103	102.5	^{101.4} 102.7	102.9
				107	106.8	^{105.5} 106.9	107.6
117.0	115.3	117.7	121.2	116	115	115	115.3
	119.9			123	121	120.5	
						127.8	
						138.8	130.5
							140

top with the type of measurement. Where possible, the data have been arranged to demonstrate the relationship between techniques. Only a brief comment will be made here regarding these measurements.

The XPS technique measures the core line shape as determined by the escaping core electron. It thus determines E_F relative to these levels and does not see the same final-state-interaction effects. There is a one eV discrepancy between ref. 57 and ref. 115. Both measurements indicate a spin-orbit splitting of about 2.8 eV. The SXA data have already been discussed. The only disagreement appears on the high energy side of the 1P_1 peak. Some of these weak structures may be attributed to sample contamination.

The columns headed "Theory" give the atomic calculations for SXA results. For the APS results the notation $[^3P_1]^*$ corresponds to the peaks AA', and so on for peaks B and C as noted. We rule out the possibility of Ce impurities for our peak D at 120.5 eV but cannot rule out the possibility that peaks D and E result from the final-state configuration $4d^9 4f^2$ in La which is a Ce-like state. As will be seen later, the main peak in the $N_{4,5}$ SXAPS results for Ce occurs at 120 eV. We would expect the $4d^9 4f^2$ configuration of La to be less bound.

The x-ray emission data (116) have an interpretation based on the SXA data. The coincidence of emission peaks with SXA peaks may be due to absorption and re-emission by the various multiplets as explained in the reference. The higher energy emission lines are relatively strong and, surprisingly, occur above the ionization threshold. They may also be connected with the broad absorption band.

M_{4,5} region In Fig. 28 we show an expanded plot of the M_{4,5} spectrum for La. The solid curve represents the clean material while the dashed line is for a contaminated surface. As before, the vertical dashed lines mark the atomic binding energies of the 3d_{5/2} and 3d_{3/2} core states according to ref. 75. The arrows pointing down mark the XPS core binding energies (57). Note that a doublet was observed there. This has not been well explained and may be due to contamination (49, 117, 118). The arrows pointing up mark the observed absorption peaks (119). The data of Fig. 28 were obtained with an emission current density of about $1.0 \times 10^{-3} \text{ A/cm}^2$, 0.5 V_{pp} modulation amplitude, and a one second time constant, with a freshly evaporated film. The noise was about equal to the width of the drawn line and the full scan took five minutes. In the figure we observe structure on the low energy side of both lines and an apparent threshold at 829.8 eV. The asymmetry in the negative portion of each feature of the solid curve may be due to oxidation or other contaminating surface compounds. This is more evident in Fig. 29 where the negative asymmetry has now developed into a shoulder. Note in this figure the correspondence between the shoulder in the upper solid curve and the negative dip of the oxide (dashed) curve. Such a line shape can be generated using two gaussian peaks of different relative intensities separated by one to two eV. Murthy and Redhead (9) observed an actual peak here, which we believe just represents a larger relative concentration of oxide. We cannot state with absolute certainty that this structure is due to partial oxidation but the data support such an interpretation. The lower solid curve in Fig. 29 is

Figure 28. SXAPS results for the La $M_{4,5}$ region

Figure 29. First- and second-harmonic spectrum for the La $M_{4,5}$ region

the second-harmonic spectrum, which verifies the existence of structure below the main peak. In such a curve, the negative peaks should correspond closely to the peaks in the total yield curve. In Fig. 29 the upper solid curve was obtained with $0.5 V_{pp}$ modulation amplitude, a 300 ms time constant, and a current density of $1.8 \times 10^{-3} \text{ A/cm}^2$ from a 30 minute old film at a pressure of 1×10^{-9} Torr. These results suggest a chemical shift, upon oxidation, of about 1.5 eV. Again it must be recalled that the curve labeled as oxide in these figures resulted from the initial evaporation rather than from exposure to oxygen and thus may not truly represent La_2O_3 , but rather some other La compound which formed on the evaporant after the electropolishing and during the initial pumpdown.

Fig. 30 shows the $M_{4,5}$ spectrum for clean La (solid line), the derivative of the absorption coefficient, α , using the data of Bonnelle et al. (119), and the derivative of the self-convolution model, using α for the density of states. For the convolution model, the threshold level was set at the onset of structure in α . Use of a slightly larger value, near the first peak for example, might be more reasonable but seems quite arbitrary. Two calculations were made, the first involving the self-convolution of α for the entire region, and the second, a convolution of the M_5 and M_4 regions separately. This last method eliminates contributions which result from the mixing of the two regions and gives a much broader M_4 peak. The interesting thing here is that the first peak in the M_4 region does not change position while the second peak does. This is due to the choice of the low energy cutoff, that is, the threshold energy. For a peak at a

Figure 30. Comparison of SXAPS model calculations for the La $M_{4,5}$ region

fixed energy E above threshold, the convolution gives two peaks, one near E and a second near $2E$, as shown in Fig. 15. This is the case for the M_4 convolution in Fig. 30. The first peak for both M_5 and M_4 in the one-electron model agrees quite well with the secondary structure on the low energy side of the SXAPS curve. This is also the case for $d\alpha/dE$.

We have already discussed the role of exchange in the $4d \rightarrow 4f$ transitions for the rare earths. Sugar (107) has performed the analogous calculation for the $3d$ core excitations. Since the exchange interaction is weaker here, the spin-orbit splitting still dominates. The results of the calculation agree quite well with the observed photoabsorption (119) so we rely again on this final-state-interaction picture.

It appears in Fig. 30 that the best agreement with $d\alpha/dE$ would be obtained if our results were systematically 2.7 eV too high. This is unlikely, however, in view of our good agreement with other SXAPS results for La (8, 9, 11). Although absolute calibration was a problem for us, this difference is well outside our uncertainty of ± 0.5 eV. We observed that the $d\alpha/dE$ peaks were below SXAPS peaks for the Cr results also, and, as discussed there, this cannot be explained in terms of a surface chemical shift.

The absorption data show a weak peak at about 830 eV followed by a strong peak at 834.9 eV (119). The M_4 region has one strong peak at 350.9 eV. In the SXAPS results we have a threshold at 829.8 eV which we associate with excitation of the 3P_1 level. A second threshold occurs at 832.2 eV which we assign to the onset of the stronger 3D_1 level. Finally, in the M_5 SXAPS spectrum we observe a third threshold at 834.8 eV. Recalling that SXAPS measures the differential yield, the zero crossing of this third

feature represents a peak in the x-ray yield. This occurs at 837.5 eV, too high to be associated with the 3D_1 level and thus represents an additional feature, which peaks 4.3 eV above the 3D_1 threshold in our spectrum. This main peak is probably associated with the 4f states above E_F as for the $N_{4,5}$ region of La. The negative portion shows a change of slope at about 840 eV. This could possibly be due to partial oxidation. Murthy and Redhead (9) observe a peak at this energy, 6 eV above threshold. We note that this depression occurs 5.2 eV above our third threshold at 834.8 eV. There may be a connection between this structure and the x-ray emission data of Mariot and Karnatak (120) which show a weak satellite at 840.6 eV, 5.9 eV above the main emission line at 834.7 eV. The latter is in good agreement with the absorption line of Bonnelle et al. (119), which implies that we are dealing with the same configuration in both absorption and emission experiments. That is, the initial x-ray emission state is the same as the final absorption state. The emission data also show an asymmetry on the low energy side of the M_5 line which Mariot and Karnatak (120) attribute to de-excitation of 4f states lying at or just below E_F . Liefeld et al. (113) observe a low energy satellite at 830.8 eV about 2.7 eV below their main emission peak. Both of these low energy structures may correspond to the absorption peak at 830 eV due to the 3P_1 4f level. However, Liefeld et al. (113) observe a satellite below the M_4 line which Mariot and Karnatak (120) do not see. This suggests that another interpretation is needed for Liefeld's data.

The absorption data have a single peak in the M_4 region at 850.2 eV. We observe a threshold at 848.5 eV which, to be consistent, we assign to

the 1P_1 level. A second threshold is observed at 851.5 eV. This main peak has a zero-crossing at 854 eV, 5.5 eV above the M_4 threshold. The M_4 region also has the depression above the main peak at 856.6 eV. The two structures may be related as for the M_5 region.

In Table 6 we summarize these data as was done for the $N_{4,5}$ region, with the implication that horizontal rows correspond to the same type of excitation. We denote in this table the thresholds, peaks and zero-crossing points of the SXAPS signals. All other measurements are peak positions. The XPS values were observed as doublets and represent the core binding energies. Such doublets were also observed in XPS studies of La halides (49, 117, 118). The emission data suggest, as do the values of ref. 75, that the 3P_1 level lies below E_F relative to the $3d_{5/2}$ state and the 3P_1 level is above E_F . The 1P_1 level is somewhat above E_F relative to $3d_{3/2}$.

We note from Figs. 28 and 30 that $d\alpha/dE$ predicts relatively equal intensities for the M_5 and M_4 regions while we measure a two to one ratio for the main peaks. However, the low energy shoulders which we attribute to the 3D_1 and 1P_1 levels do have roughly equal intensities as predicted by $d\alpha/dE$. The main peaks of the contaminated spectra, contrary to our observations for Cr, maintain the same peak intensity ratio as the clean material, suggesting an insensitivity to chemical environment. This supports their association with the shielded 4f states.

The actual mechanism involved in these 4f excitations is not well understood. Using our model of a non-interacting final-state electron, these peaks are explained as for the $N_{4,5}$ region. That is, about three eV

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Table 6. Summary of some existing data for the La 3d core excitations.
All data represent peak positions (eV) unless otherwise noted.

Experiment Reference	ATOMIC 75	XPS 57	Isoch. 113	EMIS ^a 39	EMIS ^a 120	SXA 39	SXA 119
Spectral designation							
$3P_1$			830.8	828.3 830.5		829.7	830.0
$3D_1$			833.5	834.2	834.7	833.3	834.9
$[3D_1]^*c$							
$[3D_1]^*$							
$[3D_1]^*d$							
$3d_{5/2}$	831.7	835.4					
satellite		839.4			840.6		
? ^e			847.2				
$1P_1$			849.5	850.5	850.8	849.3	850.9
$[1P_1]^*c$							
$[1P_1]^*$							
$[1P_1]^*d$							
$3d_{3/2}$	848.5	852.3					
satellite		856.3			856.6		
?							

^aSoft x-ray emission.

^bSecond-harmonic spectrum negative peak positions.

^cThreshold value.

^dZero crossing of main peak.

^eUnidentified peaks.

Theory 107	$d\alpha/dE$ 119	SXAPS 8	SXAPS 9	SXAPS our work	SXAPS our work (oxide)	SXAPS ^b our work 2 ω
829.7	829.7	830.0 ^c		829.8 ^c	832.5 ^c	
834.2	833.8		832.5 ^c	832.2 ^c		834.6
				834.8	835.5	
		835	836.1	836.5	838.1	
		836.4	837.2	837.5	839.2	837.8
			840.0	840.0		841.5
850.2	850.0			848.5 ^c	848.5 ^c	851.5
				851.5	852.5	
		850.7	852.8	853.0	854.3	
		852.5	854.1	854	855.8	854.3
			856.1	856.7		857.4
				862.5		

above the energy necessary to excite the various multiplets of the tri-positive ion, we see an enhancement due to interaction with the 4f states on neighboring atoms. For the M_4 region only one level is involved and the separation between the 1P_1 threshold and the resonance zero crossing is 5.5 eV. For the M_5 region there are two levels involved but we do not observe a doublet for the resonant peaks.

As mentioned earlier, Chamberlain and Baun (7) have suggested an interacting picture for the final-state electron in their analysis of the $M_{4,5}$ Sm SXAPS. In this scheme, the excited core electron and the incident electron form a negative ion bound state on the excited ion, being bound by the centrifugal potential barrier, and the ion with a 3d core hole. One electron then decays radiatively to fill the core vacancy with the emission of a nearly monochromatic x-ray and the other electron decays to the conduction band. For the Sm M_5 excitation two emission lines result, a lower line due to the characteristic radiation (valence band $\rightarrow$ $3d_{5/2}$ hole) and a nearly monochromatic x-ray line due to the transition, $4f \rightarrow 3d_{5/2}$. The M_4 region does not show such a doublet. The M_5 resonant line is some 2eV above the M_{α} line yet it is not clear that the 4f states are this far above E_F for Sm. For La we do not observe such a doublet even though the 4f states are thought to be above E_F . The La M_4 results suggest that the main resonant line in the M_5 region corresponds to the 3D_1 term being excited, since the zero crossing points occur about 5.3 eV above the 3D_1 and 1P_1 thresholds. The lowest term, 3P_1 , may also exhibit a resonance some five eV above threshold which overlaps with the 3D_1 excitation and cannot be distinguished.

Other La core levels The N_3 , N_2 , N_1 , M_3 , and M_2 core-level excitations of La were also observed. In Fig. 31 we show the $N_{3,2}$ region for both clean and contaminated films. There is an apparent chemical shift of about one eV to higher energy for the contaminated film. This film resulted from the initial evaporation. The N_2 and N_3 features are not clearly separated in either curve. It is apparent, however, that a strong x-ray fluorescence exists for both regions above the tabulated binding energies. This is very likely connected with the 4f states above E_F although we cannot pick out the initial threshold for the clean material. For the contaminated film, the 4f excitation has a threshold about 6 eV above the step at 187 eV. It should be noted that no significant final-state interactions are expected here since the 4p-4f overlap is small relative to the cases just discussed and the exchange interaction is much weaker. The 4f states should thus contribute a single peak to the density of states above E_F as is observed.

We have also observed some structure on the high side of the positive N_3 peak but cannot make an identification at the present time. Murthy and Redhead (9) observed additional structure in this region which they attributed to Cl contamination.

In Fig. 32 we show the M_3 , M_2 , and N_1 core-level excitations. In all cases there appears to be a step followed by a peak. The distance between the step and the peak threshold varies significantly however. In the N_1 spectrum some carbon also showed up indicating possibly a contaminated surface. The vertical lines indicate atomic core-level binding energies (75).

Figure 31. SXAPS results for the La $N_{3,2}$ region. The contaminated film results are from an earlier evaporation

Figure 32. SXAPS results for the La M₃, M₂, and N₁ regions

It appears that for the $n = 4$ shell the $4f$ peaks lie further above the atomic binding energies of Bearden and Burr (75) than do the corresponding peaks for the $n = 3$ shell. We can understand this in terms of the inner screening provided by the core electrons for the outer $4f$ orbitals. The $n = 3$ shell provides more screening than does the $n = 4$ shell so that a vacancy in the $n = 3$ shell would allow the $4f$ electrons to see a deeper potential well. The orbitals would move to smaller radii and thus move closer to the continuum threshold. This trend is observed throughout our rare earth data.

In summary, we have shown that the SXAPS data of La are not well explained by the one-electron theory. Most of the structure observed can be understood using a picture where the incident electron is a passive probe which causes excitation of the core levels similar to the photoabsorption process. The $4f$ levels, about five eV above E_F for the $N_{4,5}$ excitations and somewhat less for the $M_{4,5}$ excitations, cause some of the $d\alpha/dE$ peaks to appear at higher energies in SXAPS. Finally, certain features suggest that the incident electron can also interact with the excited core electron to form the configuration $nd^9 4f^2$ which is like the photon-excited Ce configuration and should show related effects.

Cerium

The SXAPS results for Ce were obtained using evaporated films of metallic Ce. The films were evaporated from a W wire basket at pressures below 1×10^{-8} Torr and all spectra reported here were obtained at a pressure of 3×10^{-10} Torr or lower unless otherwise noted. A spark source mass spectrometer analysis of the bulk Ce indicated no impurities above 15 ppm.

The evaporant was electropolished and loaded within 15 minutes thereafter.

Fig. 33 shows the SXAPS spectrum of a freshly evaporated Ce film from 0 to 1400 eV. As before, the vertical arrows indicate atomic core-electron binding energies (75). The sensitivity has been reduced by a factor of three compared to Fig. 23 to show the strength of the $M_{4,5}$ lines compared to the $N_{4,5}$ region. No oxygen and very little carbon is evident. Signals were observed for the N_5 , N_4 , N_3 , N_2 , M_5 , M_4 , M_3 , and M_2 core excitations although not all of these are evident in this figure. The observations made regarding line intensities for the La spectrum apply also to Ce. In addition we note that for La, the excitations occurred somewhat above the tabulated core binding energies while for Ce they tend to occur closer to or below the binding energies of Bearden and Burr (75). Looking ahead, we can say that this is a consequence of the 4f orbitals being closer to E_F .

As for La, the gaseous Ce atom is trivalent. The atomic configuration for Ce is that of Xe plus $4f5d6s^2$. The ion in the metal then is thought to contain one 4f electron. However Ce also has a tetravalent state (121) in which the single f electron also is lost. Thus we have two oxides for Ce, Ce_2O_3 , as for La, and CeO_2 . This additional complexity for Ce has revealed itself in much of the experimental data. For example, only Ce of all the light rare earths, shows major changes in the absorption spectra when exposed to air (101, 119). The studies of Fischer and Baum (39) revealed no such changes for Ce but they did occur for Yb, which also has two different valence states. Due to the vacuum conditions for many of these measurements it is quite possible that these changes reflect the difference between CeO_2 and Ce_2O_3 rather than between metal and oxide. We will discuss the evidence for this statement later.

Figure 33. SXAPS results for Ce from 0 to 1400 eV

N_{4,5} region In Fig. 34 we show the N_{4,5} region for what we feel is the clean trivalent Ce metal. By this we mean that there is a localized occupied 4f orbital on each ion. The binding energies, based on XPS results (57), of the 4d_{5/2} and 4d_{3/2} core states are indicated by the arrows pointing down. The lower portion of this figure shows an expanded spectrum of the N_{4,5} fine structure region, and the arrows pointing up mark the energies of observed SXA peaks (95, 101). The SXAPS results are quite complex compared to La and our resolution is insufficient to isolate all the expected lines. The main features do resemble La, however, in that we have a region of weak fine structure followed by a large broad band above the expected N_{4,5} threshold. The lower curve of Fig. 34 is an average of five separate runs, each on a freshly evaporated film. Consequently we will not give much attention to the finer details which may result from this averaging process. The most reproducible features consist of the threshold at 100.7 eV, a weak peak at 103.2 eV, three stronger peaks at 105.0, 107.2, and 110.0 eV and a weaker broad peak at 112.6 eV. In addition, the features at 101, 106.3, 108.2, and 113.7 eV may be significant. This low energy region is followed by a large broad peak at 120.1 eV. We do not observe a peak analogous to peak D in La (Fig. 24) but, as shown in Fig. 35, we do observe the filling of a minimum upon successive evaporations. In this figure the film labeled as contaminated resulted from the initial Ce evaporation. After a few more evaporations the solid curve was obtained. At the end of our studies the vacuum chamber was filled with oxygen to a pressure of 10⁻³ Torr and then pumped out again. The lower broken curve resulted. We note that the depression near 128 eV has returned. There are

Figure 34. SXAPS results for the Ce N_{4,5} region

Figure 35. SXAPS results for the $N_{4,5}$ region of Ce. The contaminated film results are from an early evaporation and the clean film results are from a later evaporation. The clean film was exposed to oxygen to get the results in the oxide spectrum

no major changes in these three curves in the fine structure region except possibly a chemical shift in the threshold to about 0.5 eV higher energy for the lowest curve (oxide) and a shift of one eV for the middle curve (contaminated). The number of peaks remains constant although their relative intensities have changed somewhat. Based on these results we feel that the solid curve in this figure represents a clean metallic surface. In Fig. 36 we compare the SXAPS results to the absorption coefficient, α , using the data of Rabe (95). Also shown are the derivative of α and the derivative of the self-convolution of α as prescribed by the one-electron theory. This last curve shows a peak in agreement with our main peak at 120.1 eV but also predicts a larger peak at higher energy. This is due to the existence of a large peak in α above the chosen threshold, which produces the double peak structure as was noted earlier in the Y and La discussions. The feature at 110 eV in the convolution curve would vanish if E_F were chosen to be a few eV larger. This sensitivity to E_F reflects on the fact that for Ce some 4f states lie just below E_F .

The SXA results have been explained (91, 104) quite satisfactorily using the concept of exchange-induced multiplet splitting due to the large spatial overlap of 4d and 4f wavefunctions. This was already discussed for La so we proceed to see how well the SXA data describe the SXAPS results. The $d\alpha/dE$ curve in Fig. 36 has been broadened with a 0.5 eV half-width gaussian to represent the SXAPS energy broadening. The $d\alpha/dE$ curve predicts a threshold at about 100 eV, followed by peaks at 101, 103.1, 105.5, 107.8, 109.8, and 111.2 eV. The main peak is predicted at 118.5 eV somewhat below our main peak. Due to the large number of lines observed below threshold

Figure 36. Comparison of SXAPS model calculations for the $N_{4,5}$ region of Ce

in SXA, it is quite difficult to be as conclusive about the correspondence between SXA and SXAPS. By correlating the peaks in $d\alpha/dE$ with the peaks in α , and then comparing to the SXAPS results, a tentative assignment can be made. This has been done in Table 7. The conclusion reached is that the peaks in SXAPS lie about 2.1 eV above their corresponding optical partners in $d\alpha/dE$. We note that some of the shoulders shown in Fig. 34, and noted by an S in Table 7, also fit into this scheme. This correspondence has been made on the assumption that our peaks should lie above the optical peaks for two reasons. First, the La results indicated such an analysis might also apply to Ce. Second, Chamberlain et al. (122) have made a series of studies on Ce, similar to their La studies (113), which suggest a peak in the density of states about 2.7 eV above E_F . These results from SWL measurements, and the appearance of a low energy satellite about 2.5 eV below the M_{α} and M_{β} emission lines, prompted the assignments in Table 7. Since several of the weaker shoulders in the SXAPS spectrum also fit into this same scheme, we feel that improved energy resolution in SXAPS will reveal additional structure. To eliminate possible doubts regarding the assignments in Table 7, we have averaged the ΔE values both with and without the weak structures indicated by an S. The difference in both cases is only 0.1 eV in the average separation. Part of the individual deviations from the average values reflects on the sharpness of the peaks in SXA and the broadening used for $d\alpha/dE$. For example, with one eV broadening the three peaks corresponding to G, K, and L for $d\alpha/dE$ begin to merge into one peak at 109.5 eV. The value of $\Delta E = 2.1$ eV agrees quite well with the results of Chamberlain et al. (122).

Table 7. Tentative interpretation of the fine-structure region in the $N_{4,5}$ SXAPS spectrum of Ce

	SXA ^a peaks (eV)	$d\alpha/dE^a$ peaks (eV)	APS peaks (eV)	ΔE^b	
				SXA	$d\alpha/dE$
A ^c	101.25	101	103.2	1.95	2.2
B	103.48	103.1	105.0	1.52	1.9
C	104.56	10	104.5 (S) ^d	1.74	1.8
D	105.77		106.3 (S)	1.43	1.7
E	106.06		107.2		
F	106.58	106.3 (S)	108.2 (S)	1.62	1.9
G	108.06	107.8	110	1.94	2.2
H	108.93				
J	109.70				
K	110.36	109.8	112.6	2.24	2.8
L	111.52	111.2	113.7 (S)	2.18	2.5
Total Average ΔE^e				1.8	2.1
Partial Average ΔE^e				1.9	2.2

^aData from ref. 95.

^b $\Delta E \text{ SXA}(d\alpha/dE) = \text{SXAPS} - \text{SXA}(d\alpha/dE)$.

^cSee ref. 101 for letter designation and ref. 102 for spectral term designation.

^dS = Shoulder.

^eTotal Average ΔE = average of all eight values.

Total Partial ΔE = average of peak values only.

We are left with the principal failure of the $d\alpha/dE$ curve in predicting the main SXAPS peak at 120.1 eV. We have noted that no bump analogous to peak D in the La spectrum occurred for Ce. One possible explanation now seems evident. Arguing from the good agreement for La between the main peak in $d\alpha/dE$ and the main SXAPS peak, it is possible that the main Ce

SXAPS peak results from two peaks which are not resolved, one near 118.5 eV and a second at about 2 eV higher energy. However, we expect that our resolution would reveal such a separation. Even the second-harmonic spectrum reveals only a slight change of slope in the region of the main peak.

An alternative explanation is provided by the interacting electron picture discussed earlier for La. We assume that peak D in La corresponds to the case where both the excited core electron and incident electron occupy 4f orbitals on the excited ion. This configuration is $4d^9 4f^2$. The corresponding configuration in Ce is $4d^9 4f^3$. It may be that this configuration with an unpaired 4f electron is not bound by the Ce ion potential. Then the non-interacting picture would prevail and no satellite peak would result. It is impossible to correlate this picture with an observation of fine splitting as was done for the subthreshold multiplets in La. This idea could be verified by studying other rare earth $N_{4,5}$ spectra. Using this pairing argument, we would expect satellites for Pr and Pm but none for Nd and Sm. Of course, as we increase Z , the 4f states move closer to E_F and the satellite merges into the main resonance.

We also have performed a convolution based on the two density of states model of Wendin (112). Here, the SWL data of Chamberlain et al. (122) were used to represent the $N+1$ -particle density of states on neighboring atoms which is probed by the scattered incident electron in the non-interacting picture. The absorption coefficient data of Haensel et al. (101) were used to represent the density of final states on the excited Ce ion. The results are shown in Fig. 37. Above threshold, as for La, the agreement is not exact. Below threshold, the results do not resemble the multiplet structure

Figure 37. Comparison of the Ce N_{4,5} SXAPS spectrum with the two density of states model calculation

observed and show instead something resembling a doublet. The thresholds, however, are in good agreement. The broadening which results from this convolution indicates that in this model, a sharper 4f peak may be needed for the Ce N+1-particle density of states. It is perhaps just a coincidence that this result resembles data to be presented later where a doublet was actually observed for Ce.

In Fig. 38 we show the results of correcting the Ce $N_{4,5}$ region for a non-constant beam current due to space-charge buildup. The analysis is the same as was discussed for La and the effect is to give more weight to structure observed with lower beam currents. No peak positions are significantly altered by this normalization process.

In Table 8 we summarize some of the 4d core-excitation data for Ce from XPS, emission, and absorption measurements. As for La we note some disagreement for the XPS core binding energies. The Ce data of ref. 115 may be more reliable since the resolution and vacuum conditions were somewhat better there. Also, for Ce, there may be a slight multiplet splitting which has not yet been completely analyzed (115). This splitting is more evident for heavier rare earths and is associated with the partially filled 4f shell. As for La, the emission data (116) show strong, low energy lines probably associated with the filling of 4d holes by 5p core electrons ($N_{4,5} \rightarrow O_{2,3}$). The peaks at 103.1 through 121.7 eV correspond quite well with absorption lines (106) and may be due to absorption followed by re-emission. The 4f splitting may also be responsible for some of the higher energy lines since the main absorption peak extends to nearly 150 eV. The theoretical values in the table come from atomic calculations (102) for the

Figure 38. Comparison of the measured Ce N_{4,5} spectrum with the emission-current normalized spectrum

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Table 8. Summary of some existing data for the Ce 4d core excitations.
All data represent peak positions (eV) unless otherwise noted.

Experiment Reference	ATOMIC 75	XPS 57, 94	XPS 115	EMIS ^a 116
Spectral designation ^c				
N503				83.6
N403				85.9
N402				87.0
satellite				95.0
4F(3/2)				
2G(7/2)				103.1
4G(7/2)				
4G(7/2)				105.3
4G(5/2)				106.2
4H(7/2)				
4D(3/2)				
4D(7/2)				
4F(7/2)				109.7
4H(7/2)				
2G(7/2)				
4d(5/2)	110.0	110.0	108.6	
4d(3/2)	110.0	117.7	111.5	
2G(7/2)				
2D(3/2)				121.7
2D(5/2)				
2F(5/2)				
2F(7/2)				
?				128
?				134.5
?				157
?				167

^aSoft x-ray emission.

^b $\Delta E = \text{SXAPS} - d\alpha/dE$.

^cN503 = N₅O₃, etc. 4F(3/2) = ⁴F_{3/2}, etc. 4d(3/2) = 4d_{3/2}, etc.
? = unidentified peaks.

^dA shoulder rather than a peak is observed at these values.

^eOnly one peak is observed, presumably because of broadening.

SXA 101	SXA 96, 97	Theory 102	$d\alpha/dE$ 95	SXAPS our work	ΔE^b
101.25		101.8	101.2	103.2	2.0
103.48	103.1	103.5	103.2	105.0	1.8
104.56	104.1	104.4	104.2 ^d	106.3 ^d	2.1
105.77	105.4	105.7	105.5	107.2	1.7
106.06	106.2	106.0			
106.58	107.3	106.8	106.4 ^d	108.2 ^d	1.8
108.06	107.9	108.2	107.7	110.0	2.3
108.93	108.6	108.8	108.75		
109.7	109.4	109.5			
110.36	110.2	110.1	110.0	112.6	2.6
111.52	111.2	111.7	111.2	113.7 ^d	2.5
121.7 ^d		$\left\{ \begin{array}{l} 120.4 \\ 124.4 \\ 124.8 \\ 125.3 \\ 125.4 \end{array} \right\}$	116.75		
124.3 ^e	125 ^e		118.2	120.1	1.9
	146 ^d		122.7		
			129.5		

tri-positive ion, which assume that the optically excited configuration is $4d^9 4f^2$. We have listed in Table 8 only those strong lines in the calculations which correspond to the observed absorption. In fact, a total of 24 lines are predicted (102). The peak values listed for $d\alpha/dE$ are the unbroadened derivative peaks obtained from the data of Haensel et al. (101). Even here, the average ΔE value for the differences between SXAPS and $d\alpha/dE$ peaks is 2.1 ± 0.5 eV so the broadening has little effect on this average separation determination. We thus conclude that the Ce $N_{4,5}$ SXAPS results are well explained in terms of the final state $4f$ multiplet splitting, and a $4f$ density of states peak on neighboring ions about 2 eV above E_F , using the non-interacting picture for the scattered incident electron.

$M_{4,5}$ region In Fig. 39 we show the $M_{4,5}$ spectra for a clean metallic Ce film. The lower curve shows the second-harmonic spectrum corresponding to the second derivative of the total yield. The dashed vertical lines mark the atomic core binding energies (75), and the arrows pointing down mark the XPS peak positions (57). The lower arrows show the peak positions for absorption measurements (119). A triplet is observed in SXA for both the M_5 and M_4 regions, however in the M_5 region the second and third peaks are of equal intensity and just barely resolved. In the M_4 region the three SXA peaks are successively stronger as one goes to higher energy. The second derivative curve in Fig. 39 indicates only two SXAPS peaks in the M_5 region and three in the M_4 region.

In Fig. 40 we repeat the clean $M_{4,5}$ spectrum (solid curve) and show a spectrum for our initial evaporation which, in connection with the $N_{4,5}$

Figure 39. First- and second-harmonic spectra in the $M_{4,5}$ region for a clean Ce film

Figure 40. SXAPS results for the $M_{4,5}$ region of Ce

interpretation, we assume to be contaminated. This curve shows a definite asymmetry in the negative peak which may be attributed to the appearance of an additional shoulder in the total yield at slightly higher energy. In the lower curve of Fig. 40 we show the spectrum of a clean film exposed to oxygen at a pressure of 10^{-3} Torr for about an hour. The spectrum is similar to that for clean Ce with the exception of the additional structure in the negative portion of both the M_5 and M_4 peaks. The arrows at the bottom of the figure mark the peak positions in the absorption data of Bonnelle et al. (119) for Ce exposed to air. They attribute this rearrangement of peaks to the formation of CeO_2 . Our oxide spectra do not show the additional peak which they observe at 905.6 eV and furthermore, the weak structures below each main peak still resemble the clean Ce spectrum. We conclude that the additional two small peaks may instead signal the formation of Ce_2O_3 on the surface. Such an interpretation seems somewhat speculative but there is evidence that the oxidation process for Ce may depend on the oxygen exposures involved. Helms and Spicer (123) have performed ultraviolet photoemission studies which suggest that, at low exposures, Ce_2O_3 is the stable oxide and that it forms a somewhat protective non-metallic layer, through which oxygen must diffuse to reach the bulk. On the other hand, they suggest that at larger exposures CeO_2 is the stable phase and that it is a non-protective oxide. It is not at all clear which situation applies here, so we use the $N_{4,5}$ region as a guide. After the heavy exposure to oxygen, the $N_{4,5}$ region (Fig. 35) still showed the five peaks below threshold which are indicative of the tri-positive Ce ion.

Thus we conclude that the exposure to O_2 led to the formation of Ce_2O_3 which, if quite protective and thin, may have allowed the incident electron to probe both oxide and clean metal. However this would imply that the protective layer is at most a few monolayers thick, since the 900 eV electron has a short mean free path for inelastic scattering. Another possible explanation is that we have a very small concentration mixture of CeO_2 in a matrix of Ce_2O_3 . The CeO_2 ions have the slightly larger binding energy due to reduced outer shielding. The situation here is not well understood, however, since Suzuki et al. (49) suggest that Ce_2O_3 resulted when Ce was exposed to air. Their XPS spectra in the region of 4d excitations had similar features for this oxide and for CeF_3 which differed from their CeO_2 spectra. This suggests, in agreement with our data, that Ce_2O_3 is the more stable phase for large exposures.

In Fig. 41 we show the spectrum for clean Ce (solid curve) and the derivative of the absorption coefficient, using the data of Bonnelle et al. (119) (dashed curve). We have also performed the self-convolution of α , based on the one-electron theory, and show the derivative of the self-convolution (broken line). The initial peak in each region of the convolution model is in fair agreement with structure in the SXAPS results. The remarks made earlier for the La results apply also to the convolution for Ce. We show only the results of the individual M_5 and M_4 convolutions. The results of the $d\alpha/dE$ curve indicate, however, a picture somewhat different from that for La. We note first of all that for La, $d\alpha/dE$ had about equal M_5 and M_4 intensities while for Ce the ratio is almost 1.5, in agreement with the statistical population of 6 to 4 for the $3d_{5/2}$ and $3d_{3/2}$ core states. Second, for La we had one extra structure in the SXAPS

Figure 41. Comparison of SXAPS model calculations for the $M_{4,5}$ region of Ce

results for both the M_4 and M_5 regions. For Ce we resolve two peaks in the M_5 region and two peaks with a low energy shoulder for the M_4 region. The $d\alpha/dE$ peaks are about 1.5 to 2.0 eV below the SXAPS peaks. Upon closer examination of the M_5 region, the third peak in α appears only as a change of slope in $d\alpha/dE$ near the zero crossing at 881.5 eV. This is even less evident in the SXAPS curve of Fig. 41, but the second-harmonic spectrum does indicate a slope change at 883.3 eV in Fig. 39, which is more evident in an expanded plot. Thus, for Ce we have an equal number of structures for SXAPS and $d\alpha/dE$. These results are repeated in Table 9. We see there that the initial structure for both the M_5 and M_4 regions in SXAPS occurs about 1 eV above a peak in $d\alpha/dE$, while the second and third structures, counting the slope change for M_5 , in SXAPS occur about 1.8 eV above a peak in $d\alpha/dE$. This comparison indicates that the initial structure in both regions is somewhat different from the other two. The latter two structures are consistent with the non-interacting electron picture if we place a 4f density of states peak about 1.8 eV above excitation threshold in the $N+1$ -particle density of states. The $N_{4,5}$ results suggested a value of 2.1 eV above threshold for this 4f peak. This difference between the $n = 3$ and $n = 4$ shells is consistent with the observation made earlier for La that the $n = 4$ shell structures were consistently further above the tabulated binding energies than were the $n = 3$ features.

The major difference between our La and Ce results in both the $N_{4,5}$ and $M_{4,5}$ regions is that for La it was necessary to consider an extra mechanism to explain additional features not observed in the absorption

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Table 9. Summary of some existing data for the Ce 3d core excitations.
All values listed are peak positions (eV) unless otherwise noted.

Experiment Reference	ATOMIC 75	XPS 57	Isoch. 122	EMIS ^a 39	SXA 39	SXA 119
Spectral designation ^d						
$2D_{3/2}, 2D_{5/2}$			879.5			879.3
$2G_{7/2}$			882.0	880.4	881.3	881.5
$2G_{7/2}, 2D_{3/2}$						882.2
$3d_{5/2}$	883.3	882.6				
satellite		886.3				
$4H_{7/2}$						896.4
$2G_{7/2}$			897.8			898.0
$2F_{5/2}$			900.8	899.1	899.3	899.0
$2D_{3/2}$						
$3d_{3/2}$	901.3	901.2				
satellite		904.8				

^aSoft x-ray emission.

^b ΔE = SXAPS peak value - $d\alpha/dE$ peak value.

^cSecond-harmonic spectrum negative peak values.

^dSpectral designations are from ref. 119.

^eA shoulder or change in slope.

Theory 119	$d\alpha/dE$ 119	SXAPS 119	ΔE^b	SXAPS our work (oxide)	SXAPS ^c our work 2 ω	SXA 119 (oxide)
879.5	878.5	879.4	0.9	879.5	879.7	
881.4	880.5	882.0	1.5	882.0	882.6	881.8
882.2	881.5 ^e	883.3 ^e	1.8		882.8 ^e	
		885		884.5		883.7
896.3	896.0	897.1	1.1	897.3	897.6	
897.7	897.4	899.3 ^e	1.9		898.9	
899.0	898.3	900.2	1.9	900.3	900.8	901.4
899.5						
	905.2	903	-2.2	902.5		905.6

data. For the $N_{4,5}$ region we observed the extra peaks A, B, and D which we attributed to the interacting scheme with a configuration $4d^9 4f^2$. For the $M_{4,5}$ region we observed an additional strong peak attributed to the same configuration. For Ce, however, no such additional peaks are evident. This lack of extra structure for Ce in both regions may indicate that the interacting picture for Ce, with the configuration $4d^9 4f^3$, is energetically unfavorable and that the additional nuclear charge of Pr is needed to bind the unpaired 4f electron.

Table 9 summarizes our $M_{4,5}$ results and lists the peak values observed in the XPS, x-ray emission and SXA experiments. The XPS results show doublets for the $3d_{5/2}$ and $3d_{3/2}$ core levels. As for La, these doublets may be due to oxides or halides (49). The x-ray emission data suffers heavily from self-absorption effects and inspection of the data (39) shows close correspondence between emission and absorption features. As for La, the isochromat results (122) show low energy satellites. The La results suggested that these were not due to self-absorption. They are attributed to resonant scattering into empty 4f states which are apparently below E_F since they occur below the M_α and M_β emission peaks (122). Fischer and Baum (39) suggest on the other hand that the M_α and M_β lines observed under minimal self-absorption conditions are actually $4f \rightarrow M_{4,5}$ transitions rather than valence $\rightarrow M_{4,5}$. For La and Ce we expect these to occur at higher energy than the true $M_{\alpha,\beta}$ transitions since the 4f states are above E_F . This does not seem to explain the isochromat satellites, since the average separation between the satellite and main peak is 2.5 eV for La and 2.7 eV for Ce. This means that the 4f states are the same

distance above E_F for both La and Ce. Since the SWL (122) spectra indicate that this is not the case, we conclude that the satellites are not related to the 4f states in the manner suggested.

Other Ce core levels In Fig. 42 we show the spectrum of the N_3 , N_2 , N_1 , and M_3 Ce core excitations. The upper curve shows the $N_{3,2}$ region which resembles the La $N_{3,2}$ region in many ways. The N_3 excitation has a threshold just above 195 eV followed by a peak at 205.8 eV. The fine structure in the threshold region and the shoulder on the positive peak were reproducible but have not been interpreted. We note that the peak lies relatively close to the atomic core binding energy (75) indicated by the arrow. The N_2 excitation overlaps to some extent the N_3 spectrum and is somewhat weaker. We can identify the main N_2 peak at about 221 eV, below the tabulated atomic core binding energy (75).

Very little information can be obtained from the N_1 spectrum shown in the middle of Fig. 42. Based on our experience with La, and the sensitivity used to obtain this spectrum, we believe the first peak at 288 eV is associated with the N_1 excitation. The remaining structure may be associated with carbon contamination of the surface.

For the M_3 excitation, there is a shoulder resembling a threshold at 1173 eV, followed by a threshold at 1175.7 eV for the main peak. Such structure may be an indication of the onset of transitions to 4f states 2.7 eV above E_F . A similar interpretation could be made for the shoulder in the N_3 spectrum. There the two thresholds occur at 201 and 203.8 eV, with a separation of 2.8 eV. Such an interpretation is somewhat arbitrary,

Figure 42. SXAPS results for the Ce N_3 , N_2 , N_1 , and M_3 regions

however, due to the structure below 200 eV. We did not study this region in any more detail.

Ce (IV) As was pointed out earlier in this discussion, the 4f orbital of Ce is just sufficiently bound to make the Ce ion trivalent. Vickery (124) points out that of all the lanthanides, Ce is the only one which can give rise to a stable $4+$ ion. He suggests that it is no more difficult to remove the 4f electron than it is to remove the 5d or 6s electrons. During our study of Ce it became evident that for a short time, at least, the surface of our film consisted of Ce^{4+} ions. The conditions which prompted this valency change are not clear. Three evaporations had been made and the $N_{4,5}$ spectra recorded after each consistently showed the five peaks below threshold as discussed above. The fourth evaporation yielded spectra like the dashed curve shown in Fig. 43. The pressure during evaporation did not rise above 9×10^{-9} Torr, and dropped immediately thereafter to 1.5×10^{-10} Torr. This process was repeated three more times and each film showed this same spectra. The main peak is not shifted, but the high energy side seems broader, with a weak feature around 130 eV. Moreover, the structure below threshold now appears as a doublet, with some weaker shoulders. The threshold is still in agreement with the earlier Ce data.

A scan of the $M_{4,5}$ region after the seventh evaporation resulted in the bottom curve of Fig. 44. The $M_{4,5}$ peaks show new splitting of unequal intensity. At this time the higher energy peak, at 883.7 eV was the stronger of the two M_5 features. This film sat at a base pressure of 1×10^{-10} Torr for several hours. The system was then turned on again

Figure 43. $N_{4,5}$ SXAPS spectrum for tetravalent Ce. The solid curves show the $N_{4,5}$ spectra for La and trivalent Ce metal

Figure 44. Series of spectra obtained for the Ce $M_{4,5}$ region during the transition from tetravalent to trivalent Ce. The numbers on the right indicate the film from which each spectrum was obtained, relative to the third evaporation (bottom curve)

and both the $N_{4,5}$ and $M_{4,5}$ regions still showed the new structure. A series of evaporations was then made as indicated by the curves of Fig. 44 and the intensities of the new second peaks gradually reduced, reverting to the original $M_{4,5}$ spectrum shown earlier. At the same time the $N_{4,5}$ spectrum returned to its original form, with five peaks below threshold. This sequence was originally thought to represent a mixture of Ce_2O_3 and Ce metal. The $N_{4,5}$ results however, suggest that we had a mixture of $3+$ and $4+$ ions during the sequence shown in Fig. 44 and that with successive evaporations the surface was gradually covered with $3+$ ions. The entire sequence of Fig. 44 covers a period of about 10 hours. Each individual spectrum was reproducible and only a new evaporation caused the intensity changes. We emphasize that at all times other than during evaporation, our working pressure was below 5×10^{-10} Torr. We conclude then that the films represent metallic Ce rather than oxide. This idea is supported by the $N_{4,5}$ region (Fig. 43) which shows a broad main peak without a high energy minimum which is characteristic of the contaminated films (Fig. 35). We observed this same transformation of the Ce $N_{4,5}$ fine structure in an earlier study using a different piece of Ce, but cut from the same batch as the present evaporant.

We also observed that during this series of scans the emission current was higher following successive evaporations until the sequence of Fig. 44 was begun, at which time the emission current decreased with successive evaporations. This cannot be explained by space-charge effects in the $M_{4,5}$ region and may be related to the conductivity of the sample surface,

an argument which favors the Ce^{3+} metal $\leftrightarrow$ CeO_2 transition rather than a valency change for metallic Ce.

In Fig. 43 we also show a La $N_{4,5}$ spectrum. Since the doublet of this spectrum resembles somewhat that of the dashed curve, we conclude that the Ce film during these runs consisted of Ce^{4+} ions and that the electronic configuration being studied was similar to that of La with one extra nuclear charge. The SXA data of Haensel et al. (101) lend further support to the La-like configuration for Ce. Their results for Ce oxide show two peaks, at 103.45 eV and 108.21 eV, with some weaker structure. We assume that this represents CeO_2 . Their data give peaks for $d\alpha/dE$ at 103.2 and 107.9 eV. The low energy SXAPS peaks are at 105.2, 106.7, 110.6, and 111.8 eV. We present these data in Table 10, along with the separations, ΔE , of the SXAPS peaks from the SXA and $d\alpha/dE$ peaks. The results indicate a splitting of $E = 2.4$ and 3.7 eV for the SXAPS peaks relative to the $d\alpha/dE$ peaks. This same quantity for La^{3+} was 4.4 and 5.8 eV respectively, from Table 7. If our interpretation is correct, ΔE is a rough measure of the position of the 4f states relative to the excitation threshold. The suggestion is then that the empty 4f states in Ce^{4+} are slightly further above the ionization threshold than are the 4f states in Ce^{3+} , which is what we expect. Also, the 4f states in Ce^{4+} are pulled down towards the threshold level relative to those of La^{3+} , as expected, due to the extra nuclear charge in Ce^{4+} .

The splitting of the $M_{4,5}$ peaks in Fig. 44 is 1.6 eV. For the CeO_2 data of Bonnelle et al. (119), the shift upon oxidation is about 1.8 eV for the main M_5 peak and 2.4 eV for the M_4 peak. The shift in the main

Table 10. Summary of results for the $N_{4,5}$ region of Ce (IV)

SXA ^a peaks (eV)	dα/dE ^a peaks (eV)	SXAPS peaks (eV)	ΔE ^b	
			SXA	dα/dE
103.45	103.2	105.2 ^c	1.8	2.0
		106.7	3.2	3.5
108.21	107.9	110.6	2.4	2.7
		111.8 ^c	3.6	3.9
Average ΔE			2.1	2.4
			3.4	3.7

^aUsing data from ref. 101 for Ce oxide.

^bThe ΔE values are the differences between the SXAPS values and the SXA and $d\alpha/dE$ values respectively.

^cShoulder.

$d\alpha/dE$ peaks for these data is 2 eV for M_5 and about 2.2 eV for M_4 , slightly greater than our splitting of 1.6 eV for the M_5 and M_4 doublets.

The data presented here strongly suggest that we had for some time Ce^{4+} ions in a metallic state. We cannot state with confidence the reason for this valency change nor can we rule out the existence of CeO_2 . One possible explanation is that the 4f orbital is emptied due to the elevated sample temperature. Habermann and Daane (92) have suggested this depopulation as a possible cause for the unusually high heat of sublimation for

Ce. The argument is that above room temperature, the 4f electron is thermally excited into the conduction band. If a d-symmetry orbital is occupied, the cohesive energy would be increased relative to that of La as is experimentally observed. We do not know the substrate temperature in our experiment but it is certainly well above room temperature due to the nearby W filament and to electron beam heating. However, these conditions were not altered much during the Ce runs and another explanation is probably needed. We suggest that Ce should be further studied using a heated substrate in conjunction with an Auger analysis to determine whether the surface represents metallic Ce^{4+} or CeO_2 .

Ytterbium

Our interest in Yb resulted from the moderately successful interpretation of La and Ce data in terms of the absorption coefficient. Yb metal is divalent and the ion cores have a completed 4f shell (92, 125). Upon oxidation, the ion becomes trivalent with one empty 4f orbital. The Yb SXA data of Fomichev et al. (96) show a weak peak at 171.3 eV followed by a stronger peak at 179.6 eV, slightly over five eV wide. Sugar (102) has suggested that this spectrum resulted from the oxide rather than the metal, since divalent Yb ions, having a full 4f shell, should show no absorption in this region. The transition involved in the oxide is then $4d^{10}4f^{13} \rightarrow 4d^9 4f^{14}$, which results in a singlet, $^2D_{5/2}$, excited state. The absorption measurements of Combley et al. (126) support this valency change also. They observe an M_5 absorption line ($3d \rightarrow 4f$) at 1519.9 eV in Yb_2O_3 and YbF_3 , but not in the metal. The M_5 and M_4 absorption edges are observed for all three materials. The M_4 line is not allowed optically

since $\Delta j = 2$ for $3d_{3/2} \rightarrow 4f_{7/2}$. XPS measurements (115) give core binding energies of 181.4 and 191.4 eV for $4d_{5/2}$ and $4d_{3/2}$ respectively. The electron energy loss measurements (111) agree with the SXA results in giving a single broad peak at 181 eV. This presumably also represents Yb oxide rather than metallic Yb.

Fig. 45 shows our SXAPS results for Yb in the $M_{4,5}$ and $N_{4,5}$ regions. The dashed lines mark the atomic core binding energies (75) in each region. The arrows pointing up mark the peak positions for absorption measurements (96, 126) and the double-headed arrows mark the $4d$ core binding energies determined by XPS (115). In the $M_{4,5}$ region we measure a relatively strong peak at 1524.5 eV and a weak peak at 1573.5 eV. We attribute these peaks to the excitations, $3d \rightarrow 4f$. This is perhaps evidence that optical selection rules do not hold for SXAPS where the incident electron, as a plane wave, contains all values of angular momentum. The two peaks are spin-orbit split by 49 eV, in fair agreement with the M_5 and M_4 absorption edge separation of 47.7 eV for Yb oxide (126). The data for this region are summarized in Table 11.

Our study of this region was quite limited for two reasons. The instrument did not allow accurate voltage readings above 1600 eV, and the spectra showed signs of electron-beam damage at these energies. Since the vapor pressure for Yb is quite high (92) at elevated temperatures, the system could not be baked at temperatures much above 100°C . Our early attempts to bake at 200°C resulted in failure. We then worked without baking to obtain some initial spectra.

Figure 45. SXAPS results for the $M_{4,5}$ and $N_{4,5}$ regions of Yb. The top and bottom curves were obtained prior to baking the vacuum chamber and the middle curve was obtained after a short bake at 100°C

Table 11. Summary of some existing data for the 3d and 4d core excitations in Yb. All values represent peak positions (eV) unless otherwise noted.

Experiment Reference	ATOMIC 75	XPS 115	XPS 127	EEL ^a 111	SXA 96	SXAPS our work	SXA 126	SXA 39	EMIS ^b 39
Spectral designation									
? ^c					171.3				
4d _{5/2}	184.9	181.4	181.2						
2D _{5/2}				181	179.6	184.5			
4d _{3/2}	198.1	191.4	190.0			196.5 ^d			
M _α						1524.5	1520	1515.5	1522.6
3d _{5/2}	1527.8					1550. ^e	1549		
M _β						1573.5			1566.6
3d _{3/2}	1576.3						1596.7		

^aElectron energy loss experiment.

^bX-ray emission spectroscopy.

^cUnidentified peak.

^dThe assignment of this peak to 4d_{3/2} is purely speculative.

^eA step is observed at this value rather than a peak.

The top and bottom curves of Fig. 45 were obtained at this time, at a pressure of 3×10^{-8} Torr. The middle curve was obtained after a short bake at 100°C , from a new film. The pressure after this low temperature bake was only about 1×10^{-8} Torr. We must assume that all our spectra represent Yb oxide films due to the poor vacuum. The relatively high vapor pressure also meant that electron-beam desorption was enhanced as indicated by the photocathode contamination which occurred.

The absorption edges observed by Combley et al. (126) are also indicated for the $M_{4,5}$ region in Fig. 45. The edges observed for the oxide are labelled M_5' and M_4' , and the edges observed for the metal are marked as M_5'' and M_4'' . The step observed at 1550 eV in our curve may be due to the M_5 threshold for excitation to the conduction band. We have no interpretation for the step observed at 1510 eV.

In the $N_{4,5}$ region, we observed a double peak for our initial evaporations. After the low temperature bake our films gave the broader peak shown by the middle curve of Fig. 45. The threshold for this peak is near 180 eV and is associated with excitation of the $^2D_{5/2}$ singlet. The peak has a width of 7 eV in fair agreement with the SXA results (96). The second peak, at 196.5 eV, in the bottom curve of Fig. 45 may be due to the spin-orbit split $4d_{3/2}$ excitation, contrary to the exchange splitting picture. Both curves for the $N_{4,5}$ region show a low energy shoulder near 177 eV.

The spectra shown in Fig. 45 were quite weak compared to our La results. When normalized by the emission current density and modulation potential, the La signals were about ten times stronger in the M_5 region.

The small signals obtained for Yb may result from the low density of available 4f states at E_F in Yb oxide. On the other hand, the stronger signals for the lighter rare earths may be due to resonant final states with both the excited core electron and incident electron residing on the excited ion. This interacting scheme was discussed in connection with La and cannot occur for Yb_2O_3 which has only one available 4f state.

We also observed a broad peak for Yb oxide around 40 eV as shown in Fig. 46. The 5p core state is expected (75) to be near 23 eV. The structure could not be separated convincingly from the background although it may be associated with the excitation of a $5p^5 5d^1$ configuration.

Insulators

A major goal of this work was to test the usefulness of SXAPS for insulators. From one point of view (16, 72) this question had been answered already since good spectra had been obtained for some transition metal oxides such as Sc_2O_3 (128). In the same vein, we have already shown spectra for La_2O_3 , Ce_2O_3 , and Yb_2O_3 . Such oxides first form as an outer layer and in all probability form to a depth of several atomic layers, greater than the penetration depth for unscattered medium-energy electrons. We wished to know if an evaporated film of insulating material would also give good spectra. It is not clear that this distinction between an oxidized metal surface, and a thin film of an insulating compound, should even be made here, but the fact remains that to our knowledge no SXAPS spectra had been reported for evaporated films of insulating compounds. With this in mind, we have studied evaporated films of MnF_2 , LaF_3 , CsCl and KCl .

Figure 46. SXAPS spectrum of Yb in the region of the 5p core excitations

From the outset, it was expected that charging of the sample by the electron beam would be a problem. If the results of charging were only to cause an energy shift, the line shapes might still provide useful information. It was not clear how much broadening would result from charging and how much desorption and dissociation would result from electron bombardment. Some of these questions will be addressed in the results which follow.

Potassium chloride

In Fig. 47 we show two spectra obtained from an evaporated film of KCl. The top curve covers the $L_{2,3}$ excitation region of potassium, the 2s chlorine excitation, and the 1s carbon excitation. The dominant feature is the doublet peak observed at 298 and 301 eV. A weak peak at 287.5 eV is probably due to surface carbon contamination. The dashed lines mark the atomic core-state binding energies (75). The middle curve of Fig. 47 is the KCl spectrum in the Cl $L_{2,3}$ region.

We cannot make any conclusive assignment for the observed features but, based on the absorption data for KCl, some speculation is possible. The absorption data for the chlorine $L_{2,3}$ region (129, 130) show much structure, extending from about 200 to 230 eV, which has been interpreted in terms of excitons and conduction band density of states structure. The SXAPS results show complicated structure in this region also, but the intensities here are too weak to make any assignments. The potassium $L_{2,3}$ SXA data is somewhat simpler, having two dominant peaks at 296.2 and 298.6 eV (130) which are attributed to excitons, and are indicated by the arrows pointing up in Fig. 47. The SXAPS peaks are at 198.2 and 301.0 eV, 2 eV higher in energy.

Figure 47. SXAPS results for evaporated films of KCl and MnF₂ in the regions of 2p core excitations

For an insulator, in addition to energy shifts caused by charging, the presence of a band gap would also shift SXAPS structures to a higher energy than corresponding SXA structures, because the excitation cannot occur until the scattered incident electron has enough additional energy to end up in the conduction band. That is, if we have a band gap, ΔE , and place the Fermi level at the center of the band gap, we might expect the SXAPS structure to occur at $\frac{1}{2}(\Delta E)$ higher energy than predicted by SXA. At the same time we have assumed that the extra electron does not alter the absorption spectrum. This is probably not the case as suggested by the complex carbon excitations (12, 13) and our previous discussion for rare earths. For KCl, the band gap is about 8 eV at room temperature (129) and should be slightly smaller for our heated sample. The above argument suggests that our peaks should then occur about 4 eV above the SXA peaks while we instead observe a 2 eV shift, if the peaks are in fact similar in origin.

We should also consider the role of the empty 3d bands in the SXAPS study of potassium $L_{2,3}$ excitations because, as we have already seen, the 2p excitations in the 3d metals are quite strong. The SXAPS results for Ca (28) show a peak about 6.8 eV above the L_3 threshold and this is attributed to $2p \rightarrow 3d$ excitations. For KCl, the 3d bands are about 10 to 12 eV above the vacuum level (130). The line shape for these excitations is expected to be smeared out due to the broadening of the incident electron beam energy which suffers heavily from valence bond scattering this far above excitation threshold. In Fig. 47 we do observe a step at 311 eV, about 14 eV above the first peak. We cannot say convincingly however, that this step is connected with the 3d band.

As mentioned earlier, the KCl films were very susceptible to damage due to heating, desorption, and dissociation. Very few reproducible results were obtained for KCl, even at current densities below $0.5 \times 10^{-3} \text{ A/cm}^2$. Our later work with LaF_3 also suggested that low current densities were required for studying insulators using our geometry.

In conclusion, the KCl results suggest that some useful information can be obtained from insulators using SXAPS, assuming we can avoid film damage and use sufficiently thin films to avoid charging. The potassium $L_{2,3}$ spectrum does resemble that of the x-ray absorption data in this energy range.

Manganese difluoride

We applied SXAPS to a study of evaporated films of MnF_2 in an attempt to investigate the core-level splitting of manganese core states which had been observed in XPS (131). The results were inconclusive, due primarily to the poor films obtained. MnF_2 powder was evaporated from an indirectly-heated quartz crucible. No spectra were obtained for the 2s core excitation and only a few spectra were obtained for the 2p excitations of Mn. The 2s signals are expected to be weak due to the relatively low probability for radiative decay of these core excitations (15).

The only spectra obtained were for the Mn $L_{2,3}$ region. Even here, the background was not reproducible and we cannot be very confident of these data. The lower curve of Fig. 47 shows a typical spectrum for the $L_{2,3}$ excitations. We see the two spin-orbit split levels at 641 and 651.7 eV. Each peak appears to have a low energy satellite with a threshold at 634 and 646 eV respectively. The background was decreasing here for unknown

reasons.

The XPS results for the 2p excitations of MnF_2 single crystals show slight asymmetries which have been interpreted (132) in terms of multiplet splitting due to the half-filled 3d shell. The spectrum in Fig. 47 was obtained with $2 V_{pp}$ modulation which gave insufficient resolution to see these core-level effects. We can, however, make some comparisons with our Ag-Mn results discussed earlier and the results of Park and Houston for Mn metal (3). In Table 12 we list the SXAPS peak positions for the $\text{Mn } L_{2,3}$ excitations in the metal, fluoride, and dilute alloy, along with the spin-orbit splitting, ΔE . The XPS results (132) indicate an increase in splitting for the fluoride. Since we do not observe this increase for our films, we must allow the possibility that we have caused dissociation of the molecule by heating and electron bombardment, resulting in some other Mn compound. Our observed splitting agrees very well with that of the metal and the dilute alloy. The shift of the peaks to higher binding energy is as expected for the fluoride, and the peaks for the alloy occur 0.5 eV higher still in energy. In that case, however, the shift may be connected with the formation of localized states a few eV above E_F .

As for KCl, we conclude that the effects of charging seem minor for thin film insulators studied with SXAPS. However, we were not successful in observing core-level multiplet splitting which is observed for single crystals. We also suspect that large scale dissociation occurred in these films.

Table 12. Comparison of SXAPS data for the 2p core excitations of Mn in metallic Mn, MnF_2 , and Ag-Mn. All values are peak positions (eV). ΔE is the spin-orbit splitting

Experiment Reference	ATOMIC 75	Mn (metal) 3 28		MnF_2 our work	Ag + Mn (5%) our work
Spectral designation					
$3d_{5/2}$	640.3	639.7	640.1	641	641.5
$3d_{3/2}$	651.4	650.3	651	651.7	652.1
ΔE	11.1	10.6	10.9	10.7	10.6
ΔE (XPS) ^a	-	11.18		12.07	-

^a ref. 131.

Cesium chloride

The initial motivation for studying CsCl was to see how the Cs 4f levels, far above E_F , would contribute to the SXAPS measurements. Also, we would be able to further test SXAPS for manifestation of exciton effects in insulators.

The films were evaporated using a W wire basket. Based on prior measurements from a similar source, the films were probably several thousand angstroms thick. The measurements were made at pressures of 1×10^{-7} Torr, using beam current densities of about $1 \times 10^{-4} \text{ A/cm}^2$. This corresponded to about 200 μA emission current for our target area. Even with this low current we suspect that considerable film damage occurred within

a few minutes since the background signals were observed to change considerably following each evaporation, achieving equilibrium only after 30 minutes or even longer. Presumably we caused dissociation of the CsCl surface layers by electron bombardment, with the Cl gas leaving the target while the Cs atoms remained on the substrate forming some other compound. Although we could not observe the target during the runs, upon opening the vacuum we observed that the CsCl on the walls of the evaporation chamber was white, as expected for polycrystalline CsCl, while the material on our substrate was considerably discolored, being somewhat brown in appearance. We present the data with the possibility that we did not have CsCl, but rather some other compound.

In Fig. 48 we show our results for the energy region from 70 to 170 eV. The upper solid curve shows the SXAPS results and the vertical lines mark the atomic core binding energies for the $4d_{5/2}$ (N_5), $4d_{3/2}$ (N_4), and $4p_{3/2}$ (N_3) levels of Cs (75). We observe a threshold near 80 eV, followed by a broad peak at 120 eV. The peak extends over 70 eV and has shoulders near 95 eV and 105 eV. The peak observed above 160 eV was not as reproducible as the main peak but may correspond to excitation of the $4p_{3/2}$ Cs core state. The broken line shows the photoabsorption data for CsCl (133). This curve has a threshold near 74 eV, followed by several peaks on the rising slope of a strong, broad absorption band. Not all of these peaks are completely understood, although some of them may correspond to excitons, and a few peaks can be identified as spin-orbit split pairs. The strong, broad absorption peak is associated with the Cs $4d \rightarrow 4f$ transitions which extend far above threshold and are broadened by the presence

Figure 48. SXAPS results for the 4d core excitations of Cs in CsCl. The absorption coefficient (ref. 133), its derivative, and the derivative of its self-convolution are also shown for comparison

of continuum states. This broad peak also extends over 70 eV similar to the SXAPS results. The SXA N_3 excitation is observed at 161.5 eV. The dashed curve shows $d\alpha/dE$, which is dominated primarily by the fine structure region of α . This curve has been broadened with a gaussian of 1.0 eV width. The dash-dot curve of Fig. 48 shows the derivative of the self-convolution of α . The convolution smears out most of the fine structure in α , and consists primarily of a broad peak near 120 eV.

An interpretation of our results is difficult due to the uncertainty regarding our sample composition. We feel relatively certain, however, that the broad peak is connected with the $4d \rightarrow 4f$ excitations based on the threshold position and width of the peak. The success of the convolution model suggests that both electrons involved here are probing the same density of states contrary to the scheme discussed for the rare earths where two different densities of states were involved. For La we saw that the population of the $4f$ states by $4d$ electrons resulted in three multiplets; two were pulled below the ionization threshold, and the third, above threshold, was broadened by autoionization. Nilsson et al. (52) have performed SXAPS measurements on Ba metal and oxide. They still observe three multiplets, but for Ba, the $4f$ levels are further above E_F and the exchange interaction does not quite pull the 3D_1 and 3P_1 terms below threshold. We do not expect to have Cs metal, but may still be seeing the same mechanism. If we make such an interpretation anyway, the broad peak at 120 eV is connected with the 1P_1 resonance and the two shoulders may be associated with the 3P_1 and 3D_1 levels which are also broadened by interaction with continuum states. If we measure the position of the main peak

Table 13. Comparison of the main peak positions in SXAPS and SXA relative to the atomic core binding energies for the 4d excitations of Xe, Cs, Ba, La, and Ce. All energies are in units of eV.

	ATOMIC ^a	SXAPS	ΔE (SXAPS) ^b	SXA	ΔE (SXA) ^b
element					
Xe	65 ^c	-	-	101 ^d	36
Cs	77.6 ^e	120	42.2	104 ^f	26.4
Ba	91.2 ^e	110 ^g	18.8	107.4 ^h	16.2
La	98.9	115	16.1	117 ^d	18.1
Ce	110.0	120	10.0	125 ^d	15.0

^aref. 75.

^b $\Delta E = \text{SXAPS (or SXA)} - \text{ATOMIC}.$

^cestimated.

^dref. 97.

^eaverage.

^fref. 132.

^gref. 52.

^href. 134.

above the tabulated atomic binding energies (75) for these elements, we get the values shown in Table 13. The Cs SXAPS figure seems too large. The photoabsorption data indicates a less rapid increase in ΔE where we list the position of the main SXA peak above the same tabulated binding energies.

In Fig. 49 we show the CsCl SXAPS spectrum from 705 to 775 eV. As mentioned earlier, our geometry was arranged in the latter stages to provide better shielding of the detector from the evaporation source. A mask permitted deposition of the material only in the center of the substrate so that a portion of the stainless steel was never covered. In this case, we benefitted from the arrangement because the Fe $L_{3,2}$ peaks from the stainless steel could be observed in every run of the Cs $M_{4,5}$ region. These two peaks always occurred at the positions shown, 709.4 and 721.9 eV. We were thus assured that no change occurred in the work function of the W filament due to Cs contamination. The vertical arrows mark the binding energies (75) of the Fe $L_{3,2}$ and Cs $M_{4,5}$ atomic core states. The two peaks at 749.3 and 763.3 eV were present in all runs. The single peak at 737 eV did not always appear as sharp as shown in this particular run, but was nevertheless always present. The two weak peaks at 756 and 769 eV were not always present and may be dependent on film damage, although they were also observed for some freshly evaporated films. We will not consider them further.

In Fig. 49 we have indicated the two high energy peaks by the connected arrows labeled C which point out the 14 eV splitting. This agrees with the atomic $M_{4,5}$ spin-orbit splitting. The thresholds indicated by the coupled arrows B and A seem to fit this picture although the threshold at 759 eV was not always clear, as is the case in Fig. 49. The structures labeled A have thresholds about 2.2 eV above the values of ref. 75. The thresholds of the two main peaks are 19.5 eV and 17.2 eV higher still, and the main

Figure 49. SXAPS spectrum of CsCl from 705 to 775 eV

peaks occur about 21.5 eV above their mates in the A couple. We do not feel that charging of the film is responsible for much of this 21.5 eV shift, since the peaks, C, did not shift with time, nor did they shift when the emission current was changed by a factor of two. The results in Fig. 49 were obtained with an emission current of 0.8 mA, but unshifted peaks were also obtained with currents of 0.2, 0.4, and 1.0 mA as well. On the other hand, the peaks at 756 and 769 eV were not observed with 0.4 mA and may be due to some charging. The peak at 737 eV did occur with reduced intensity at 0.4 mA emission current.

A possible interpretation for these data can be made if we recall the atomic nature of the $d \rightarrow f$ transitions. We associate the thresholds, A, with the initial excitation of the $4d$ electrons to the conduction band states. The main peaks, C, then correspond to $d \rightarrow f$ transitions where the localized f states are about 20 eV above excitation threshold. These peaks might not be observed if we had a band picture rather than an atomic one, since it has been suggested (5, 16) that SXAPS peaks this far above threshold would be completely smeared out due to the energy broadening of the exciting beam, brought about by inelastic scattering and other energy loss mechanisms prior to core-level excitation. The picture of localized $4f$ states some 20 eV above excitation threshold is also consistent with our $N_{4,5}$ results, since the convolution of a peak, ΔE above E_F , results in a large peak at $2\Delta E$ above E_F . The $N_{4,5}$ data suggest that $\Delta E \approx 21$ eV for the strong $4f$ transitions, in agreement with SXA and our $M_{4,5}$ results. The $M_{4,5}$ peaks are only about 5 eV wide. A similar narrowing of line

shapes was observed for La and is presumably the result of less exchange interaction for the $n = 3$ shell than for the $n = 4$ shell.

We have indicated that charging of our films did not manifest itself in the form of energy shifts or severe broadening. We do believe that serious film damage did occur due to the electron beam and this is demonstrated in Fig. 50. Here we show the spectra from a fresh film, from 0 to 300 eV for different biasing voltages, V_B . It was explained in Chapter III that the target and filament were biased above ground to prevent thermionically emitted electrons from entering the detector through the grounded wire mesh. In Fig. 50 we show spectra for several values of V_B ranging from 16.6 to 43.2 V. Several runs were taken and the number at the left hand side indicates the run number in this sequence. Two trends were observed. First, a large negative peak seemed to appear and move to higher energy as V_B was increased. The negative peak was sufficiently strong to make the $N_{4,5}$ maximum appear as a doublet for high V_B . Second, the two runs with 43.2 volts indicate that the negative peak decreased with time, and in fact, after several hours of exposure, very little difference was noted for changes in V_B . The source of this negative peak was evident in the total yield curves shown in Fig. 51. These curves represent the total d.c. current being measured by the detector as a function of electron beam energy. The values of V_B are noted for each spectrum and the vertical arrows mark the position of the large negative peak in the differential yield curves of Fig. 50. The $N_{4,5}$ threshold is also indicated in Fig. 51. All the curves here were taken with an emission current density of 7×10^{-5} A/cm². A shoulder, just barely detectable in the 16.6 V curve, is seen to

Figure 50. Dependence of the SXAPS spectrum of CsCl on the bias voltage of the emitter in the low energy region

Figure 51. Dependence of the total yield curve of CsCl on the bias voltage of the emitter in the low energy region

grow and move almost linearly with increasing V_B to higher energies. Since the 16.6 V curve is nearly free of this shoulder, and since the corresponding negative peak would appear about 30 eV below the $N_{4,5}$ threshold, we feel that the differential yield curves are free of this interfering structure for a 16.6 V bias, and give a reliable line shape for the true x-ray yield. We believe that the moving shoulder is not connected with x-ray fluorescence, but rather with an ion current, possibly due to Cl gas leaving the target. This suggestion is made for two reasons. The negative peak disappears with increasing exposure time, suggesting a depletion of the source, while the Cs line shape is not much affected. Also, we measured the synchronous current to the photocathode as a function of V_B . Here, with the photocathode near ground potential, we were collecting primarily positive ion currents. A large peak was observed to move in the same manner as the shoulder of Fig. 51. With the standard detector arrangement and zero collecting voltage on the stainless steel pin, the same peak was observed with a weaker intensity. We do not completely understand the bias-voltage dependence of this moving peak, but feel that the data with 16.6 V bias, are more reliable than the other spectra.

Lanthanum trifluoride

We studied the SXAPS spectra of LaF_3 thin films, evaporated from a polycrystalline source in a W wire basket. As for the other insulators studied, we found that charging, if it occurred, did not cause large energy shifts of the main peaks. However, even with low beam current densities we suspect that film damage did occur.

Our interest in LaF_3 was two-fold. First, the studies would give more information on the usefulness of SXAPS for insulators since, from SXA data (95) we again had a rough idea of what our spectra would look like. Second, and more important, the study could help to identify more clearly the nature of the transitions occurring in La metal.

In Fig. 52 the solid curve shows our results for the $N_{4,5}$ region of LaF_3 , obtained with a vacuum pressure of 2×10^{-8} Torr. In the same figure we show our earlier results for La metal (dashed curve), and contaminated La (broken line). The agreement between these three curves is quite good. They all show the two peaks below threshold which we have previously assigned to the 3D_1 and 3P_1 multiplets, shifted 5 eV towards higher energy. They all have the main peak near 115 eV, assigned earlier to the 1P_1 resonance. The agreement of these three main features is the strongest argument in support of the atomic description for these transitions. The 4f states are sufficiently localized about the ion core, being well screened by the outer electrons, to make the multiplet splitting nearly insensitive to chemical changes in the environment. There are, however, some differences in these curves. Most noticeable is the peak near 121 eV which appears in the metal and the fluoride, but not in our contaminated films. We also do not resolve a splitting of the two low energy peaks in the fluoride. There may be a slight chemical shift in the fluoride and contaminated spectra relative to the metal results, but it is on the order of 0.5 eV or less, and thus below our resolution capability. The SXA data for LaF_3 indicates a chemical shift of only 0.1 eV (135) for the 3P_1 and 3D_1 levels.

Figure 52. Comparison of the SXAPS results for the N_{4,5} region of LaF₃, metallic La, and La₂O₃

In Fig. 53 we show our results for the $M_{4,5}$ region of LaF_3 (solid curve), and include for comparison our earlier results for the metal and contaminated La films. Using the zero crossing of the main peaks, we observe a chemical shift, relative to the metal, of 1.5 eV for the fluoride, and 2.0 eV for the contaminated films. The metal and fluoride results have similar line shapes, but the threshold structure in the M_5 region for LaF_3 seems less resolved. This apparent broadening is also indicated by the full width at half maximum for the M_5 peaks, which is 1.5 eV for La metal and 2.0 eV for LaF_3 . Also, the shoulder for the M_4 region of the fluoride seems less resolved. The LaF_3 results were obtained with 0.5 V_{pp} modulation amplitude and an emission current density of 1.8×10^{-4} A/cm² (0.5 mA), so the broadening is not due to potential modulation, but may be evidence of energy broadening due to charging of the film. The broadening could also be inherent to LaF_3 but we cannot make this distinction using these results alone. Since we observe broadening in this region, we expect it to occur in the $N_{4,5}$ region also. Thus we cannot say convincingly that the 3P_1 and 3D_1 fine splitting is absent for LaF_3 , especially since there is evidence of a shoulder in the first $N_{4,5}$ peak. However, the second peak always showed better resolution of the splitting in our metal film spectra and this LaF_3 peak is nearly structureless.

The $M_{4,5}$ results, aside from broadening, are the same for both metal and fluoride with one notable exception. In the fluoride results we observe a depression in the negative peaks near 843 and 859 eV. Our metal results had a similar depression at times, as shown in Fig. 29, but there we attributed the dips to slight oxidation since they occurred near 840.5 and 857 eV, in agreement with the negative peaks of our contaminated films.

Figure 53. Comparison of the SXAPS results for the $M_{4,5}$ region of LaF_3 , metallic La, and La_2O_3

It is possible then, that this depression in the $M_{4,5}$ spectrum is a characteristic of the anion. To understand this better, we review the photoemission results for the rare earth halides.

Several workers have reported on photoemission from rare earth halides (49, 117) and other rare earth compounds (118). The 3d, and possibly the 4d, core excitations have high energy satellites with intensities, relative to the main line, which vary quite strongly for different anions. For example, the satellite of LaF_3 is quite weak, but becomes stronger than the main peak as one goes from F^- to O^- to Cl^- to Br^- . These results have been interpreted (117, 118) in terms of an electron transfer from the anion 2p shell to the La 4f shell as a consequence of the core-hole creation. The argument is similar to that used for SXA in that the core hole may deepen the ionic potential sufficiently to pull some of the 4f orbitals below the 2p valence band level of the anion. The transfer occurs and the position of the photoemission satellite above the main peak is then a measure of the 2p binding energy of the anion, relative to the lowered 4f level of the metal ion. The separation is greatest for F^- (3.2 eV), and decreases as the satellite intensity increases, being 2.3 eV for O^- and 2.4 eV for Br^- .

In the XPS 4d excitations (49, 117) the spin-orbit splitting is comparable to the multiplet splitting so the satellites overlap with the neighboring peaks, but intensity variations are still observed. Since the 4d vacancy is not as well screened as the 3d vacancy, the effective nuclear charge increases to a lesser extent with the 4d vacancy, and the satellites are expected to be weaker.

We do not expect this charge mechanism to be as strong in SXAPS or SXA where the excited core electron remains in the 4f states rather than leaving the metal. However, for the $M_{4,5}$ region of LaF_3 we have the most favorable conditions for charge transfer since we have a large electron affinity for F^- , and good screening of the 3d vacancy.

It is possible then, that the depression in the negative peaks of the LaF_3 $M_{4,5}$ region is due to the charge-transfer mechanism. The depression occurs about 4 eV above our zero crossing values which is comparable to the splitting observed in the photoemission results (49, 117, 118).

The comparison of our LaF_3 results with our earlier La metal results raises more questions than we can answer. In the metal we have a conduction band which can carry off the scattered electron, even at threshold excitation, in our non-interacting picture. We used this to explain peaks A', B', C and possibly D in Fig. 24, while peaks A and B were attributed to a $4d^9 4f^2$ configuration. In the insulators, the continuum states occur at higher energy so the broadening due to autoionization is reduced for peak C, as experimentally observed for La_2O_3 and LaF_3 . In the non-interacting picture, this peak would be shifted corresponding to the new edge of the conduction band. We do not observe a shift of the main peak but the onset for the fluoride does occur about 1 eV higher than in the metal, and even higher for the oxide, suggesting the change in position of the conduction band edge relative to the 1P_1 level. For LaF_3 , $d\alpha/dE$ peaks at 115.7 eV, using the data of Rabe(95), which agrees so well with our peak at 115.4 eV that we believe that the non-interacting picture is still satisfactory. We have no way of confirming that our sample was truly LaF_3 since additional

broad peaks above both the $N_{4,5}$ and $M_{4,5}$ regions could be made to appear by subjecting the films to electron bombardment at densities of about 1×10^{-3} A/cm² for several hours. The data presented here, however, did not show these additional peaks. In addition, we observed structure near 680 eV, probably due to the fluorine 1s excitation, but these peaks were quite weak and not reproducible.

We do not completely understand the mechanism for peak D in the $N_{4,5}$ region. If this peak in the metal and the fluoride were related to 4f states, it should also appear in the oxide since the 4f states are quite insensitive to chemical changes in the environment. If the peak is due to the same mechanism in both metal and fluoride, it may correspond to a virtual state which broadens by autoionization, similar to the 1P_1 state, since the peak sharpens considerably in the fluoride, where presumably the continuum has been pushed to higher energy. However, since the peak does not occur in the oxide, this transition would have to depend on the anion rather than on the metal ion. The charge transfer process just discussed fits this picture, but as stated earlier, we don't expect such a strong transfer interaction in the 4d region. This also would require that the metal peak be due to a different mechanism than charge transfer, possibly a resonance of the $4d^9 4f 5d$ configuration.

We do not have a better interpretation for these results at the present time. It is possible that a study of $LaCl_3$ would further this analysis. If the peak near 121 eV is due to a charge-transfer mechanism, we would expect, based on the photoemission results, to see a different line

shape for peak D in LaCl_3 . We do not, however, believe that this mechanism is responsible for the 121 eV peak.

In summary, our results for LaF_3 are quite similar to our results for metallic La. This supports the interpretation of these spectra in terms of atomic-like $d \rightarrow f$ transitions. We observed very little evidence of charging and film damage when low emission current densities were used. The secondary structure in the high energy region of both the $N_{4,5}$ and $M_{4,5}$ spectra was observed to change as one goes from metallic La to La_2O_3 and LaF_3 . This may be evidence for a transition which depends weakly on the local environment of the La ion.

CHAPTER V. CONCLUSIONS

In the preceding chapter a great deal of data were discussed and it is useful here to recall our initial goals in this work. Briefly, we sought a model for SXAPS which would explain the results for the rare earths as well as the transition metals, hopeful of improving on the one-electron theory discussed in Chapter II. The results of this work showed that the two density of states model was superior to the one-electron theory in that the SXAPS spectrum often could be interpreted using this model with the existing SXA and SWL data. This is not of much use to us in interpreting SXAPS spectra of materials for which the other data are lacking, since a deconvolution of the spectrum is not possible when we have two unknown densities of states. Such applications of SXAPS must wait for advancements in the theory of low energy electron scattering in solids.

We also were interested in the nature of the electronic transitions involved in SXAPS. The main conclusion reached for most of the materials studied here, is that the excitations are much more localized than was expected. For the rare earths this is primarily a consequence of the localized 4f orbitals which, upon creation of a 3d or 4d vacancy, are lowered sufficiently to be bound within the centrifugal barrier. Even for the transition metals, the measured SXAPS spectra are better described by a model with two localized densities of states than by the self-convolution of a density of itinerant band states. Admittedly, the differences in this case are not as large as for the rare earths, but they do effect the bandwidths and binding energies obtained from the measured spectra. The convergence of the two models is due to the fact that the SXA spectrum tends to resemble the SWL spectrum as the role of final-state interactions decreases.

For Y the low intensity signals were attributed to reduced transition matrix elements, due primarily to the reduced overlap of the 3p and 4d wavefunctions. The Y line shape suggested, based on the one-electron theory, a density of states maximum about 4 eV above E_F . Our studies of La and Ce showed that SXAPS cannot uniquely determine the position of the 4f states relative to E_F in the ground state configuration. This results primarily from the contraction of the 4f orbitals in the presence of a core hole. For La the position of these states relative to the excitation threshold varied between 3 and 5 eV, while for Ce the separation was from 1.5 to 2 eV, depending on which inner shell contained the core hole. Also for Ce we observed a spectral change which we attribute to the formation of tetravalent Ce ions. We suspect that the film was metallic in this case, but we cannot rule out the formation of CeO_2 . We also observed weak 3d and 4d excitations in Yb_2O_3 , and associated them with a single vacant 4f state. The 3d excitations showed a peak which is forbidden for optical excitations, confirming the lack of dipole selection rules for electron excitation in SXAPS.

Finally, we sought to test SXAPS as a tool for studying insulating compounds. The results suggest that useful information can be obtained by using thin films to avoid charging, and low current densities to avoid film damage. Our results for KCl, CsCl, and LaF_3 were in good agreement with the SXA data. The role of the $d \rightarrow f$ excitations in LaF_3 changed very little from that for metallic La, although secondary structures were observed for LaF_3 and La_2O_3 which may depend on the anion involved.

REFERENCES

1. B. Dev and H. Brinkman, Ned. Tijdschr. Vacuumtechn. 8, 176 (1970).
2. J. E. Houston and R. L. Park, J. Chem. Phys. 55, 4601 (1971).
3. R. L. Park and J. E. Houston, Phys. Rev. B 6, 1073 (1972).
4. P. O. Nilsson and J. Kanski, Phys Lett. A 41, 217 (1972).
5. P. O. Nilsson and J. Kanski, Surf. Sci. 37, 700 (1973).
6. J. Kanski and P. O. Nilsson, Phys. Lett. A 45, 399 (1973).
7. M. B. Chamberlain and W. L. Baun, J. Vac. Sci. Technol. 11, 441 (1974).
8. W. E. Harte, P. S. Szczepanek, and A. J. Leyendecker, Phys Rev. Lett. 33, 86 (1974).
9. M. S. Murthy and P. A. Redhead, J. Vac. Sci. Technol. 11, 837 (1974).
10. K. N. Ramachandran and C. D. Cox, J. Vac. Sci. Technol. 11, 579 (1974).
11. P. S. Szczepanek and W. E. Harte, Phys. Lett. A 49, 377 (1974).
12. J. E. Houston and R. L. Park, J. Vac. Sci. Technol. 8, 91 (1971).
13. J. E. Houston and R. L. Park, Solid State Commun. 10, 91 (1972).
14. J. C. Tracy, Appl. Phys. Lett. 19, 353 (1971).
15. J. C. Tracy, J. Appl. Phys. 43, 4164 (1972).
16. R. L. Park and J. E. Houston, J. Vac. Sci. Technol. 11, 1 (1974).
17. D. J. Nagel, in Band Structure Spectroscopy of Metals and Alloys, edited by D. J. Fabian and L. M. Watson (Academic, London, 1973), p. 457.
18. D. Coster and R. de L. Kronig, Physica (Utrecht) 2, 13 (1935).
19. T. Aberg and J. Utriainen, Phys. Rev. Lett. 23, 1346 (1969).
20. T. Aberg and J. Utriainen, J. de Phys. Suppl 32, C4-295 (1971).
21. T. Aberg, Phys. Rev. A 4, 1735 (1971).
22. R. D. Evans, The Atomic Nucleus (McGraw - Hill, New York, 1955) p. 617

23. W. Bambynek, B. Crasemann, R. W. Fink, H. U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. V. Rao, Rev. Mod. Phys. 44, 716 (1972).
24. C. B. Duke and C. W. Tucker, Jr., Surf. Sci. 15, 231 (1969).
25. E. Bauer, Z. Phys. 224, 19 (1969).
26. R. H. Good, Jr. and T. J. Nelson, Classical Theory of Electric and Magnetic Fields (Academic, New York, 1971) p. 164.
27. T. M. Apostol, Mathematical Analysis (Addison - Wesley, London, 1964) p. 219.
28. J. Kanski, Ph. D. thesis (Chalmers University of Technology, Goteborg, Sweden, 1974)(unpublished).
29. J. M. Ziman, Principles of the Theory of Solids (Cambridge U. P., Cambridge, England 1969) p. 221.
30. R. B. Leighton, Principles of Modern Physics (McGraw - Hill, New York, 1959) p. 422.
31. E. Merzbacher, Quantum Mechanics (Wiley, New York, 1967) p. 452.
32. L. Hedin, B. I. Lundqvist, and S. Lundqvist, in Electronic Density of States, Natl. Bur. Std. Spec. Publ. No. 323, edited by L. H. Bennett (U. S. GPO, Washington, D. C., 1971) p. 319.
33. G. A. Rooke, in Electronic Density of States, Natl. Bur. Std. Spec. Publ. No. 323, edited by L. H. Bennett (U. S. GPO, Washington, D. C., 1971) p. 287.
34. B. Coqblin, J. de Phys. Suppl. 32, C1-599 (1971).
35. J. Appel, Phys. Rev. B 8, 1079 (1973).
36. The material was obtained from Carborundum Co., Refractories and Electronics Div., Tech. Ceramics Plant, Latrobe Penn. 15650.
37. R. G. Musket and S. W. Taatjes, J. Vac. Sci. Technol. 9, 1041 (1972).
38. W. B. Nottingham, Phys. Rev. 47, 806(A) (1935).
39. D. W. Fischer and W. L. Baun, in Advances in X-Ray Analysis, edited by J. B. Newkirk, G. R. Maller, and H. G. Pfeiffer (Plenum, New York, 1968), Vol 11, p.230.
40. W. L. Baun, M. B. Chamberlain, and J. S. Soloman, Rev. Sci. Instrum. 44, 1419 (1973).

41. W. L. Baun, M. B. Chamberlain, and J. S. Soloman, Rev. Sci. Instrum. 44, 1421 (1973).
42. M. B. Chamberlain and W. L. Baun, Rev. Sci. Instrum. 45, 545 (1974).
43. D. J. Pocker, Rev. Sci. Instrum. 45, 1271 (1974).
44. S. Andersson, H. Hammarqvist, and C. Nyberg, Rev. Sci. Instrum. 45, 877 (1974).
45. J. J. Brophy, Basic Electronics for Scientists (McGraw - Hill, New York, 1966) p. 268.
46. Instruction and Maintenance Manual - Ithaco Model 353 (Ithaco, Inc., Ithaca, New York, 1969).
47. D. E. Eastman, in Techniques of Metals Research, edited by E. Passaglia (Interscience, New York, 1972), Vol. 6, p. 411.
48. Operating and Service Manual - Model 6427B DC Power Supply (Hewlett - Packard, Palo Alto, California, 1966).
49. S. Suzuki, T. Ishii, and T. Sagawa, J. Phys. Soc. Jpn. 37, 1334 (1974).
50. R. L. Park and J. E. Houston, J. Vac. Sci. Technol. 10, 176 (1973).
51. C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949).
52. P. O. Nilsson, J. Kanski, and G. Wendin, Solid State Commun. 15, 287 (1974).
53. J. E. Houston and R. L. Park, Rev. Sci. Instrum. 43, 1437 (1972).
54. J. E. Houston, Rev. Sci. Instrum. 45, 897 (1974).
55. J. E. Houston, Surf. Sci. 38, 283 (1973).
56. T. M. Apostol, Mathematical Analysis (Addison - Wesley, London, 1964) p. 489
57. I. Nagakura, T. Ishii, and T. Sagawa, J. Phys. Soc. Jpn. 33, 754 (1972).
58. C. Webb and P. M. Williams, Phys. Rev. Lett. 33, 824 (1974).
59. D. E. Eastman, Solid State Commun. 8, 41 (1970).
60. R. L. Park, J. E. Houston, and D. G. Schreiner, J. Vac. Sci. Technol. 9, 1023 (1972).

61. J. V. Florio and W. D. Robertson, *Surf. Sci.* 18, 398 (1969).
62. J. C. Tracy and P. W. Palmberg, *J. Chem. Phys.* 51, 4852 (1969).
63. R. M. Lambert and C. M. Comrie, *Surf. Sci.* 38, 197 (1973).
64. J. E. Houston and R. L. Park, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972) p. 895.
65. J. T. Grant, T. W. Haas, and J. E. Houston, *J. Vac. Sci. Technol.* 11, 227 (1974).
66. R. Konishi, G. Murata, and S. Kato, *Surf. Sci.* 44, 287 (1974).
67. J. E. Houston, R. L. Park, and G. E. Laramore, *Phys. Rev. Lett.* 30, 846 (1973).
68. J. E. Houston and R. L. Park, *Phys. Rev. B* 5, 3808 (1972).
69. J. E. Houston and R. L. Park, *J. Vac. Sci. Technol.* 9, 579 (1972).
70. G. Ertl and K. Wandelt, *Phys. Rev. Lett.* 29, 218 (1972).
71. R. G. Musket, *J. Vac. Sci. Technol.* 9, 603 (1972).
72. R. L. Park and J. E. Houston, *J. Appl. Phys.* 44, 3810 (1973).
73. J. C. Tracy, *J. Appl. Phys.* 44, 4788 (1973).
74. D. W. Fischer, *Phys. Rev. B* 4, 1778 (1971).
75. J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* 39, 125 (1967).
76. J. P. Petrakian, J. P. Palmer, and G. Rassigni, *Appl. Opt.* 9, 2115 (1970).
77. M. J. Lynch and J. B. Swan, *Austral. J. Phys.* 21, 811 (1968); V. V. Zashkvara, M. I. Korsunskii, V. S. Red'kin, and V. E. Masyagin, *Fiz. Tverd. tels* 11, 3667 (1969) [*Sov. Phys. - Solid State* 11, 3083 (1970)].
78. D. C. Langreth, *Phys. Rev. Lett.* 26, 1229 (1971).
79. G. E. Laramore, *Phys. Rev. Lett.* 27, 1050 (1971).
80. G. E. Laramore, *Solid State Commun.* 10, 85 (1972).
81. C. F. Fischer, *Atomic Data* 4, 301 (1972).
82. M. O. Krause, *Chem. Phys. Lett.* 10, 65 (1971).

83. C. Webb and P. M. Williams, Phys. Rev. B 11, 2082 (1975).
84. P. W. Anderson, Phys. Rev. 124, 41 (1961).
85. P. A. Wolff, Phys. Rev. 124, 1030 (1961).
86. H. P. Myers, L. Wallden, and A. Karlsson, Philos. Mag. 18, 725 (1968).
87. M. R. Steel and D. M. Treherne, J. Phys. F 2, 199 (1972).
88. C. Norris and L. Wallden, Solid State Commun. 7, 99 (1969).
89. C. Norris, J. Appl. Phys. 40, 1396 (1969).
90. L. F. Wallden, D. H. Seib, and W. E. Spicer, J. Appl. Phys. 40, 1281 (1969).
91. A. F. Starace, Phys. Rev. B 5, 1773 (1972).
92. C. E. Habermann and A. H. Daane, J. Chem. Phys. 41, 2818 (1964).
93. F. Herman and S. Skillman, Atomic Structure Calculations (Prentice - Hall, Englewood Cliffs, New Jersey, 1963).
94. S. Suzuki, I. Nagakura, T. Ishii, T. Satoh, and T. Sagawa, Phys. Lett. A 41, 95 (1972).
95. P. Rabe, Ph. D. thesis (Universitat Hamburg, 1974) (to be published).
96. V. A. Fomichev, T. M. Zimkina, S. A. Gribovskii, and I. Zhukova, Fiz. Tverd. Tela 9, 1490 (1967) [Sov. Phys. - Solid State 9, 1163 (1967)].
97. T. M. Zimkina, V. A. Fomichev, S. A. Gribovskii, and I. I. Zhukova, Fiz. Tverd. Tela 9, 1447 (1967) [Sov. Phys. Solid State 9, 1128 (1967)].
98. I. Nagakura, O. Aita, K. Ichikawa, S. Suzuki, S. Kono, T. Ishii, and T. Sagawa, Third Int. Conf. Vacuum - Ultraviolet Radiation Physics, Tokyo, 1971 (unpublished).
99. R. C. Vickery, Chemistry of the Lanthanons (Butterworths Scientific, London, 1953) p. 207.
100. R. Smith, M. Piacentini, and D. W. Lynch, Phys Rev. Lett. 34, 476 (1975).
101. R. Haensel, P. Rabe, and B. Sonntag, Solid State Commun. 8, 1845 (1970).
102. J. Sugar, Phys Rev. B 5, 1785 (1972).

103. J. L. Dehmer and A. F. Starace, Phys. Rev. B 5, 1792 (1972).
104. J. L. Dehmer, A. F. Starace, U. Fano, J. Sugar, and J. W. Cooper, Phys. Rev. Lett. 26, 1521 (1971).
105. A. F. Starace, J. Phys. B 7, 14 (1974).
106. D. W. Lynch and C. G. Olson, Proc. Int. Conf. Vacuum - Ultraviolet Radiation Physics, Hamburg, 1974 (Vieweg - Pergamon, Braunschweig, 1974) p. 258.
107. J. Sugar, Phys. Rev. A 6, 1764 (1972).
108. F. Combet - Farnoux, X-ray Processes in Matter, Conf. Proc., Helsinki, Finland, 1974; F. Combet - Farnoux and M. Lamoureux, Proc. Int. Conf. Vacuum - Ultraviolet Radiation Physics, Hamburg, 1974 (Vieweg - Pergamon, Braunschweig, 1974) p. 89.
109. J. Daniels, C. V. Festenburg, H. Raether, and K. Zeppenfeld, Springer Tracts Mod. Phys. 54, 77 (1970).
110. F. Wooten, Optical Properties of Solids (Academic, New York, 1972) p. 81.
111. P. Trebbia and C. Colliex, Phys. Status Solidi B 58, 523 (1973).
112. G. Wendin, Proc. Int. Conf. Vacuum - Ultraviolet Radiation Physics, Hamburg, 1974 (Vieweg - Pergamon, Braunschweig, 1974) p. 252.
113. R. J. Liefeld, A. F. Burr, and M. B. Chamberlain, Phys. Rev. A 9, 316 (1974).
114. U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).
115. S. P. Kowalczyk, N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley, Chem. Phys. Lett. 29, 491 (1974).
116. V. A. Fomichev, S. A. Gribovskii, and T. M. Zimkina, Fiz. Tverd. Tela 15, 201 (1973) [Sov. Phys. - Solid State 15, 138 (1973)].
117. A. J. Signorelli and R. G. Hayes, Phys. Rev. B 8, 81 (1973).
118. C. K. Jorgensen and H. Berthou, Chem. Phys. Lett. 13, 186 (1972).
119. C. Bonnelle, R. C. Karnatak, and J. Sugar, Phys. Rev. A 9, 1920 (1974).
120. J. M. Mariot and R. C. Karnatak, J. Phys. F 4, L223 (1974).

121. D. Brown, Halides of the Lanthanides and Actinides (Wiley, London, 1968) p. 3.
122. M. B. Chamberlain, A. F. Burr, and R. J. Liefeld, Phys. Rev. A 9, 663 (1974).
123. C. R. Helms and W. E. Spicer, Appl. Phys. Lett. 21, 237 (1972).
124. R. C. Vickery, Chemistry of the Lanthanons (Butterworths Scientific, London, 1953) p. 60.
125. L. Brewer, J. Opt. Soc. Amer. 61, 1101 (1971).
126. F. H. Combley, E. A. Stewardson, and J. E. Wilson, J. Phys. B 1, 120 (1968).
127. S. B. M. Hagstrom, P. O. Heden and H. Lofgren Solid State Commun. 8, 1245 (1970).
128. R. L. Park, Surf. Sci. 48, 80 (1975).
129. F. C. Brown, C. Gahwiller, H. Fujita, A. B. Kunz, W. Scheifley, and N. Carrera, Phys. Rev. B 2, 2126 (1970).
130. L. N. Mazalov, S. M. Blokhin, and E. E. Vainshtein, Fiz. Tverd. Tela 8, 2420 (1966) [Sov. Phys. - Solid State 8, 1926 (1967)].
131. S. P. Kowalczyk, L. Ley, R. A. Pollak, F. R. McFeely, and D. A. Shirley, Phys. Rev. B 7, 4009 (1973).
132. S. P. Kowalczyk, L. Ley, F. R. McFeely and D. A. Shirley, Phys. Rev. B 11, 1721 (1975).
133. M. Cardona, R. Haensel, D. W. Lynch, and B. Sonntag, Phys. Rev. B 2, 1117 (1970).
134. P. Rabe, K. Radler, and H. W. Wolff, Proc. Int. Conf. Vacuum - Ultra-violet Radiation Physics, Hamburg, 1974 (Vieweg - Pergamon, Braunschweig, 1974) p. 247.
135. S. Suzuki, T. Ishii, and T. Sagawa, J. Phys. Soc. Jpn. 38, 156 (1975).

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