Review

X-ray and electron microscopy of actinide materials

Kevin T. Moore*

Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

ABSTRACT

Actinide materials demonstrate a wide variety of interesting physical properties in both bulk and nanoscale form. To better understand these materials, a broad array of microscopy techniques have been employed, including transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDXS), high-angle annular dark-field imaging (HAADF), scanning electron microscopy (SEM), wavelength dispersive X-ray spectroscopy (WDXS), electron back scattered diffraction (EBSD), scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning transmission X-ray microscopy (STXM). Here these techniques will be reviewed, highlighting advances made in the physics, materials science, chemistry, and biology of actinide materials through microscopy. Construction of a spin-polarized TEM will be discussed, considering its potential for examining the nanoscale magnetic structure of actinides as well as broader materials and devices, such as those for computational magnetic memory.

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1. Introduction

Actinides are the 14 elements relegated to the bottom of the Periodic table. Across the series, the 5f electrons progressively fill in a manner similar to the 4f electrons in the rare earth series, but with more active bonding in the light actinides. Scientific interest in these electrons is fervent due to their strongly correlated nature. However, while the nuclear processes are well understood given their role in energy, the physical and chemical properties of the actinides remain obscure compared to lighter elements because they are difficult to handle. Between the numerous unanswered scientific questions on basic physical properties and a potential resurgence of nuclear power due to rising energy demand, the actinides are an exciting and burgeoning class of materials. As with any materials, the ability to identify and characterize micro- and nanoscale physical properties is imperative for advanced understanding and application. This level of interrogation can be achieved through a variety of means, but microscopy offers a direct and powerful method to examine actinide materials at small spatial scales. In a world where cutting-edge science and engineering depends on ever smaller sizes, this mean microscopy must play an integral role in the advancement of actinide science.

In this review, a variety of X-ray and electron microscopy techniques will be considered in regards to actinide materials, including transmission electron microscopy (TEM) in both static and scanning mode, electron energy-loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDXS), high-angle annular dark-field imaging (HAADF), scanning electron microscopy (SEM), wavelength dispersive X-ray spectroscopy (WDXS), electron back scattered diffraction (EBSD), scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning transmission X-ray microscopy (STXM). Particular attention will be paid to micro- and nanoscale chemical and structural characterization of these materials, a facet that while being present for decades for lighter elements is just coming to fruition for the actinide elements. In reviewing microscopy techniques, advances made in the physics, materials science, chemistry, and biology of actinide materials will be highlighted, including radiological waste management; electrical transport phenomena; phase transformations and equilibria; chemical reactions; microstructure of weld joining; and electronic, magnetic, and crystal structure. The review will be concluded with an examination of spin-polarized TEM, a future tool to examine the nanoscale magnetic structure of ferromagnetic materials, including the actinides.

This review is meant to focus on advances in microscopy of actinide materials. For in-depth treatments of the physics and chemistry of the actinides, there are several books, such as Freeman and Darby (1974), Freeman and Lander (1984), and Morris et al. (2006) as well as review articles, such as Santini et al. (1999, 2009), Schwartz et al. (2009b), Moore and van der Laan (2009), and van der Laan and Moore (2010).

2. The unique world of actinide materials

When considering the actinides, it is good to start with the elemental metals as they are the most simple. Typical metals exhibit high-symmetry structures, such as face-centered cubic, hexagonal close packed, and body-centered cubic. However, the light actinides exhibit low-symmetry structures that are typical of minerals: tetragonal, orthorhombic, and monoclinic (Moore and van der Laan, 2009). These low symmetry structures are the result of narrow bands. Unlike lighter metals that are bound by s electron states, which tend to form bands on the order of 10 eV, and the d electron states, which form bands on the order of 6 eV, the f band is only about 2 eV wide. The fact that narrow bands cause low-symmetry crystal structures was first illustrated by Söderlind et al. (1995), where the total energy of different crystal structures was examined as a function of calculated bandwidth using density-functional theory for four separate metals, each with different electron bonding states: Al (2p bonding), Fe (3d bonding), Nb (4d bonding), and U (5f bonding). All four metals exhibited low-symmetry crystal structures when the bandwidth of bonding electron states was narrow, such as found in the 5f states of the actinides at ambient pressure. On the other hand, high-symmetry structures were found for wide bands, similar to 4d and 5d metals at ambient pressure.

The symmetry reduction due to narrow bands shown by Söderlind et al. (1995) illustrates that the crystal structure of a metal distorts through a Peierls-like mechanism. The original Peierls distortion model was formulated in a one-dimensional lattice, where a row of equidistant atoms can lower its total energy by forming pairs. The lower periodicity causes the degenerate energy levels to split into two bands with lower and higher energies. The electrons occupy the lower levels, so that the distortion increases the bonding and reduces the total energy. In one-dimensional systems, the distortion opens an energy gap at the Fermi level making the system an insulator. However, in the higher dimensional systems, the material remains a metal after the distortion because other Bloch states fill the gap. This mechanism is effective if there are many degenerate levels near the Fermi level, that is, if the energy bands are narrow with a large density of states. This indeed is the case for the light actinide metals, Th, Pa, U, Np, and Pu.

Beyond the complex crystal structure of the light actinide metals, actinide materials in general exhibit strong electron correlations, meaning one-particle theoretical approaches often fail to properly describe the electronic and magnetic structure of the materials. Such a failure may in turn yield incorrect physical properties, such as bulk modulus, shear constants, and electrical and thermal transport. Advanced theoretical approaches, such as dynamical mean-field theory, have proved useful in this regard (Kotliar et al., 2006; Marianetti et al., 2009) and some thoughtful implementations of density-functional theory have been able to capture much of the physics of Pu (Söderlind and Sadigh, 2004; Söderlind, 2008), which is notoriously difficult for theory. Whether using standard one-particle approaches, such as density-functional theory, or advanced computational techniques, such as dynamical mean-field theory, each needs a robust and accurate record of experimentally recorded physical properties from which to extract parameters; otherwise, theorists are forced to make one or multiple approximations. This is one of the areas microscopy can make great strides, namely to benchmark the unique electronic, magnetic, and crystal structure of actinide materials. As it turns out, this class of materials is not only complex in static form, but changes occur over time, making theory and experiment even more difficult.

Most actinide materials accumulate lattice damage over time from self-induced irradiation due to nuclear decay. This comes in the form of α, β, and γ decay that occur in different amounts, depending on element and isotope. For example, α decay occurs in 239Pu, where a He atom is ejected with an energy of ~5 MeV and a uranium atom recoils with an energy of ~86 keV (Wirth et al., 2002). The He atom creates little damage to the lattice; however, the U atom dislodges thousands of plutonium atoms from their normal positions in the crystal lattice, producing vacancies and interstitials known as Frenkel pairs. Within ~200 ns most of the Frenkel pairs annihilate, leaving a small amount of damage in the lattice. A molecular dynamic simulations of this process in face-centered cubic 8-Pu is shown in Fig. 1, which is based on the molecular embedded atom method (Kubota et al., 2007). In this image, the pristine lattice is illustrated as open space for visualization purposes. The damage imparted to the lattice, which
occurs on a time scale of 2 ns, is shown by the trajectories of corresponding particles that are color-coded to indicate kinetic energy. While an appreciable amount of this damage quickly anneals out, over time, the remaining damage accumulates in the form of defects, such as vacancies, interstitials, dislocations, and He bubbles (Hecker, 2004; Schwartz et al., 2005). What this means is that not only are actinide elements intrinsically complicated, but lattice damage accumulates over time due to self irradiation, further complicating the physics of the materials. This also means that special handling procedures are necessary given the radioactive nature of the materials.

3. Sample preparation of actinide materials

Apart from a few isotopes, actinide elements are radioactive to varying degrees. In order to safely handle, prepare, and transfer actinide materials for microscopy, an inert-atmosphere glove box has been built that interfaces with vacuum-transfer holders, as shown in Fig. 2(a). Regardless of the sample or the final destination, the same glove box is employed for actinide material sample preparation and only the type of vacuum-transfer specimen holder changes depending on the type of experiment. Through this glove box samples are prepared for electron microscopy, synchrotron radiation, diamond anvil cell compression, low-temperature magnetic susceptibility, and differential scanning calorimetry. Supplies and samples are moved into and out of the glove box via an anti-chamber that can be either evacuated or purged with nitrogen. Regardless of the sample or the final destination, the same glove box is employed for actinide material sample preparation and only the type of vacuum-transfer specimen holder changes depending on the type of experiment. Through this glove box samples are prepared for electron microscopy, synchrotron radiation, diamond anvil cell compression, low-temperature magnetic susceptibility, and differential scanning calorimetry. Supplies and samples are moved into and out of the glove box via an anti-chamber that can be either evacuated or purged with nitrogen. (b) The vacuum-transfer TEM specimen holder docked at the airlock attached to the glove box. Once the TEM sample is prepared and loaded, it is pumped down and vacuum transferred to the TEM, never being exposed to atmospheric conditions.

Fig. 2. (a) The dry-train glove box used for actinide sample preparation that achieves a base-line reading of ~0.2 ppm for O₂ and ~1 ppm H₂O with an inert atmosphere of nitrogen. Through this glove box samples are prepared for electron microscopy, synchrotron radiation experiments, diamond anvil cell compressions, and differential scanning calorimetry. Supplies and samples are moved into and out of the glove box via an anti-chamber that can be either evacuated or purged with nitrogen. (b) The vacuum-transfer TEM specimen holder docked at the airlock attached to the glove box. Once the TEM sample is prepared and loaded, it is pumped down and vacuum transferred to the TEM, never being exposed to atmospheric conditions.

Starting off with the simple technique of bright-field imaging, we find there is a great deal that can be learned about actinide materials, including phase morphology (Zocco et al., 1990; Hecker
et al., 2004), defects (Hecker, 2004), chemical reactions (Moore et al., 2006), and impurity phases (Moore et al., 2002a). However, due to the highly reactive nature of many actinide materials, the issue of sample-preparation-induced artifacts is, as is so often the case in TEM investigations, a first and foremost priority.

4.1.1. Sample-preparation-induced phases

As with any TEM investigation, proper sample preparation is of utmost importance. A few sample-preparation artifacts are usually not an issue when using an electron microscope, since one can simply avoid these unwanted byproducts. Of course if sample-preparation artifacts become overwhelming, then useful TEM analysis becomes difficult to impossible. One problem with actinide materials, particularly metals, is their propensity for reaction with gases, such as O, N, and H; this often results in sample-preparation-induced phases of oxides, nitrides, and hydrides, respectively. This problem is illustrated in Fig. 3, where ion-milled samples of Np (a), Pu (b), and Am (c) metal are shown. In each case, the metals contain varying amounts of hydride precipitates that were produced during sample preparation via ion milling. The vacuum of the ion mill, which is on the order of $5 \times 10^{-6}$ torr, is not low enough to preclude reactions with gases, often resulting in sample-preparation-induced phases. Electro-polishing does not impart as many impurity phases when preparing actinide metals, however since it often takes a considerable amount of material to perfect a polishing solution, ion-beam milling is frequently the only choice for TEM sample preparation of rare actinide materials. Ironically, sample-preparation-induced phases are sometimes helpful because they are previously unexamined phases and unknown spectra and diffraction can be measured. However, unwanted phases sometimes contaminate the microstructure or the material of interest and this can become especially detrimental for synchrotron radiation experiments where the resolution is not sufficient to avoid the unwanted phases.

4.1.2. Nanoscale He bubbles

As discussed in Section 2, most actinide materials accumulate damage over time due to self-induced irradiation (Hecker, 2004; Schwartz et al., 2005). In the $\alpha$ decay process, a He atom is ejected and a uranium atom recoils. While the He atom creates little damage to the lattice, the remnant He accumulates over time, migrates through the lattice, and creates nanometer-sized He bubbles. The bubbles influence physical properties, such as strength and ductility, and continually change due to perpetual self-irradiation, so understanding their size, number density, etc., as a function of time is important.

He bubbles in $\delta$-Pu due to self-induced irradiation damage and He growth is shown in the bright-field TEM image in Fig. 4(a). Clearly near atomic resolution is needed to find and examine these bubbles given that their average size is a few nanometers. One issue that comes into play with using a 300 keV field-emission-gun TEM to collect this data is beam coherence and, concomitantly, where to measure the edge of the bubbles. No clear answer was achieved after numerous image simulations, and so all bubbles are measured from full width half maximum of the bright center of each bubble recorded at 1.7 $\mu$m under focus. This yields

![Image](image-url)
consistency in measurements such that trends in bubble size (and number density) can be examined with material age. This is precisely the case shown in Fig. 4(b), where bubble diameter as a function of age is shown for 18–42 year old Pu material. This graph reveals the need for data in the earliest periods, within the first year, to validate the theoretical curves with and without cascade effects that are plotted over the experimental data points.

4.1.3. Precipitate microstructure

When Pu is alloyed with a few percent of trivalent metals such as Al, Ga, Ce, or Am, the readily machinable fcc δ phase can be retained in a metastable state at room temperature (Hecker, 2004; Schwartz et al., 2009a,b). Examination of the Pu-rich side of the Pu–Ga binary phase diagram shows that δ-Pu should separate into α + Pu3Ga at room temperature. However, kinetics limits the transformation such that δ-Pu is stable for thousands of years, even with self-radiation damage (Hecker and Timofeeva, 2000). However, when the metastable fcc Pu with a few atomic percent Ga is cooled to below −120°C, an isothermal martensitic transformation occurs to the monoclinic α' phase (The prime simply means there is Ga trapped in the lattice). A time-temperature-transformation (TTT) diagram for a Pu–0.56 wt.% Ga alloy shows there are two noses on the TTT curve, one at −130°C and one at −155°C, suggesting that there are two distinct thermally-activated mechanisms existing for this transformation. A maximum of about 25% transformation to α' occurs, beyond which little additional transformation is observed. This is most likely due to the large amount of plastic deformation and internal stress that must occur during the ~20% volume reduction in the δ → α' martensitic transformation. TEM affords a direct means to examine the transformation microstructure and the concomitant damage due to the large volume change from δ- to α-Pu.

A two-phase mixture of α' plates and δ fcc matrix coexist after the Pu–Ga alloy has been cooled to −120°C for 10 h. The α'/δ orientation relationship was examined via TEM and reported as:

\[ (1\ 1\ 1)_{\delta} \parallel (0\ 2\ 0)_{\alpha'} \]
\[ [1\ 1\ 0]_{\delta} \parallel [1\ 0\ 0]_{\alpha'} \]

by Zocco et al. (1990). The α' plates in the micrograph in Fig. 5(a) are easily seen due to the strong mass contrast caused by the 20% volume difference between α' and δ. In previous theoretical examinations, the macroscopic habit plane of α' plates was shown to be near \( (1\ 2\ 3)_\delta \) (Adler et al., 1986). Assuming a habit plane of \( (1\ 2\ 3)_\delta \), 24 variants of α' are produced in the fcc matrix due to symmetry operations. Our optical microscopy and TEM experiments have repeatedly revealed not 24, but rather ~4 variants. An elastic phase-field simulation of the growth and intersection of α' plates in a single crystal of δ is shown in Fig. 5(a) (Krenn et al., 2004; Moore et al., 2007a), where there are 24 variants as would be expected from \( (1\ 2\ 3)_\delta \) habit plane. However, the micrograph in Fig. 5(a) shows fewer variants, and in fact looks very much like plates on a \( (1\ 1\ 1) \) habit plane when looking parallel to a \( <1\ 1\ 1> \) direction of an fcc crystal.

The volume reduction that occurs in the δ → α' martensitic transformation is approximately 20%, so the amount of damage that occurs during transformation is accordingly large. In order to better understand this, calculations and transmission electron microscopy were again performed. Elastic-plastic finite element calculations can be used to visualize the stress induced by the δ → α' martensitic transformation, and this is shown in the left side of Fig. 5(b) (Krenn, 2004; Krenn et al., 2004; Moore et al., 2007a). Here, the compressive and tensile stresses are shown for a fcc matrix that has first grown an α' plate, then
reverted back to fcc δ phase. The large and isolated strain fields near the tip of the α′ plate are clear in the color computed image in Fig. 5(b). Examining the dislocation density in a two-phase Pu–Ga alloy using TEM in Fig. 5(b), there are six to seven times more dislocations near the α′/δ interface in the image right compared to the matrix away from any α′ plates in the image center.

As discussed in Section 2, many actinide materials exhibit low-symmetry crystal structures like minerals. In fact, an examination of the microstructure of some monoclinic minerals shows striking similarities to the α′ plates in Pu–Ga alloys. This is illustrated in Fig. 6, where the two images in the left column are Pu–Ga alloys and the two images in the right column are pyroxenes, a single-chain silicate that is abundant in the Earth’s crust and upper mantle. The electron micrographs of the intergrown pyroxenes augite (Ca rich) and pigeonite (Fe rich) have a hook-like structure (Moore et al., 2001a,b). In the case of the minerals, both are monoclinic in crystal symmetry; however, the Pu–Ga alloy is a monoclinic secondary phase in an fcc matrix. Regardless of this difference, both systems exhibit a hook-like structure with growth along the primary monoclinic directions a, b, and c. No detailed study has yet been performed on this, but the images alone show fascinating trends in the growth of monoclinic phases in a host crystal.

4.2. Electron diffraction and dark-field imaging of charge density waves in α-U

A charge density wave (CDW) is a low-energy ordered state that forms in low-dimensional or low-symmetry materials that have a high density of states at the Fermi level. When these materials are cooled to sub-ambient temperatures, a periodic charge modulation forms that is defined by the characteristic spatial frequency q. The CDW is commensurate with the atomic lattice when q is a rational fraction or multiple of the lattice constant; it is incommensurate when q is irrational. The atomic lattice itself often distorts by a few percent due to the CDW, resulting in a cooperative state where the lattice and electron charge each distort to achieve a reduced free energy of the system. The magnitude of q is determined by the Fermi surface nesting vector of the material, where q connects parallel areas of electron pockets and holes in momentum space. When the CDW forms, a gap opens in the Fermi surface along the areas connected by the nesting vector. Low-dimensional materials and low-symmetry metals or alloys often have anisotropic Fermi surfaces with prominent nesting vectors, which opens the possibility of CDW formation upon cooling. While these charge modulations are small, they can alter lattice parameter, resistivity, elastic response, and thermal expansion, meaning CDWs clearly influence the physical properties of the crystal.

Fig. 6. A comparison of the two-phase microstructure of a Pu–Ga alloy (left column) and the mineral pyroxene (right column). In the case of Pu–Ga, the monoclinic α′ phase grown in an fcc host. In the case of the pyroxenes, monoclinic pigeonite grows in a monoclinic augite host. The lines in pigeonite are stacking faults. Striking is the similarity in microstructure between two entirely different materials, each with a monoclinic second phase.
Charge density waves often form in surfaces (Carpinelli et al., 1996) and layered materials (Fournel et al., 1986; Kim et al., 2008) due to low dimensionality; however, they seldom form in the bulk of elemental metals. Chromium (Fawcett, 1988) and uranium (Smith et al., 1980; Lander et al., 1994) are the only known pure elemental systems that exhibit a bulk spin or CDW, respectively. Potassium was reported to have a CDW (Giebultowicz et al., 1986), but this has been largely discounted (Pintschovius et al., 1987). Elastic constant measurements of α-U to liquid-helium temperature show a large change in $c_{11}$ at 43 K, revealing a phase transformation at that temperature (Fisher and McSkimin, 1961). It turns out this is a CDW that is clearly observed in the phonon dispersion curves, where cooling to 30 K causes the $\Sigma_4$ branch in the [100] direction to condense, or reduce in frequency (Crummett et al., 1979; Smith and Lander, 1984). At this temperature, superlattice reflections appear due to charge ordering that is incommensurate with the atomic lattice. Neutron diffraction experiments show there are in fact three separate CDWs—43 K ($\alpha_1$), 37 K ($\alpha_2$), and 22 K ($\alpha_3$)—where $\alpha_1$ and $\alpha_2$ are incommensurate with the lattice and $\alpha_3$ is commensurate (Marmeggi et al., 1990). First-principles calculations show the strong nesting of the narrow 5f bands in the Fermi surface for the $\alpha_1$ phase, where partial gaps are opened at the Fermi surface (Fast et al., 1998).

Large single crystals are needed to reveal the CDW in α-U. For example, specific heat measurements on single crystal α-U show clearly resolved peaks at the three CDW transition temperatures (Lashley et al., 2001); however, these peaks are unresolved in polycrystalline samples due to varying elastic strains between different metal grains (crystallites) in the microstructure (Manley et al., 2002). In other words, the CDW peaks are washed out in specific heat measurements of polycrystalline samples because slightly different elastic strains in each grain cause the small CDW peak positions to vary in temperature. This variation of CDW onset temperature between different grains causes the overall signal to be smeared out over enough temperature range to loose resolution of the CDW peak. This issue can be circumvented by searching for CDWs with scattering techniques with high spatial resolution (Kim et al., 2005).

Transmission electron microscopy has been employed for α-U at low temperature to examine the CDW superlattice reflections using electron diffraction (Chen and Lander, 1986). In this work, the sample was cooled using liquid He to between 18 and 26 K, producing diffraction patterns similar to the one shown in Fig. 7(a). In this [0 1 0] zone axis pattern recorded at 18 K, the primary α-U reflections are marked with red circles while the CDW reflections are the weak reflections at $(h + 1/2), 0, l = $ odd. Dark-field imaging performed using the CDW superlattice reflections revealed several interesting facts about the ordered state. First, different CDW superlattice reflections were produced by different areas of the sample, meaning there were distinctive domains, as shown in Fig. 7(b) and (c). Second, there was a distinct memory effect, where the sample could be cycled from room temperature to low temperature, repeatedly producing the same domain structure. Finally, 100 reflections appeared in the diffraction pattern at 18 K, a possible result of the loss of C-centered symmetry that occurs in the orthorhombic Cmcm α-U crystal when the CDWs forms. This, however, is not entirely clear from their work and may be due to double diffraction from the heavy U atoms. The results of Chen and Lander (1986) illustrate the strength of TEM to search for and examine CDWs on the nm to μm scale in polycrystalline materials. As a final note, due to their low crystal symmetry and high density of states, it was postulated that CDWs may form in α-Np and α-Pu. Both metals were cooled to 10 K in a liquid He TEM holder by Moore et al. (2008) in hopes of finding such an ordered state, but none was found.

Fig. 7. (a) Selected-area diffraction pattern of α-U at 18 K with [0 1 0] orientation, where the red circles denote the primary Bragg reflection of the metal. (b) and (c) A pair of dark-field images showing a contrast reversal when different CDW reflections are used to form the image. From Chen and Lander (1986).

### 4.3. High resolution imaging of the PuCoGa$_5$ superconductor

The discovery of superconductivity to 18.5 K in PuCoGa$_5$ (Sarrao et al., 2002) was a significant event to both the actinide and charge transport communities. The structure of PuCoGa$_5$ is part of a large class of materials known as the 115 group, where the number represents the stoichiometric character $X_1Y_1Z_5$. The superconducting state in PuCoGa$_5$ is delicate and readily effected by impurities and defects. Evidence of this is given by the fact that self-induced irradiation damage causes the superconducting transition temperature to drop ~0.2 K per month in PuCoGa$_5$, slowing in rate as defects accumulate over time (Sarrao et al., 2002; Booth et al., 2007; Jutier et al., 2007, 2008).

Atomic resolution imaging is a viable tool for examining the crystal lattice of PuCoGa$_5$ as self-induced irradiation damage accumulates over time. An example of this shown in Fig. 8, where (a) is a bright-field image that illustrates the overall microstructure, (b) is a high-resolution image with areas of lattice damage due to self-induced irradiation, and (c) is an experimental
high-resolution image with a unit cell of PuCoGa$_5$ and a simulated high-resolution image. These are merely preliminary results on a single sample; there is no data yet available of atomic-level irradiation damage as a function of time and how this correlates with the drop in superconducting transition temperature.

4.4. Electron energy-loss spectroscopy

Electron energy-loss spectroscopy is a powerful tool for examining the electronic structure of a material. In regards to actinide materials, it offers many positive attributes. First, the TEM utilizes small samples, which allows one to avoid the handling of appreciable amounts of toxic and radioactive materials. Second, it allows one to do in-house experiment rather than taking radioactive material to a multi-user synchrotron radiation facility. Third, the technique is bulk sensitive due to the fact that the electrons traverse ~40 nm of metal, which is the appropriate thickness for quality EELS spectra of actinide materials. A few nanometers of oxide do form on the surfaces of the TEM samples, but this is insignificant in comparison to the amount of metal sampled through transmission of the electron beam. Finally, as pointed out in Section 4.1.1, actinide metals readily react with hydrogen and oxygen, producing unwanted phases in the material during storage or preparation for experiments. The TEM has the spatial resolution to image and identify secondary phases, ensuring examination of only the phase(s) of interest.

4.4.1. Comparison with X-ray absorption spectroscopy

EELS spectra collected in the TEM are, within error, identical to XAS spectra. At first this may not seem correct, since in XAS the transitions are electric-dipole whereas in EELS there is also an electric-quadrupole transition due to momentum transfer (Reimer, 1995; Egerton, 1996). However, the work by Moser and Wendin (1988, 1991) on the $O_{4,5}$ ($5d - 5f$) and $N_{4,5}$ ($4d - 5f$) edge of Th shows that as the energy of the incident electron is increased, the EELS spectral shape became more similar to XAS, and at around 2 keV they are close to identical. The incident energy of the TEM electron source used to collect the EELS spectra is 297 keV, ensuring the electron transitions are close to the electric-dipole limit. The use of apertures that remove high-angle Bragg and plural scattering (Moore et al., 1999a,b) further refine the quality of EELS, providing spectra that are practically identical to XAS for transition metals (Blanche et al., 1993), rare earths (Moore et al., 2004), and actinides (Moore et al., 2007b,c). Looking specifically at actinides, direct comparison of Th and U $O_{4,5}$ edge can be made between EELS (Moore et al., 2003) and XAS (For Th: Cukier et al., 1978; Aono et al., 1981. For U: Cukier et al., 1978; Iwan et al., 1981). Similar comparisons can be made for the $N_{4,5}$ edge of U for EELS (van der Laan et al., 2004) and XAS (Kalkowski et al., 1987). In all cases, the EELS and XAS spectra are identical within error.

This equivalence between EELS and XAS is becoming stronger now that monochromated TEMs are available that have an energy resolution comparable to monochromatized synchrotron radiation (Hill et al., 1988; Brown, 1997; Walther and Stegmann, 2006). In fact, some TEMs can even resolve better than 50 meV (Brink et al., 2003), which is close to the energy of phonon excitations. An example of monochromated EELS with 100 meV energy resolution as compared to synchrotron XAS is shown in Fig. 9. The $N_{4,5}$ ($4d - 4f$) and $M_{4,5}$ ($3d - 4f$) transitions of $\gamma$-Ce are shown for EELS spectra acquired in a monochromated TEM, XAS from the Advanced Light Source at the Lawrence Berkeley National Laboratory, and many-electron atomic spectral calculations (Moore et al., 2004). Note the similarity between spectra, particularly the two experimental spectra, which clearly illustrates that EELS in a TEM is practically identical to synchrotron-radiation-based XAS. Ironically, a monochromated source is not needed for EELS measurements on actinides, since the intrinsic core-hole lifetime broadening for the actinide $d \rightarrow f$ transitions is ~2 eV (Kalkowski et al., 1987). Nonetheless, the comparison of EELS in a monochromated TEM and synchrotron-radiation-based XAS in Fig. 9 firmly illustrates the equivalence of techniques when a high primary electron energy is utilized for EELS.

4.4.2. The $O_{4,5}$ edge

To investigate the $5f$ states of actinide elements using EELS or XAS, transitions from $d$ core states are utilized because they directly probe the $f$ states due to the electric-dipole transitions $\Delta l = \pm 1$. The selection rules for these transitions strongly limit the
final states that can be reached from the initial 5f\(^n\) state, which means that the spectrum becomes a fingerprint of the initial state. These transitions to the 5f states can be excited using either a 3d (M\(_{4,5}\)), 4d (N\(_{4,5}\)), or 5d (O\(_{4,5}\)) core level, each yielding different spectral behaviors.

The O\(_{4,5}\) (5d \(\rightarrow\) 5f) edges of Th, U, Np, Pu, Am, and Cm metal are shown in Fig. 10(a), where all the edges are normalized to the same peak intensity (Butterfield et al., 2008; Moore and van der Laan, 2009). While the spectrum for each elemental metal is distinctively different, they all contain a broad edge that is often referred to as the giant resonance (Wendin, 1984). This edge is preceded by a narrow structure in Th, U, and Np that is typically referred to as a pre-peak. The giant resonance is ill-defined for the actinide O\(_{4,5}\) (5d \(\rightarrow\) 5f) transition because the core 5d spin–orbit interaction is smaller than the core–valence electrostatic interactions (Ogasawara et al., 1991; Ogasawara and Kotani, 1995, 2001). This effectively smears out the transitions, encapsulating both the O\(_4\) (5d\(_{3/2}\)) and O\(_5\) (5d\(_{5/2}\)) peaks within the giant resonance, and making distinction between them difficult or even impossible. The dipole-allowed transitions are contained within the giant resonance, whereas the pre-peak is a result of the finite spin–orbit interaction (Moore and van der Laan, 2007).

Fig. 9. The N\(_{4,5}\) (4d \(\rightarrow\) 4f) and M\(_{4,5}\) (3d \(\rightarrow\) 4f) transitions for y-Ce metal as acquired by EELS, XAS, and many-electron atomic spectral calculations. Of particular importance is the fact that the XAS and EELS from a monochromated TEM are essentially identical in both resolution and spectral shape. This means that comparison between the techniques, as well as to multi-electronic atomic calculations, is entirely justified. From Moore et al. (2004) and Moore and van der Laan (2009).

Fig. 10. (a) The experimental O\(_{4,5}\) (5d \(\rightarrow\) 5f) EELS edges for Th, U, Np, Pu, Am, and Cm metal. In each case the ground-state \(\alpha\) phase was examined. (b) Calculated actinide O\(_{4,5}\) absorption spectra with 5d core spin–orbit interaction for the ground state configurations \(f^7\) to \(f^9\) using a Fano line shape broadening for the giant resonance. The calculations in (b) are convoluted using a Fano line shape broadening of \(\Gamma = 2\) eV for the giant resonance and a Lorentzian line shape of \(\Gamma = 0.5\) eV for the pre-peak structure, where the cross-over between these two regions is assumed to be at a relative excitation energy of 5 eV. From Butterfield et al. (2008) and Moore and van der Laan (2009).

Multiplet theory can be used to calculate core-level spectra for EELS and XAS of the M\(_{4,5}\), N\(_{4,5}\), and O\(_{4,5}\) edges given by the transitions \(f^7\) \(\rightarrow\) \(d^0\) or \(f^9\). These calculations are performed in the same way as the M\(_{4,5}\) and N\(_{4,5}\) absorption edges for the rare earths (Thole et al., 1985; Starke et al., 1997), only the parameters are different. Contrary to band-structure calculations, the multiplet structure is calculated in intermediate coupling, which treats spin–orbit, Coulomb, and exchange interactions on equal footing (van der Laan, 2006). The calculated actinide O\(_{4,5}\) spectra are shown in Fig. 10(b) for the ground state configurations \(f^7\) \(\rightarrow\) \(f^9\). The calculated spectra in (b) reproduce the general trends in the EELS data in (a) very well. First, the pre-peaks in the Th and U O\(_{4,5}\) EELS edge are produced in agreement with the experimental EELS (Moore and van der Laan, 2009) and XAS (Kalkowski et al., 1987) spectra. Second, the width of the calculated O\(_{4,5}\) edge reduces by about half when going from \(n = 5\) to 6, which is exactly what we observe between Pu and Am in the O\(_{4,5}\) EELS.

To better understand the actinide O\(_{4,5}\) edges, it is instructive to consider the shape of the 4f rare earth N\(_{4,5}\) (4d) edges and the 3d transition metal M\(_{2,3}\) (3p) edges, which also exhibit a giant resonance similar to the actinide O\(_{4,5}\) edge. In all three of these cases, the core–valence electrostatic interactions dominate the core spin–orbit interaction. The 4f metals show a pre-peak structure that is similar to the light actinides and is largely insensitive to the local environment (Dehmer et al., 1971; Starace, 1972; Sugar, 1972), meaning the pre-peak structure changes little with bonding environment. The 3d metals show a pre-peak structure that is strongly dependent on the crystal field and hybridization (Thole and van der Laan, 1988a,b; van der Laan, 1991). Since the 5f localization is between those of 4f and 3d, the O\(_{4,5}\) pre-peak behavior for the actinides is expected to show only a mild dependence on the environment. Indeed, examining the O\(_{4,5}\)
edge of $\alpha$-U and UO$_2$ in Moore and van der Laan (2007) shows there is only a slight change in the pre-peak structure where a small shoulder appears on the high energy side of the peak at about 98 eV in UO$_2$. The U $O_{4.5}$ edge has also been used for empirical identification of uranium oxides and fluorides, where the spectral structure could differentiate between U$^{4+}$ and U$^{6+}$ (Rice et al., 1999).

4.4.3. The N$_{4.5}$ edge

For the actinide N$_{4.5}$ ($4d-5f$) edge the situation is entirely opposite from the O$_{4.5}$ edge: the 5$d$ spin–orbit interaction is dominant over the 5$d$5$f$ electrostatic interaction. Therefore, the 4$d_{5/2}$ and 4$d_{3/2}$ peaks, or ‘white lines’, are well separated by the large core spin–orbit splitting that is on the order of 40 eV and considerably larger than the electrostatic interaction. Due to this large splitting, the 5$f$ spin–orbit interaction per hole can be directly examined for a particular actinide material by the spin-orbit sum rule (Thole and van der Laan, 1988a,b; van der Laan and Thole, 1996; van der Laan et al., 2004). The branching ratio of the spectra is extracted from the spin-orbit-split core-level edges gathered from the N$_{4.5}$ ($4d-5f$) peaks. Electric-dipole selection rules allow two kinds of transitions: N$_5$ ($4d_{5/2} - 5f_{5/2,7/2}$) and N$_6$ ($4d_{3/2} - 5f_{5/2}$). Since an electron from a $d$ core state can only be excited into spin-0 $f$ states, this leads to differences in the branching ratio that can be interrogated using the spin-orbit sum rule.

The N$_{4.5}$ edge for each metal is shown in Fig. 11(a), where each spectrum is normalized to the N$_5$ ($4d_{5/2}$) peak height. Immediately noticeable is the gradually growing separation between the N$_5$ and N$_6$ peaks from Th to Cm, in pace with the increase in 4$d$ spin-orbit splitting with atomic number. Also noticeable is that the N$_5$ ($4d_{5/2}$) peak reduces in intensity going from Th to Am, but then the trend reverses, giving a larger intensity for Cm. The behavior of the N$_5$ peak in the EELS spectra in Fig. 11(a) directly reflects the filling of the angular momentum levels in the 5$f$ state. Selection rules govern that a 4$d_{5/2}$ electron can only be excited into an empty 5$f_{5/2}$ level, which means that the ratio of the N$_5$ ($4d_{5/2}$) and N$_6$ ($4d_{3/2}$) peak intensities serves as a measure for the relative occupation of the 5$f_{5/2}$ and 5$f_{7/2}$ levels. The N$_5$ peak reduces rapidly as the atomic number increases because the majority of the 5$f$ electrons are occupying the 5$f_{7/2}$ level. By the time Am is reached, the N$_5$ peak is almost extinct since the 5$f_{7/2}$ level is close to full with six 5$f$ electrons (there is only a minor amount of electrons in the 5$f_{5/2}$ level). Thus, there is little room for an electron from 4$d_{5/2}$ to be excited into the 5$f_{5/2}$ level. For Cm, the N$_5$ peak then increases relative to the N$_6$ peak.

For the $f$ shell, the number of electrons, $n_f$, and the expectation value of the angular part of the spin–orbit interaction, $\langle w^{110} \rangle$, is given as

$$n_f = n_{7/2} + n_{5/2}, \quad (1)$$

$$\langle w^{110} \rangle = \frac{3}{2} (l - s) = n_{7/2} - \frac{3}{2} n_{5/2}, \quad (2)$$

where $n_{7/2}$ and $n_{5/2}$ are the electron occupation numbers of the angular-momentum levels $j = 7/2$ and 5/2 (Thole and van der Laan, 1988a;b; van der Laan and Thole, 1996; van der Laan et al., 2004). Thus, $\langle w^{110} \rangle$ reveals the proper angular momentum coupling scheme for a given material. The branching ratio $B = n_{5/2}/n_{7/2}$ is obtained by calculating the second derivative of the raw EELS spectra, then integrating the area beneath the N$_5$ and N$_6$ peaks above zero, which yields the integrated intensities $I(N_5)$ and $I(N_6)$. The experimental branching ratio for Th, U, Np, Pu, Am, and Cm metal are listed in Table 1. For each metal the value of the branching ratio is fed into the spin-orbit sum-rule, yielding the spin–orbit interaction per hole. For the $d-f$ transition, the sum rule is given as

$$\langle w^{110} \rangle = \frac{14}{14 - n_f} - \Delta = -\frac{5}{2} \left( \frac{B - \frac{3}{2}}{\frac{3}{2}} \right), \quad (3)$$

where $\Delta$ represents a small correction term for the sum rule calculated using Cowan’s relativistic Hartree–Fock code (Cowan, 1981; van der Laan and Thole, 1996). The results of the spin-orbit analysis for the EELS spectra of each metal are given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Metal</th>
<th>$n_f$</th>
<th>$B$</th>
<th>$\langle w^{110} \rangle/(14 - n_f) - \Delta$</th>
<th>$n_{5/2}$</th>
<th>$n_{7/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>1.3</td>
<td>0.646 (003)</td>
<td>-0.115 (008)</td>
<td>1.28</td>
<td>0.02</td>
</tr>
<tr>
<td>U</td>
<td>3</td>
<td>0.688 (002)</td>
<td>-0.215 (005)</td>
<td>2.35</td>
<td>0.66</td>
</tr>
<tr>
<td>Np</td>
<td>4</td>
<td>0.740 (005)</td>
<td>-0.350 (013)</td>
<td>3.24</td>
<td>0.76</td>
</tr>
<tr>
<td>Pu</td>
<td>5</td>
<td>0.826 (010)</td>
<td>-0.565 (025)</td>
<td>4.32</td>
<td>0.68</td>
</tr>
<tr>
<td>Am</td>
<td>6</td>
<td>0.930 (005)</td>
<td>-0.825 (013)</td>
<td>5.38</td>
<td>0.62</td>
</tr>
<tr>
<td>Cm</td>
<td>7</td>
<td>0.794 (003)</td>
<td>-0.485 (008)</td>
<td>4.41</td>
<td>2.59</td>
</tr>
</tbody>
</table>

Each branching ratio value is an average of between 10 to 20 EELS spectra, with the standard deviation given in parenthesis. The sum rule requires a small correction factor, which is $\Delta = -0.017$, $-0.010$, $-0.005$, $0.000$, $0.005$, and $0.015$ for $n_f = 1, 3, 4, 5, 6, \text{ and } 7$, respectively. The experimental electron occupation numbers $n_{5/2}$ and $n_{7/2}$ of the $f_{5/2}$ and $f_{7/2}$ levels are obtained by solving Eqs. (1) and (2).
In order to analyze the spin-orbit analysis of the EELS spectra, several steps are followed. First, the $N_{4.5}$ edges are calculated in each coupling limit using many-electron atomic spectral simulations. The results for intermediate coupling are shown in Fig. 11(b) for a number of f electron counts (van der Laan and Thole, 1996). Next, a plot of $(w^{1/2})/(14 - n_f)$ against the number of $f$ electrons in made for the atomic calculations in the three theoretical angular-momentum coupling schemes, $LS$, $jj$, and intermediate, which is shown in Fig. 12. From here, the experimental EELS results are plotted as blue points, generating the following results. Th metal falls close to all three curves, which is due to the fact that it takes two electrons to tangle and with barely more than one $5f$ electron in Th there is little difference between the coupling mechanisms. U falls directly on the $LS$ coupling curve, Np between the $LS$ and intermediate curve, and Pu, Am, and Cm all fall on or near the intermediate coupling curve. The intermediate curve is strongly shifted towards the $jj$ limit for Pu and Am, indicating the strong preference of the $5f$ electrons for the $5f_{5/2}$ level in these two metals. However, at Cm there is a sudden and pronounced shift in the intermediate coupling curve toward the $LS$ limit.

The electron occupation numbers $n_{7/2}$ and $n_{5/2}$ can be calculated by subtracting the values of $n_f$ and $(w^{1/2})$ in Eqs. (1) and (2). The experimental and theoretical results are listed in Table 1 and displayed in Fig. 12, where the number of electrons in the $5f_{5/2}$ and $5f_{7/2}$ levels as calculated in intermediate coupling using the atomic model are drawn with black and red lines, respectively. Again, the experimental EELS results are indicated with blue points. Apart from the slight deviation in the lighter actinides, U and Np, which is caused by delocalization of the $5f$ states and thus indicates a departure from the atomic model, the EELS results are in excellent agreement with the theoretical curves. Fig. 12 clearly shows that for the actinide metals up to and including Am, the $5f$ electrons strongly prefer the $5f_{5/2}$ level. However, this changes in a striking manner at Cm, where not only does the electron occupation sharply increases for the $5f_{5/2}$ level, but even decreases for the $5f_{7/2}$ level. 

The results shown in Figs. 11 and 12 lead to several conclusions, namely the spin-orbit sum rule is sensitive to the degree of delocalization of the $5f$ states, intermediate coupling for the $5f$ states as obtained from atomic calculations is the appropriate scheme for Pu, Am, and Cm, and these three metals have $f$ electron counts near $5f^6$, $5f^5$, and $5f^5$, respectively. The spin-orbit analysis and magnetic calculations of Moore et al. (2007b) also explain why the crystal structure of curium is stabilized by magnetism, as first proposed by the density-functional theory results of Heathman et al. (2005). Thus, the experimentally acquired EELS spectra have been used in conjunction with theory to extract and benchmark quantum mechanical aspects of the $5f$ states of actinide metals, in turn relating them to physical properties of the materials.

4.4.4. The $M_{4.5}$ edge

The actinide $M_{4.5}$ (3d − 5f) edge is similar to the $N_{4.5}$ edge, where the $d_{3/2}$ and $d_{5/2}$ peaks appear as two white lines separated by the large spin-orbit splitting of the core 3d states that is on the order of 200 eV. The edge for actinide elements resides in the energy range between 3000 and 6000 eV, meaning for a TEM with a post-column energy filter the lenses must be adjusted to work beyond the standard 3000 eV energy loss. This is routinely done by Buck and others (Buck and Fortner, 1997; Fortner et al., 1997; Buck et al., 1997, 2004, 2009; Colella et al., 2005) in regards to investigating actinide contamination and storage of nuclear fuels. The valence states of uranium in synthetic and natural brannerite samples were studied using the actinide $M_{4.5}$ (3d − 5f) edge as acquired via EELS in a TEM (Colella et al., 2005). The spectra were collected at LN2 temperature in order to minimize the effects of electron beam reduction of $U_6^{2+}$ and $U_5^{5+}$. Three natural brannerites from different localities, each of which were entirely amorphous due to cumulative self-induced irradiation from $\alpha$ decay events over geological time periods, as well as three additional synthetic brannerites. One of the natural brannerites is show in the SEM image in Fig. 13(a), where a reaction front can be seen due to environmental weathering. A TEM micrograph and inset diffraction pattern in Fig. 13(b) shows the amorphous nature of the material. These natural and synthetic brannerites were analyzed using the EELS $M_{4.5}$ branching ratio, $B = l(M_3)/(l(M_5) + l(M_4))$, against the number of $f$ electrons, and calibrated using a number of U sample standard: UO$_6$, CaUO$_4$, SrCa$_2$UO$_6$, Ti$_2$O$_6$, and Y$_{0.5}$U$_{0.5}$Ti$_2$O$_6$. The spectra were collected as shown in Fig. 13(c), then the background was removed from the raw spectra using a second derivative. Thus, as done for the $N_{4.5}$ edge, the second derivative of the raw $M_{4.5}$ EELS spectra is calculated, then the area beneath the $M_4$ and $M_5$ peaks is integrated above zero, yielding the integrated intensities $I(M_4)$ and $I(M_5)$. This process is illustrated in the inset of Fig. 13(c). The results of Colella et al. (2005) for the brannerites and standards is shown in Fig. 13(d), revealing a non-linear relationship between the branching ratio and the number of $f$ electrons of U in solids. It also gives a curve with which one may take a given branching ratio and extract an f-electron count, which is often an important parameter for first principles calculations.

4.5. Energy dispersive X-ray spectroscopy of zirconia–thoria–urania ceramics

Energy dispersive X-ray spectroscopy, particularly in scanning mode, is a robust technique for elemental analysis that has been used for metal alloys (Moore et al., 2002a,b), mineralogy (Popvic...
et al., 2007), and biology (Leapman and Andrews, 1991) with great success. For actinide materials it is quite useful for isotopes that are less radioactive; however, for more strongly radioactive elements the technique become more difficult. When the sample radiation is large, spurious peaks are created in the EDXS spectra that must be removed by first recording a spectrum with the beam off the sample, then subtracting it from the spectrum recorded with the beam on the sample, each with the same acquisition time. High background radiation from the sample may also produce a considerable dead time for the detector, resulting in a low count rate and poor counting statistics. Finally, high X-ray emission from the sample can flood the detector causing the automated control shutter to close. This forces one to “find a balance” between the amount of signal received and the amount of background radiation. A balance is practically found by reducing the size of the sample, shielding some of the sample from the detector, or inserting the EDXS detector just enough to get signal but not enough to flood the detector.

Zirconia–thoria–urania ceramics, which hold potential as fuel for generation IV reactors, have been examined by Curran et al. (2003) using energy dispersive X-ray spectroscopy in a TEM. Their results are shown in Fig. 14 for Zr6Th3U with 0.5 wt.% MgO, where (a) is a bright-field image, (b) a Th elemental map, (c) a Zr elemental map, and (d) a U elemental map. The results show that while U is fairly uniform in its distribution (as well as Mg, which is not shown), Th and Zr are isolated to opposite grains. The overall stoichiometry, Zr6Th3U, was held to a Th–U ratio of 3:1 for reactor physics considerations; however, their analysis clearly shows little solubility of Th and Zr. This is an example where EDXS was fairly straight-forward due to reasonable sample radiation. However, EDXS work on 239Pu, which is considerably more radioactive, has proven to be difficult to record and analyze (Moore et al., 2002a).

4.6. Energy-filtered imaging of ThO2 stained bacteria

Having spent an appreciable amount of time discussing hard materials it is attractive to consider actinides in the context of soft materials. To this end, we will consider in this section how cationic hydrous thorium dioxide colloids can be used as a matrix stain of glycoaminoclycans of tissues (Groot, 1981; Winkler et al., 2001) and for staining bacteria for use in EFTEM imaging (Lünsdorf et al., 2006; Hegermann et al., 2008). With biology and biological engineering being a burgeoning field for the next century, it will be all the more important to consider how actinides may play a role in advancing the field.

![Fig. 13](image13.png)

Fig. 13. A series of images and data from brannerites samples. (a) An SEM image of a natural brannerite, where a reaction front can be seen due to environmental weathering. (b) A TEM micrograph and inset diffraction pattern showing the amorphous nature of the material. (c) The M4,5(3d → 5f) EELS spectra from brannerite. The inset shows how the background was removed from the raw spectra using a second derivative. (d) The EELS M4,5 branching ratio, \( B = \frac{I(M_5)}{I(M_4)+I(M_5)} \), vs. the number of f electrons, and calibrated using a number of U sample standard: UO2, CaUO4, SrCa2UO6, UTi2O6 and Y0.5U0.5Ti2O6. From Colella et al. (2005).

![Fig. 14](image14.png)

Fig. 14. A series of TEM data sets from Zr6Th3U with 0.5 wt.% MgO. (a) Bright-field image, (b) Th elemental map, (c) Zr elemental map, (d) a U elemental map, acquired using energy dispersive X-ray spectroscopy. Notice that Th and Zr separate in different phases, while U is homogenously distributed. From Curran et al. (2003).
Conventional and energy-filtered TEM imaging of Th-stained bacteria was performed by Lünsdorf et al. (2006). Results are shown in Fig. 15(a) and (b), which are *Pseudomonas aeruginosa* cells that have been contrasted after aldehyde fixation while growing in suspension then embedded with thorium dioxide. Higher magnification images, as shown in Fig. 15(b), reveal ultrastructural details of the outer cell surface near the macromolecular level. They show the morphology of thorificated cells is similar to those which were conventionally stained. EFTEM imaging was performed using the O$_{4,5}$ edge, as shown in the inset in Fig. 15(b). A standard three-window removal method was employed to create the elemental maps (Egerton, 1975). A bright-field image and Th elemental map are shown in Fig. 15(c) and (d), respectively. Thorium-rich regions clearly appear in Fig. 15(d) as the green-colored regions. The Th O$_{4,5}$ edge serves well for EFTEM imaging, since it is a high-intensity edge due to the $d \rightarrow f$ transition and O-type edges can yield spatial resolution of 2.4 nm with inelastically scattered electrons (Golla and Kohl, 1997).

The work of Lünsdorf et al. (2006) thus shows that application of cationic hydrous ThO$_2$ colloids for examining bacteria is highly effective for EFTEM. Because of the good diffusibility of Th, it stains and outlines electro-negative charges within these biopolymers, allowing robust EFTEM imaging of *Pseudomonas aeruginosa* cells. In situ whole-mount application of cationic hydrous thorium dioxide colloids for tracing acidic groups of bacterial slime matrices also works well for *E. coli* cells. From Lünsdorf et al. (2006).

4.7. High-angle annular dark-field imaging of uraninite nanoparticles

High-angle annular dark-field imaging can be performed in a conventional or dedicated scanning TEM when equipped with an annular dark-field detector. High-angle, incoherently scattered electrons are recorded, giving strong sensitivity to variation in atomic number, thus the often used term “Z-contrast imaging”. This, of course, makes the technique of great interest for actinides, especially when they are contained in a matrix of lighter elements. What is more, HAADF can be performed in tandem with analytical techniques, such as EXDS and EELS, meaning structural and chemical information can be recorded in tandem.

Uraninite nanocrystals in an atmospheric aerosol have been examined by Utsunomiya et al. (2002, 2009) and Utsunomiya and Ewing (2003). In their studies, the distribution of a trace amount (1–10 ppm) of uranium was examined in airborne particulates from mainly coal-fired power plants. Electron microscopy results are shown in Fig. 16, where (a) is a bright-field image that does not clearly reveal the structure or composition of the nanoparticles. However, the HAADF image shown in Fig. 16(b), which is of the boxed area in (a), clearly shows the heterogeneous distribution of U-rich nanoparticles. Using higher magnification TEM imaging, the nanoparticles were subsequently identified as uraninite, UO$_2$ $\cdot$ $\alpha$ encased in well-crystallized graphite, as shown in Fig. 16(c). Finally, the high-resolution image in Fig. 16(d), with insets of the particle magnified and a Fourier transform of the particle, yield lattice spacings that match uraninite. This instance discussed here
of U ($Z = 92$) encased in carbon ($Z = 6$) affords a clear example of when and how HAADF can be a powerful tool for examining actinide materials.

5. Scanning electron microscopy

Scanning electron microscopy, which is a surface sensitive technique, is naturally suited for examining large-scale structural morphology through secondary electron imaging, crystal orientation through backscattered electrons, and chemistry using a myriad of spectroscopy techniques. As often is the case, SEM investigations combine several of these techniques, therefore each will be discussed in the next two sections.

5.1. Wavelength dispersive X-ray spectroscopy of nuclear fuel pellets

When spent nuclear fuel is reprocessed, the fuel rods are sectioned and the nuclear material is separated from the cladding through dissolution. The remaining solid waste, which comes from the zirconium alloy cladding, are sections called (hulls) and must be disposed. Any remaining radioactive material on the hulls complicates storage and disposal. Accordingly, it is of interest to understand how well the dissolution process works and in turn identify and characterize any remaining nuclear materials. An SEM with imaging and spectral capabilities, which can operate on the nanometer to millimeter scale, is a prefect tool for such investigations.

Wavelength dispersive X-ray spectroscopy is a technique that counts the number of emitted X-rays of a specific wavelength Bragg diffracted from a crystal. A combination of SEM and WDXS was employed by Lamontagne et al. (2008) to examine spent fuel hulls from a French UO$_2$ fuel rod with Zircaloy cladding. An optical micrograph of a section of a cladding hull is shown in Fig. 17(a). Examining the inner surface of the hull in Fig. 17(b) reveals the impression of a pellet interface, which is shown at high magnification in (c). The hull impression was subsequently examined using WDXS elemental mapping of Zr, U, and Pu, as shown in (d), (e), and (f), respectively. While the Zr distribution is fairly uniform with a somewhat higher concentration in the cladding surrounding the pellet impression, the U and Pu distribution is clearly higher at the center of the pellet impression. It is the remains of such fuel pellets, and the associated U and Pu, which make disposal and storage of these hull more difficult than if the radioactive elements entirely dissolved away.

5.2. Electron backscattered diffraction of U metal welds

Electron backscattered diffraction performed in an SEM yields the crystallographic orientation of material. It is highly useful for elucidating texture or preferred orientation in polycrystalline material (Schwartz et al., 2009a) and has been used on actinides for examining the microstructure of Pu–Ga alloys (Boehlert et al., 2003), the shape memory effect of deformation structures in a U–14 at.% Nb alloy (Clarke et al., 2008), and deformation twinning (Field et al., 2009) and recrystallisation in α-U (McCabe and Teter, 2006). Here, focus will be on the recrystallisation of uranium in regions that have been electron beam welded (Scott et al., 2009).

Depleted U is used for a multitude of components, such as military armament. During fabrication, joining of two parts is often required, meaning they must be welded. Electron beam welding is...
frequently utilized because the welds are precise. They are also performed in a partial vacuum, which ensures less reaction of the weld joint with gases while the metal is liquid. However, the resultant microstructure of welded areas depends on numerous parameters, such as electron beam power, energy flux distribution, welding speed, focal location, focal spot size, and convergence angle (Cary and Helzer, 2005). This, in turn, influences mechanical properties, such as strength and ductility. Accordingly, characterization of weld joints is paramount in order to understand how the resultant microstructure influences performance.

Recrystallisation of uranium in electron-beam welded regions was examined by Scott et al. (2009). A schematic image and a series of stitched SEM images of a weld are shown in Fig. 18(a). From this image it is clear that a change occurs in the microstructure when moving from the cast (body) uranium on the left, to the heat affected zone (HAZ) in the center, to the weld center on the right. While this image shows the grain size is dramatically reduced in the weld center, it does not give any crystallographic information. EBSD data taken from the red box in Fig. 18(a) is shown in Fig. 18(b). Significant variation in crystallographic orientation is observed between grains as well as inter-granular deformation twins that were likely caused during rapid cooling from the β to α phase (Scott et al., 2009). These results exemplify why weld joints are often heated for a period after welding so as to remove residual stress and to create a more uniform microstructure through grain growth.

6. Scanning tunneling microscopy of UO₂ reactions with oxygen

Scanning tunneling microscopy provides an image of the atomic arrangement of a surface by sensing corrugations in the electron density of the surface that arise from the positions of surface atoms (Binnig and Rohrer, 1986; Bai, 2000). The technique is based on quantum tunneling, where a finely sharpened tungsten tip is brought near the surface of a material and a bias applied between the tip and sample can allow electrons to tunnel through the vacuum. An image is created by measuring the current as the tip is scanned across the surface, where the tunneling current is a function of tip position, applied voltage, and the local density of states of the sample. STM in the context of actinides, which are often reactive and radioactive, can be difficult since the technique requires extremely clean surfaces, sharp tips, excellent vibration control, and sophisticated electronics. Besides these difficulties, the technique can be versatile since it can be performed at various temperatures with gas and liquid exposures. In the case of UO₂, which insulates at ambient temperature, STM work must be done at elevated temperature (400–500 °C) so that the material conducts, a requirement of STM.

STM has been used by Castell, Muggelberg, and others to examine the surface of UO₂ and its reaction with oxygen (Castell et al., 1996, 1998, 2000; Muggelberg et al., 1998a,b, 1999; Dudarev et al., 2000; Castell, 2003). UO₂ single crystals are grown through a process of pressing granulated UO₂ into cylinders, followed by sintering at 1700 °C for 10 h. The grain size increases over time, then millimeter grains are harvested through disintegration into fragmentary single crystals by heating to 2100 °C in flowing dry hydrogen for 1 h in a refractory metal furnace (for the full recipe, see Brook and Harrison, 1975). When cleaved along (1 1 1), voids are revealed that are typically of micrometer dimensions. A low-voltage SEM image of one of these voids is shown in Fig. 19(a). The voids exhibit clear (1 1 1) and (0 0 1) facets, and some appear to have reached their thermodynamic equilibrium Wulff shape (Castell et al., 2000; Castell, 2003). The atomic structure of the (1 1 1) cleaved surface can be examined by STM, as shown in the empty states image in Fig. 19(b). The charge density and empty state distributions can be calculated for the UO₂ (1 1 1) surface using LSDA + U and compared to the experimental image in Fig. 19(b). These results of Dudarev et al. (2000) shown in Fig. 19(c) reveal the comparison of experimental STM images and simulated
charge density/empty state distributions are not straightforward. This is not surprising, since as stated in Section 2 calculating the electronic, magnetic, and crystal structure of actinide materials is often difficult due to strong electron correlations.

An interesting facet of STM is the ability to examine the reaction of the UO₂ surface with oxygen. On the UO₂ (1 1 0) surface U dimer pairs form in double rows with slight overstoichiometry, as shown in Fig. 19(d). It has been shown that excess oxygen can stabilize the (1 1 0) surface through the formation of variable U–O superstructures (Campbell and Ellis, 1970). The STM image and schematic diagram in Fig. 19(d) relay a structure that could be the initial stage of an ordered, but unstable, superstructure on the UO₂ + x(1 1 0) surface that depends on the temperature and excess interstitial oxygen (Muggelberg et al., 1998a). Exposure to oxygen does not change this surface structure as it is incorporated interstitially without any influence on the uranium lattice positions. However, when molecular oxygen is adsorbed onto a UO₂(1 1 0) surface and the crystal is subsequently annealed in UHV at 750 °C for 1 h, a different type of oxygen superstructure is observed in STM, as shown in Fig. 19(e). The structure has changed compared to Fig. 19(d) because some of oxygen adsorbates diffused into the subsurface bulk interstitial positions, which is illustrated in the schematic drawing in Fig. 19(e). Results of these types are of great importance for understanding how UO₂, both on and off stoichiometry, changes when exposed to an environment with oxygen and elevated temperatures.

7. Atomic force microscopy of anisotropic resistance in UO₂

Atomic force microscopy is fundamentally based on the operation of the STM, where a probe composed of Si or SiN is mounted on a cantilever and moved across a sample surface. When the probe nears the sample surface it is deflected, in turn bending the cantilever. A laser, which is reflected from the top of the cantilever to an array of photodiodes, measures changes. This technique is sensitive to van der Walls, electrostatic, magnetic, and capillary forces among others. Each of these properties is important for actinide materials, since they govern physical properties.

The anisotropy of local electrical conductivity in UO₂+x was examined using current-sensing AFM by O’Neil et al. (2008). Their results are shown in Fig. 20, where (a) is an SEM image of the sample. The SEM image clearly shows there are three distinct types of surface features: Smooth featureless grains, faceted grains showing surface steps or ridges, and grains comprising a mixture of both features. In order to examine the local resistance, current-sensing AFM images were acquired in different areas of the sample and at different magnifications, as shown in Fig. 20(b) and (c). The conductivity image reveals higher conducting regions as bright and lower conducting regions as dark. Immediately noticeable is that the faceted grains exhibit high electrical conductivity while the smooth grains consistently exhibit low or no conductivity. Grains with both smooth and faceted features exhibit enhanced electrical
conductivity near the facets. The images also show there is enhancement of conductivity in the grain boundaries. Close examination of Fig. 20(c) shows that within the facetted regions themselves there are both conducting and non-conducting areas. The data in the images is supported by plots in Fig. 20(d) showing the dependencies of tip current vs. tip bias taken at the various locations. The curves, numbered 1–4 and taken from areas labeled in Fig. 20(b) and (c), correspond to (1) ridges on a facetted grain, (2) inclined facets of the pyramidal structure, (3) a flat terrace on the pyramidal facetted structure, and (4) the top of a smooth non-facetted region. Curves 1 and 2 confirm that the facetted structures are conducting, while curves 3 and 4 show the flat regions are not. Thus, the results of O’Neil et al. (2008) establish a clear correlation between surface morphology and electrical conductivity.

8. Scanning transmission X-ray microscopy of Cm-bearing microparticles

X-ray microscopy forms images and spectra using soft X-rays produced at synchrotron radiation sources. The resolution of X-ray microscopy, while better than optical microscopy, is less than electron microscopy. However, the interaction of uncharged X-rays is far less than charged electrons, meaning much thicker samples can be examined in transmission. What is more, radiation damage produced by STXM is often less than that imparted by TEM electron sources, especially with soft materials (Bluhm et al., 2006). In comparison to EELS, soft X-rays produced by synchrotrons afford extremely high energy resolution for XAS. What is more, STXM experiments do not necessitate ultra-high vacuum and can be performed on liquids as well as air-sensitive materials and complexes, meaning \textit{in situ} experiments can be undertaken in a manner similar to environmental TEM.

STXM is now routinely applied to actinides both in hard and soft matter (Rothe et al., 2004; Tyliszczak et al., 2005; Nilsson et al., 2005; Plaschke et al., 2005; Fillaux et al., 2006, 2007a,b; Shuh, 2007; Janousch et al., 2008; Vigier et al., 2008; Minasian et al., 2009). Radioactive material is safely handled by encapsulating particles between silicon nitride windows, which allow the passage of X-rays. David Shuh and collaborators at the Advanced Light Source work routinely with all actinides isotopes. STXM yields direct information and speciation of light-element bonding to actinides by XAS, which makes it a powerful tool for biological materials (Glasauer et al., 2009) and chemical complexes (Copping et al., 2009).

An example of STXM applied to a chemical complex is shown in Fig. 21, which is $^{248}\text{Cm(phenanthroline)}_2$. A Cm $N_{4,5}$ XAS spectrum

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{Fig_19.png}
\caption{A series of STM images and calculations from UO$_2$. (a) A low-voltage SEM image of voids found when a large single crystal was cleaved along (1 1 1). The void exhibits clear (1 1 1) and (0 0 1) facets. (b) Empty state STM image showing the atomic lattice. (c) The charge density and empty state distributions calculated for UO$_2$ (1 1 1) surface using LSDA + U. (d) Empty state STM images showing U dimer pairs that form in double rows on the (1 1 0) surface of slightly overstoichiometric UO$_2$. A schematic image of the surface is shown. (e) Empty state STM images of a UO$_2$ (1 1 0) surface. The structure has changed compared to (d) because some of oxygen adsorbates diffused into the subsurface bulk interstitial positions, as shown in the schematic drawing. From Muggelberg et al. (1998a,b), Dudarev et al. (2000), Castell et al. (2000), and Castell (2003).}
\end{figure}
Fig. 20. A series of AFM images and data. (a) An SEM image of the UO$_2$ sample used for acquisition of AFM images. (b) Current-sensing AFM image of a region of the UO$_2$ sample in (a). The Z-scales were 2000 nm (topography) and 40 nA (current). An external bias of 250 mV was applied. (c) Current-sensing AFM image: Z-scales were 1200 nm and 2.5 nA, with an external bias of 50 mV. (d) Dependence of tip current vs. tip bias taken at various locations on the UO$_2$ surface, as noted in (b) and (c) with numbers 1–4. From O'Neil et al. (2008).
is shown that was acquired from the complex using STXM at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The overall spectrum agrees well with the Cm $N_{4,5}$ EELS spectrum in Fig. 11(a). The scanning X-ray probe can also form images, as shown in the insets of Fig. 21. A normal-contrast image is shown in the left inset that was formed using X-rays with 853.3 eV energy. A corresponding Cm elemental map can be formed by acquiring a second image at the $N_5e$ edge at 863.8 eV. The 853.8 eV image is subtracted from the 863.8 eV image, yielding a chemical image based on the intensity in the Cm $N_5$ edge. The regions of high Cm content appear as white regions in the chemical map in the right inset, and these are marked with white arrows in both images. Thus, not only can chemical images be formed, but the spectra themselves may be analyzed as done with the $N_{4,5}$ EELS spectra in Section 4.4.3, examining the angular momentum coupling of the 5$f$ states. This technique will undoubtedly become useful for other actinide materials, such as nuclear fuels, as well prove useful for tomography, revealing the three-dimensional structure of actinide particles.

9. The future: measuring spin and orbital magnetic moments with spin-polarized TEM

In Section 4.4.3 it was shown that the spin–orbit interaction, $(l \cdot s)$, can be obtained from the branching ratio of the $N_{4,5}$ EELS spectra. However, it is not possible to address the expectation value of the orbital and spin magnetic moments, $(l_z)$ and $(s_z)$, respectively, without polarized radiation. Normally one examines these through X-ray magnetic circular dichroism (XMCD) at a synchrotron radiation source (van der Laan et al., 1986; van der Laan, 1998; Thole et al., 1992). In this technique, two XAS spectra are acquired in a magnetic field, one with left circularly polarized light and one with right circularly polarized light. The difference of these two spectra is a dichroism spectrum that can yield magnetic moments of an atom, such as its spin and orbital magnetic moment. For transition metals the L edge (2$p$ – 3$d$) is employed as exemplified in Fig. 22(a) for Fe, for rare earths it is the M edge (3$d$ – 4$f$), and for the actinides it can be either the N edge (4$d$ – 5$f$) or the M edge (3$d$ – 5$f$). In each case, the transitions are into unoccupied electron states of an atom that are directly responsible for the magnetic properties of a material, as schematically illustrated in the inset in Fig. 22(a) for the Fe L$_{2,3}$ transition.

The magnetic structure of actinide materials has been examined with XMCD using both the N edge (Okane et al., 2008) and the M edge (Kucera et al., 2002; Okane et al., 2008). The technique has also been used to examine various multilayers of U with transition and rare earth metals, such as Fe and Gd (Kernavanois et al., 2004; Wilhelm et al., 2007; Springer et al., 2008). An example of XMCD on U is shown in Fig. 22(b), where the upper panel is the M$_{4,5}$ edge acquired using both left and right polarized light. The lower panel shows the dichroic (difference) signal for a series of multilayers, where the subscript next to the element denotes the number of atomic layers and the subscript outside the brackets indicates the number of repeat layers. The results show that the dichroic signal is larger for multilayers with less U, becoming strongest for the sample with only nine layers. XMCD is element and transition
selective, meaning it can be used for the exact atom of interest, such as U in this multilayer work. However, the experimental setup used at the synchrotron radiation source shown in the inset of Fig. 22(b) does not yield the spatial resolution needed to examine each individual elemental layer within a multilayer; the spatial resolution is simply not near enough. Future plans have a solution for this.

Dichroic information can be obtained at the nanoscale in a TEM if the electron source is polarized. This can be achieved through the use of a photoemitting source driven by a laser that is polarized via a grating. This would enable the nanometer-scale acquisition of element and transition selective EELS that can yield the spin and orbital magnetic moments of a given atom species. Magnetic circular dichroism has been detected using EELS in a standard TEM by Schattschneider et al. (2006). In this process, an unpolarized electron beam traverses a ferromagnetic material, producing magnetic dichroism in the momentum resolved EELS spectra. It is promising to be able to achieve dichroism in a standard TEM; however, the dichroic signal is considerably weaker than that achieved using a polarized source, and specific sample orientations must be used since particular scattering conditions are required. A TEM with a spin-polarized source would be a more robust and versatile tool, and to this end we plan to construct the first spin-polarized TEM.

Several fundamental issues would need to be addressed in the construction of a spin-polarized TEM. First, what would the source be and would it be bright enough? A negative electron affinity GaAs photoemitting source driven by a pulsed laser yields a brightness of \(4.4 \times 10^8\) AC m\(^{-2}\)sr\(^{-1}\) at 100 keV, which is brighter than LaB\(_6\) at 7 \(\times\) 10\(^6\), W hairpin filament at 5 \(\times\) 10\(^5\), pointed W filament at 2 \(\times\) 10\(^5\), and a heated field emission source at 10\(^7\)–10\(^8\) (Pierce, 1995). What is more, a GaAs source can achieve a \(\sim 30\) meV resolution (Feigerle et al., 1984), meaning the energy resolution would be outstanding even compared to today's monochromated TEMs. Thus, a GaAs photocathode would yield both high brightness and an intrinsically narrow energy spread of the emitted beam. Second, can the standard electromagnetic lenses in a TEM properly operate when a planar source is utilized rather than a point source? This is not yet settled, but preliminary calculations suggest the condenser, objective, and projector lenses should function suitably, albeit with slightly higher aberrations. Third, would the objective lens be electromagnetic or electrostatic? If the former is used, the \(\sim 1\) Tesla field produced near the sample from the pole piece will surely influence the magnetic structure in some manner, possibly aligning the magnetic moment and destroying any domain structure. If the latter is employed, the probe quality and resolution will be compromised. This choice has yet to be finalized. A balance would need to be found, since the sample would need to be magnetically field cooled in order to lock in magnetism, but a field will also damage magnetic domain features which could be of interest. The cooling aspect can easily be handled with their an LN\(_2\) or liquid helium holder. The field would be a more difficult engineering issue and will be resolved in the future. Surely there are other issues to address, but these are front and center when considering the construction of a spin-polarized TEM. None, however, appear insurmountable.

Engineering problems aside, a spin-polarized TEM would be able to interrogate the magnetic structure of materials at the nanoscale. Scientific and engineering issues ranging from the behavior of magnetism at transformation interfaces and defects to the nanoscale magnetic structure of magnetic memory devices could be addressed. It would be indispensable for examining the magnetic structure of transition metal, rare earth, and actinide multilayers, such as those considered by Kernavanois et al. (2004), Wilhelm et al. (2007), and Springell et al. (2008). The spin-polarized TEM would be comparable with synchrotron radiation sources and STM, yet with different strengths and weaknesses. It would have a better spatial resolution than a synchrotron source, but would be less bright. Compared to STM, it would be more bulk sensitive and be able to examine insulators, but would be less sensitive. In the end, it is not that any one would be better than the other, but rather that all three would be a symbiotic suite of experimental tools with which to investigate the magnetic structure of materials, including the actinides.

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References


Brook, R.J., Harrison, K.T., 1975. The Achievement of Spectacular Grain Growth in \(\text{UO}_2\) Fuel. UKAEA, Harwell.


Moser, H.R., Wendin, G., 1991. Theoretical models for intensities of


Plaschke, M., Rothe, J., Altmaier, M., Denecke, M.A., Fanghanel, T., 2005. Near edge X-


