MASTER

OPTICAL TECHNIQUES FOR ACTINIDE RESEARCH

by

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Abstract

In recent years, substantial gains have been made in the development of spectroscopic techniques for electronic properties studies. These techniques have seen relatively small, but growing, application in the field of actinide research. Photoemission spectroscopies, reflectivity and absorption studies, and x-ray techniques will be discussed and illustrative examples of studies on actinide materials will be presented.

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Résumé

Ces dernières années, des progrès substantiels ont été réalisés dans le développement de techniques spectroscopiques d'étude des propriétés électroniques.

Les applications de ces techniques dans le domaine de la recherche sur les actinides sont relativement mineurs mais d'importance croissante.

Des études de spectroscopie de photoémission, d'absorption et réflexion et des techniques de rayons X sont ici présentées et des exemples d'études des matériaux actinides sont aussi exposés pour illustrer le sujet.

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I. Introduction

In recent years, significant advances have been made in the development of spectroscopic techniques and their exploitation for materials research. However, for the actinide materials, this field of research remains virtually unexplored. Because of the obvious value that these techniques have for investigation of electronic properties, and because of the rich variety of electronic structure phenomena that can be found in actinide materials, it is certain that the spectroscopic techniques will become more vigorously exploited as the specialized capabilities required for handling actinide materials become available.

Those experiments which might properly be called "optical" or "spectroscopic" comprise an inappropriately long list for this presentation. In general, nearly any photon experiment might qualify as an "optical spectroscopy". For this presentation we will simply choose to discuss a few "optical spectroscopic" techniques which are useful for elucidating electronic structure in actinide materials. Other spectroscopic techniques not included in this brief list may nicely complement those discussed here. Related spectroscopies such as Auger electron spectroscopy, electron energy loss spectroscopy and ion neutralization spectroscopy might also be appropriate for this discussion but will not be considered. We shall limit the discussion to reflectivity, x-ray and ultra violet photoemission, and x-ray absorption and emission spectroscopies.⁽¹⁾

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Due to space limitations, this discussion of spectroscopic techniques will necessarily be very incomplete and somewhat qualitative to emphasize the kind of information that can be obtained. Only illustrative examples will be presented. Subtleties in the techniques and analyses cannot be adequately discussed.

The valence band spectrum obtained by x-ray photoemission spectroscopy (XPS) usually provides a reasonably accurate direct measure of the occupied density of states. Because of this apparent interpretative simplicity, XPS is a very good first experiment for studying electronic structure of the occupied states in metals. The technique also lends itself to the study of both itinerant and local valence states. Chemical bonding information can be obtained from XPS core level studies. (Due to the wide variety of information available from XPS studies, somewhat more attention will be devoted to the XPS studies than to the complementary spectroscopies.)

With the knowledge of valence band states obtained from XPS, excellent follow-up spectroscopies are UPS and optical reflectivity both of which can provide information about the empty conduction states as well as the occupied valence states. The techniques often contain too much information for reasonably straightforward analysis and data interpretation may demand extensive theoretical support. The x-ray absorption and emission techniques also nicely complement the above spectroscopies. Both conduction and valence electron structure information can be obtained. Synchrotron radiation from electron storage rings can provide a very high intensity radiation source over a spectral range from the infrared to x-ray region. The high intensities and

continuous scanning capabilities afforded by synchrotron radiation can contribute substantially toward improving all of the above spectroscopies. To the authors knowledge, however, no electronic structure studies of actinide materials have been reported using synchrotron radiation.

II. Electron Emission Spectroscopies

The photoemission spectroscopies depend upon the energy analysis of electrons emitted from a sample surface as the result of photons of known energy impinging on the sample. Measurement of the emitted electron flux as a function of kinetic energy gives a "mapping" of the occupied density of states $n(E)$. For valence band studies using XPS, the photoemitted electrons are excited to final states far above the Fermi level E_F where the energy bands are expected to have essentially plane wave character. Thus, the measured spectrum should be sensitive to the occupied states with little distortion from $\vec{k}$ dependence in the empty conduction bands. The observed XPS spectrum for a given metal will contain distortions from the actual density of states because of matrix elements effects. For itinerant states, this distortion is usually small.

With ultra violet photoemission spectroscopy (UPS), valence and conduction band structure information is convoluted and crystal momentum $\vec{k}$ becomes an important parameter so that one does not measure a simple $n(E)$ but rather a joint density of states that is dependent on $\vec{k}$. Contributions to the observed spectrum depend upon the location within the Brillouin zone where the transition occurs. Thus, UPS is more dependent on details of the band structure than is XPS. These details can be interpreted with the aid of suitably accurate and detailed energy band calculations. Additional electronic structure information can be obtained from angular

resolved photoemission (ARP) spectroscopy. It appears that one can continuously map out energy dispersion relations throughout the Brillouin zone. For the itinerant ferromagnet iron, an ARP study was able to follow dispersion relations for both the majority and minority spin bands.⁽²⁾ The demonstration of this application of UPS is very recent and has not yet been exploited for any actinide systems.

The cross section for photoemission of electrons of a given angular momentum character depends upon the energy of the exciting photons. Thus, from photon energy dependence studies, one can obtain information about the angular momentum character of the occupied states. Figure 1 shows photoemission spectra for UO_2 taken with 21.2 eV(He I), 40.8 eV(He II), and 1253 eV(Mg $K\alpha$) radiation.⁽³⁾ Peak B consists primarily of O 2p derived electrons while peak A corresponds to localized U 5f electrons in the $5f^2$ ground state configuration.⁽⁴⁾

As discussed above, the valence band XPS spectrum is often a very accurate representation of the itinerant valence electron states in a solid. For local states occupying a partially filled shell, as are often encountered in actinide compounds and the heavy actinide elements, however, the interpretation of XPS spectra is different. One no longer measures a ground state property of the material but rather a spectrum of the possible (or accessible) excited states of the localized electrons. Since the localized electrons in a partially filled shell are strongly correlated, the excitation of one of those electrons is felt by the remaining members of the shell. Excitations, (representing the possible angular momentum coupling schemes and possible configuration changes), of the local electron system provide a channel for absorption of some of the energy of the incident photon. The observed

spectra are thus a measure of accessible multiplets which can be excited by the incident photon during the process of photoemission.

XPS multiplet spectra have been observed and analyzed in numerous studies of lanthanide systems.⁽⁵⁾ The simplest systems are probably the elemental lanthanide metals where a relatively small portion of the total XPS spectrum (near E_F) is contributed by itinerant or band electrons. Essentially all observed features can then be analyzed with multiplet theory. For the actinides, no XPS (or UPS) measurements have been reported for elemental metals. Only data for actinide oxides have been so analyzed. Figure 2 shows XPS spectra for dioxides of Np, Pu, and Am compared with the theoretically computed free ion multiplet spectra broadened to simulate experiment.⁽⁶⁾ There is substantial correspondence between the calculated and observed spectra. However, a potentially more fruitful experiment would provide similar measurements for the metals. Experimentally, better resolution should be obtained so that more spectral detail would be available for analysis. The O 2p orbitals, which overlap the multiplet spectra in the oxides, would be absent. And most importantly, the multiplets should provide direct input into assessing the extent to which the 5f electrons are localized.

Chemical bonding information in compounds can be obtained from the measurement of XPS core level binding energies. The binding energies of the electron core levels of an atom are dependent upon the local charge environment at the atomic site. That local charge is determined by the distribution of molecular orbitals in the compound. Figure 3 illustrates the effect for the U 4f levels of U_3O_8 where chemically shifted peaks corresponding to U^{4+} and U^{6+} ionization states are observed.⁽⁷⁾

III. Reflectivity and Absorption

Reflectivity experiments, typically spanning the spectral region from the near infrared (1 eV or less) to a few tens of electron volts, have been extensively applied to the study of the electronic structure of a wide range of materials. Modulation techniques contribute a large subset to the reflectivity and absorption spectroscopies. Reflectance studies have seen limited application in the field of actinide research. Studies on oxides of light actinides and on some elemental metals have been reported.⁽⁸⁾

The measured parameters of interest [usually obtained by Kramers-Kronig inversion of the reflectivity $R(\omega)$] are the components of the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. ϵ_2 relates directly to the electron band structure. Photons at energy $\hbar\omega$ can excite electrons from all occupied valence states between E_F and $E_F - \hbar\omega$ into conduction states between E_F and $E_F + \hbar\omega$. $\epsilon_2(\omega)$ is thus a convolution of the state densities of the valence and conduction bands within energy $\hbar\omega$ modulated by electric dipole selection rules and momentum conservation ($\vec{k}$ dependence) considerations. A quantitative first-principles calculation of $\epsilon_2(\omega)$ is difficult and costly requiring, as a starting point, a determination of the energy bands $E(\vec{k})$ throughout the Brillouin zone and the wave functions $\psi_{\vec{k}}(E)$. However, electronic structure information can often be inferred from positions and intensities of spectral features even when available theoretical input is severely limited. Figure 4, for example, shows the components of $\vec{\epsilon}(\omega)$ for UO_2 as measured by J. Shoenes⁽⁹⁾ and the energy level scheme which he proposes to account for the observed features.

The positions and intensities of spectral features, selection rules and sum rules are discussed to support the proposed model. It is argued that both localized 5f states and itinerant band states contribute to the observed spectrum. In support of the model, Gubanov, Rosen and Ellis⁽¹⁰⁾ (GRE) have examined UO_2 within the framework of theoretical molecular cluster models and confirm several features of the proposed electron energy level scheme. They obtain the expected band gap, d-electron, crystal field splittings, and energies of major features. The contribution which the localized 5f electrons make to the spectrum of $\epsilon_2(\omega)$ probably remains most uncertain. Shoenes argues that, like XPS, multiplet excitations in the $5f^{n-1}$ system provides a channel for absorption of incident radiation when a localized $5f^n$ electron is excited to a higher band. Shoenes argues that, for the f^1 final state, only two (spin-orbit split) levels are expected. The proposed spin-orbit splitting of 1.1 eV exceeds, by over a factor of two, the spin-orbit splitting obtained by GRE. GRE argue that excitations within crystal field (or ligand field) split 5f levels (concurrent with the $f \rightarrow d$ transitions) can account for the observed spectral structure.

Another technique applicable to the study of insulators containing localized 5f electrons (such as UF_4 or CaF_2 containing dissolved actinide ions), is transmission or fluorescence optical absorption spectroscopy where transitions within a given f^n multiplet are excited.⁽¹¹⁾ This is an electric dipole forbidden process (for Russell-Saunders states) so that absorption coefficients are weak and cannot be observed when interband absorption processes occur. For suitable systems, however, this technique probably provides the most direct information about the 5f electron excitation spectrum. The large number of observable transitions provides redundant information from which the 5f ground state can be specified as well as the appropriate crystal field parameters.

IV. X-ray Techniques

X-ray emission and absorption spectroscopies provide alternative means for examining the valence and conduction bands of solids. When electrons are excited from a core state to the conduction band by x-rays, the absorption spectrum provides a measure of conduction band states that are accessible for electric dipole excitations. Similarly, de-excitation from valence band states to an empty core level produces an emission spectrum that is dependent on the band structure of the occupied valence states. The combination of absorption and emission spectra, then, should provide valuable information about the electronic states in the vicinity of E_F . Additional information about the valence (or conduction) bands can be gained by examining spectra associated with transitions to (or from) different core states thus exploiting the angular momentum selectivity afforded by electric dipole selection rules.

Absorption and emission studies have been reported for uranium and plutonium metals and for ThO_2 and UO_2 .⁽⁸⁾ For the metals, rather featureless, single peaks in both the absorption and emission spectra ($4d_{3/2}$ core levels) are attributed to 5f electron states. Results are shown in Fig. 5 for $\alpha\text{-Pu}$.⁽¹²⁾ For localized 5f valence states, more complexity may be encountered in the x-ray spectra because of the possibility of exciting transitions within the local 5f system.

Appearance potential spectroscopy⁽¹³⁾ (APS) is a tool similar to the x-ray techniques that is also useful for investigating conduction electron structure. Electrons are excited from core levels to the conduction band by an incident electron beam. The electron energy near excitation threshold is plotted against x-ray emission intensity. The emission monitors the rate of core hole production and hence the excitation probability of the incident electron

beam. This excitation probability is related to the conduction band density of states. Figure 6 shows conduction electron APS results of Houston and Park for α -uranium metal⁽¹⁴⁾ plotted with XPS valence band data.⁽⁴⁾ These experimental results are compared with the f-electron contribution to the total density of states as computed by Freeman et al.⁽¹⁵⁾. This comparison was made [rather than total $n(E)$] since the f electrons probably dominate the XPS spectrum,^(3,4) and in the conduction band region, the calculated f-electron $n(E)$ is similar to the total $n(E)$. The relative scaling of the XPS and APS spectra is arbitrary. Furthermore, as we have seen in other spectroscopic experiments involving 5f states, the tendency toward localization may introduce interpretation complexities. Nonetheless, the agreement between theory and experiment shown in Fig. 6 is encouraging.

V. Bonding of Metal Oxides in Silicate Glass

Recently, work has been undertaken at Argonne National Laboratory to investigate the bonding of metal oxides in sodium silicate glasses. Some results on uranium oxides and Fe_2O_3 dissolved in $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ will be presented to illustrate an approach for obtaining bonding and structural information for these amorphous materials.

The silicate glasses are important for the actinide community because they have remarkably high solubilities for numerous metal oxides from all regions of the periodic table and thus are attractive candidate materials for long term storage of radioactive wastes. Many active nuclear species with great variation in atomic number must be stored. Fundamental information about the bonding properties of metal oxides in the silicate glasses can provide useful input for evaluating the confinement integrity of glass storage systems.

When UO_2 is dissolved into sodium silicate glass, with the sample melting done in air environment, we find that essentially all uranium appears in the +6 ionization state. If the preparation is conducted in vacuum, then uranium retains the +4 ionization state. These results are illustrated in Fig. 7. For the vacuum melt (curve a), the peak near the valence band edge is a measure of the occupancy of localized 5f electrons. No 5f occupancy appears in the air melt (curve b-nor in a glass sample prepared with UO_3) indicating that the uranium is in the +6 oxidation state.⁽⁴⁾ Similar conclusions can be drawn from examining the 4f core levels where the +6 ionization state appears at the higher binding energy (Fig. 7-insert). [Probably only +4 or +6 ionization states would be expected, consistent with observations of Verbist et al.⁽⁷⁾ for oxides of uranium.]

The oxidation state of uranium in the amorphous silicate matrix can be readily discerned. It also appears, from a detailed study of the O 1s line, that additional information pertaining to the bonding of the oxide in the matrix can be obtained. In essence, the procedure is to monitor the rate of oxygen bond alteration in the matrix silicate caused by incorporating a metal oxide.

The behavior of UO_2 (or UO_3) in the silicate glass appears to be dramatically different from the behavior of Fe_2O_3 dissolved in the glass. The XPS results indicate that no apparent disruption of the oxygen bonds in the glass matrix is observed when UO_2 (or UO_3) is added. Rather the XPS data are consistent with the conclusion that the uranium oxides enter the glass as a simple mixture. In contrast, for Fe_2O_3 glass, matrix oxygen bonds are clearly disrupted to permit the Fe^{3+} ion to bond to three oxygens of the glass matrix.⁽¹⁶⁾

The arguments are best illustrated for Fe_2O_3 where matrix bond alteration occurs. Figure 8(b) illustrates O 1s levels for $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$.⁽¹⁷⁾ Figure 8(a) shows the O 1s line for the iron glass. Subtracting the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ contribution from the iron glass spectrum, we obtain the difference spectrum shown in Fig. 8(c). Had the Fe_2O_3 entered the glass matrix without chemical rearrangement (e.g., as a simple mixture), one would expect the difference spectrum to exhibit a simple Gaussian line shape. Rather, the shape of Fig. 8(c) indicates that oxygen 1s bonds of the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ are destroyed on addition of Fe_2O_3 to produce a new bonding site, apparently associated with Fe-O bonds. To obtain a simple (Gaussian) line shape (curve d) by subtraction of curve b from curve a, curve b must be scaled by a factor whose magnitude implies that for each added molecule of Fe_2O_3 , three oxygen bonds of the disilicate matrix are broken and replaced by bonds to the iron atoms. That is, the original oxygen bonds in the disilicate [corresponding to Fig. 8(b)] are consumed to produce Fe-O-Si bonds in the iron glass.

For UO_2 , simply subtracting the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ contribution from the $(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)_{0.8} (\text{UO}_2)_{0.2}$ spectrum produces a simple difference lineshape which cannot be improved by relative scaling. Thus, no bond alteration in the matrix glass can be observed. Probably, molecular units of UO_2 (or UO_3) are contained in open regions of the amorphous matrix without formation of strong molecular orbitals between the matrix and oxide.

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Figure Captions

- Figure 1. Photoemission spectra for UO_2 taken at photon excitation energies of 21.2 eV (He I), 40.8 eV (He II), and 1253 eV (Mg K α). The U 5f electrons (peak A) have a very different dependence on photon energy than the O 2p's (peak B). (See Ref. 3.)
- Figure 2. XPS spectra of localized 5f states in light actinide oxides compared to the calculated final state multiplet spectra. (See Ref. 6.)
- Figure 3. XPS spectra for the spin-orbit split U 4f levels in U_3O_8 . Chemically shifted peaks corresponding to U^{4+} and U^{6+} ions are observed. (See Ref. 7.)
- Figure 4. The real (solid line) and imaginary (dashed line) parts of the dielectric function $\hat{\epsilon} = \epsilon_1 + i\epsilon_2$ for UO_2 displayed vs. photon energy. The band model shown is proposed to account for the observed spectral features. (See Ref. 9.)
- Figure 5. X-ray absorption and emission spectra for α -Pu metal. (See Ref. 12.)
- Figure 6. The calculated f-electron density of states⁽¹⁵⁾ (histogram) for α -U compared with XPS measurements⁽⁴⁾ below E_F and with APS measurements⁽¹⁴⁾ above E_F .
- Figure 7. XPS valence band and U 4f (insert) spectra for $(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)_{0.8} \cdot (\text{UO}_2)_{0.2}$ when (a) the melt was done in vacuum and (b) the melt was done in air. For the vacuum melt, the U^{+4} ionization state dominates; for the air melt, the U^{6+} state dominates.

Figure Captions (Contd.)

Figure 8. XPS O 1s lines for (a) sodium disilicate containing Fe_2O_3 and (b) for sodium disilicate. The simple difference spectrum (c) indicates that O 1s bonds of the disilicate matrix are broken by the added Fe_2O_3 . The scaled difference (d) indicates that 3 bonds of the matrix are broken for each added molecule of Fe_2O_3 .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8