# **Understanding** Actinides through the Role of 5*f* Electrons

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#### Introduction

Studies of the actinide elements and compounds were (and are) motivated by the need to characterize their structural and thermodynamic properties for the development of nuclear fuels and the treatment of waste, whether it be for long-term storage or ideas involving transmutation in high-powered accelerators. For the most part, tables giving these data exist, although the data for transuranium compounds are rather sparse. A much more difficult task is to understand the data and develop theories that have predictive power in this part of the periodic table. In doing this, however, we are confronted with the extremely complicated electronic structure of the 5fshell and the great paucity of high-quality data on materials containing transuranium isotopes.

Research on uranium, both the element and compounds of it, is conducted in many parts of the world because uranium is a nontoxic material (at least in the quantities used for basic research) and can be handled in university laboratories. Our lab has projects on uranium because of our collaborations with European laboratories (as well as laboratories in the United States and Japan); however, our primary focus is on transuranium materials, which *cannot* be investigated in many places.

Because our European Commission lab is situated in Karlsruhe at an institute that specializes in transuranium materials, mostly connected with the nuclear-fuel industry in the areas of fuel development, fuel characterization, or aspects of the nuclearwaste problem, we have an infrastructure for handling transuranium isotopes (principally Np, Pu, Am, and Cm). Thus, this article focuses particularly on work from our own laboratory. We give a brief review of the basic research activities on actinide elements and compounds, revealing the varying nature of the 5*f* electrons across this last, and least explored, row of the periodic table. We emphasize our efforts on Np, Pu, and Am, and how such studies can enhance our understanding of the complete series. We start with the importance of preparation and then describe measurement techniques including those to characterize structural, magnetic, transport, and surface properties.

#### **Preparation and Transport Studies**

Our effort starts with preparation. Many different materials science techniques exist, but our laboratory has devoted a considerable effort to producing high-purity single crystals of actinide compounds,1 which these high-level physics experiments demand. Techniques such as mineralization, zone-refining and the Czochralski process for the metallic compounds, and vapor transport for the oxides, can be used to produce crystals and to increase the purity, thus assuring the stoichiometry. Some of these materials are shown in Figure 1. The crystals are then characterized by x-ray, scanning electron microscopy, and microprobe analysis techniques.

A key transport property is the electrical resistivity of a material, measured both as a function of temperature and pressure.



Figure 1. (a) Single crystals of mixed (U, Np)O<sub>2</sub> oxide obtained by the vapor-transport technique. (b) Single crystals of PuSb grown by mineralization. (c) Czochralski growth of crystals of the intermetallic  $PuFe_2$ . (d) Pu-Am cast for resistivity and magnetization measurements.

Figure 2 shows the resistivity of PuTe as a function of temperature and pressure.<sup>2</sup> These experiments require very small samples, for example, a small flake of the order of 100  $\mu$ m in size, which has to be cleaved inside a glovebox from a larger piece, and mounted between diamond anvils with the necessary leads. PuTe is particularly interesting from a basic point of view, as the 5f states form a narrow band with strong correlations between them. Surprisingly, none of the Pu monochalcogenides, including PuTe, show magnetic order at low temperature, and this aspect of their behavior, and the fundamental difference between them and comparable lanthanide compounds, has interested theorists for many years.3,4 More recent theories<sup>4</sup> are able to explain the initial increase in the resistivity (see Figure 2) with increasing pressure and even the sudden decrease in the resistance when PuTe transforms<sup>5</sup> from the NaCl (B1) to the CsCl (B2) crystal structure at about 11 GPa. Moreover, they predict that the high-pressure phase of PuTe will be magnetic. There is a chance that this has been seen<sup>2</sup> as a slight inflection point in the resistance versus temperature R(T)curve (see the arrow marked at 15 K in Figure 2), but this needs to be confirmed by other measurements.

#### Structural Studies at High Pressures

As mentioned in the article by Hecker in this issue, across the elements in the actinide series there is an extraordinary change of volume (shown in the inset of Figure 3), which has been known for more than 50 years. The minimum for U, Np,



Figure 2. Temperature-dependence of the electrical resistance of PuTe at selected pressures of up to 24.3 GPa. (From Reference 2.)



Figure 3. Relative volume V (where  $V_0$  is the volume at zero pressure) versus pressure curve for americium. The inset shows the atomic volume at ambient pressure across the actinide series. (From Reference 8.)

and Pu is commonly attributed to the fact that the 5*f* electrons, which are added as one progresses across the series from Pa onward, participate in the bonding of the element and thus contribute to the cohesive properties and decrease the volume. A similar effect is found in the transitionmetal series, where the cohesion involves d electrons. There is, however, a sudden increase in the volume at Am and then a progression that appears to suggest a rareearth-like series, in which the 5f states are localized and do not participate in the bonding.<sup>6</sup> Pu and Am might then be capable of exhibiting a transition to the "other" state, larger in the case of Pu and smaller in the case of Am.

We shall discuss in the following section how one can make Pu larger (by examining Pu atoms on the surface), but here we concentrate on making Am smaller, which is best done with pressure experiments. Of course, this has been attempted for many years,7 but recently8 new synchrotron experiments have shown the richness of the phase diagram of Am under pressure. The details of the volume versus pressure curve are shown in Figure 3. The delocalization of the 5f states in Am actually starts at about 15 GPa (150 kbar), where there is a transformation from Am(II), which is fcc, to Am(III), which has the same facecentered orthorhombic structure as the high-temperature form of  $\gamma$ -Pu. There is then a further contraction of the volume

(by  $\sim$ 7%) when entering the Am(IV) phase, which remains up to 100 GPa. These results are in disagreement with theory,<sup>9</sup> but work is in progress to reconcile these differences. It should be realized that experiments of this sort, which are now under way on Cm and Cf, provide an enormously important test for first-principles theories. These theories must take into account all the complications of the relativistic nature of the 5*f* electrons, together with the strong spin-orbit corrections, and they are at the frontier of condensed-matter theory today.

#### Surface Studies

Our surface characterization is based mainly on photoelectron spectroscopy techniques, namely, XPS (x-ray photoelectron spectroscopy) and high-resolution UPS (ultraviolet photoelectron spectroscopy), which also provide direct information about basic features of electronic structure, such as the degree of delocalization of the 5*f* states. The spectroscopy study can be performed on bulk materials, but a real breakthrough was the implementation of a sputter-deposition technique that allows the preparation of thin layers of transuranium materials. This technique yields materials that do not suffer from surface segregation of oxygen, which seriously affects surfaces of bulk samples. Moreover, it provides larger flexibility in variations of stoichiometry and microstructure, and it allows us to follow the variations of

properties when the thickness is reduced down to a monoatomic layer.

To gain information on the electronic structure of Pu monochalcogenides, we studied PuSe,<sup>10</sup> which has properties very similar to PuTe, as discussed earlier. Figure 4 shows the valence-band spectra of PuSe layers deposited on Si, in comparison with PuSb and Am, the latter having the 5*f* states localized, yielding the maximum intensity at about 2-eV binding energy. The low density of states at the Fermi level is indicated by a weak emission around zero energy. In contrast to this situation, PuSe shows three sharp features at low binding energies, the highest one located at the Fermi level. These three features are strongly dependent on the quality of the surface. They are reduced at an excess of Pu and disappear for deposition on a substrate cooled to T = 77 K (i.e., for presumably amorphous PuSe). The same variations are observed for bulk PuSe and for a surface depleted by Se due to Ar ion etching. The comparison with spectra taken at lower photon energy (hv = 21.2 eV), for which the 5*f* photoexcitation cross section is negligible, demonstrates that all three features are related to the 5*f* electronic states. But the mechanism responsible for the sharp features still remains unclear. As they also appear in some other Pu-based systems (at identical energies but various intensities), it seems that they are related not to details of a particular band structure, but more probably to a rather general many-electron phenomenon.<sup>11</sup>

The interesting position of Pu metal just at the verge of the 5f localization is reflected in dramatic variations of its electronic structure with the crossover from three-dimensional to two-dimensional systems. Figure 5 shows the spectra of the valence band, recorded for a photon energy of 40.8 eV for Pu deposited on a Mg substrate.11 As Mg does not react or intermix at the interface during the sputterdeposition process with Pu, ultrathin Pu layers of controlled thickness can be prepared. The features of this dramatic localization process can be observed in the electronic structure below five monolayers' thickness. For the "thick" layer, one can see the spectral intensity representing a 5f band, increasing up to the Fermi level cutoff. The reduced thickness leads to a new spectral feature around 1.7 eV below the Fermi energy  $E_{\rm F}$ ; at the same time, the itinerant 5*f* states leading to the high intensity at  $E_{\rm F}$  are gradually suppressed. This broad maximum is undoubtedly of 5*f* origin, as shown by comparison with spectra of different photon energies, and corresponds roughly to the 5*f* emission found in PuSb.

We interpret this broad maximum, with the support of the Pu-4*f* core level spectra, as being due to the emission from the 5*f* states, which become localized as a result of the reduced Pu coordination number in the monoatomic layer. For such a Pu layer, one can thus expect very different cohesion, lattice parameters, and other physical properties as compared with the bulk. For the intermediate state of the localization process, one can clearly distinguish the three features close to the Fermi level, observed already in PuSe.

The 5*f* localization due to the reduced thickness, which diminishes the number of nearest neighbors and thus the effective 5f-5f overlap, can be understood as the opposite process to the loss of localization of Am under pressure (at which the compression increases the overlap of the 5f wave functions centered on nearest neighbors). The reduced number of nearest Pu



Figure 4. Ultraviolet photoelectron spectroscopy valence-band spectra of (a) PuSb, (b) PuSe, and (c) Am. Blue lines represent spectra for  $h\nu = 40.8 \text{ eV}$ , black lines represent spectra for  $h\nu = 21.2 \text{ eV}$ . For PuSb (a), the red line represents the difference spectrum. For higher binding energies than 5 eV, the difference spectrum is negative due to a higher secondaryelectron background for  $h\nu = 21.2 \text{ eV}$ in this energy range.



Figure 5. Photoelectron spectra of valence band of Pu layers of variable thickness, recorded with 40.8-eV photon energy. The spectral feature originating from the localized 5f states is emphasized by the darker shading. (From Reference 11.)

neighbors should, however, affect the 5*f* localization, even in the surface layer of bulk Pu metal. We indeed observed, due to the extreme surface sensitivity of photoelectron spectroscopy, that the freshly prepared  $\alpha$ -Pu surface adopts the character of  $\delta$ -Pu with more localized 5*f* states. The fact that the kinetics of this process is increasing with increasing temperature points to a real reconstruction of surface crystallography in favor of a structure accommodating more localized (i.e., bigger) surface Pu atoms. Interestingly, the stability of the  $\delta$ -Pu surface at the surface of  $\alpha$ -Pu was predicted theoretically.<sup>12</sup>

The capabilities of reactive sputtering, during which the deposited material is exposed to a gas in ionized atomic form, can be used to prepare and study systems that cannot be prepared by standard vacuum techniques. Thus, for example, layers of higher nitrides and oxides could be synthesized for U and Th  $(U_2N_3, Th_3N_4)$ . In analogy to uranium, for which UO<sub>2</sub> prepared by exposure of U layers to molecular oxygen can be further oxidized to UO<sub>3</sub> by atomic oxygen, we were able to follow how such an oxidation process increases the O content in PuO<sub>2</sub>. The existence of a higher Pu oxide (presumably water-soluble) has serious consequences for nuclear-waste storage considerations.<sup>13</sup>

#### **Magnetism and Its Many Forms**

The filling of the 5f shell and the subsequent application of Hund's rules lead to the prediction of magnetism in the actinide series, just as is found in the lanthanides. Surprisingly, none of the elements are magnetic until one reaches Cm. This is now understood exactly in the same manner as already explained in the section on "Structural Studies at High Pressures" for the participation of the 5*f* states in the cohesive properties. The 5f states in the early elements form bands, rather than localized states, and these bands are too wide to sustain spontaneous magnetism. Arguments to understand this are based on work by Stoner (and others) on the 3d series and date back 50 years.6 However, the situation is more complicated in the actinides as, in addition to the spin moment, the 5f states also have a large orbital contribution to the magnetism simply because, as they are *f* electrons, they have a large angular momentum term (l = 3).<sup>14</sup> Mägnetism does appear in many U, Np, and Pu compounds, and fundamental studies of such magnetic properties<sup>15</sup> represent another perspective on our efforts to understand the 5f electrons and their interaction both with each other and with other electron states in the solid. An important requirement for magnetic studies is the

availability of single crystals; this is a major motivation for crystal production in our laboratory.

Characterization of magnetic properties initially requires a magnetometer. Detailed

magnetization curves for crystals of less than 1 mg have been obtained with a SQUID (semiconducting quantum interference device) magnetometer. For the magnetism of Np compounds, the Mössbauer



Figure 6. The upper diagrams show the triple-**k** (left) and single-**k** (right) magnetic configurations. The main figure shows a schematic phase diagram for the  $(U_{0.25}Pu_{0.75})Sb$  sample as a function of field (H) and temperature (T). Note that the Néel temperature  $T_N$  is ~90 K. T' and H<sub>c</sub> refer to the temperature and critical field, respectively, at which the configuration changes from single-**k** to triple-**k**. Red (blue) areas imply that the triple-**k** (single-**k**) configuration dominates. (From Reference 19.)

effect with the <sup>237</sup>Np nucleus<sup>16</sup> may be effectively used to gather useful information, and this is used routinely with Np compounds. Other techniques important in magnetic studies are resistance and magnetoresistance. A specific-heat apparatus will be added to our lab later in 2001. This will greatly expand our capability to characterize magnetic properties and is essential for the research into "nearly" magnetic properties such as many of the so-called heavy-Fermion compounds. These have been found widely in uranium compounds and surely exist also in transuranium compounds. More sophisticated experiments involve the use of neutrons, x-rays, or muons that are produced at large facilities (e.g., at synchrotron sources). For these, special encapsulation procedures have been developed, and the experiments are allowed to take place in some user facilities, provided that the amounts are small and all the regulations are followed.

Magnetic ordering in the actinides takes many forms, but in high-symmetry crystal structures, such as those compounds with the NaCl fcc structure, a common form of the magnetic structure is the so-called multi-k configuration, where k is a wave vector defining a Fourier component of the magnetic configuration.<sup>17</sup> In the upper part of Figure 6, we show the configurations with the so-called single- $\mathbf{k}$  (1 $\mathbf{k}$ ) and triple-k (3k) symmetry. The first has tetragonal symmetry, whereas the second has cubic symmetry. The precise configuration that a compound develops is a signature of how the 5f electrons are arranged on the Fermi surface and may be loosely thought of as a measure of how the 5f electrons mix with the valence electrons in the compound.18 USb is known to have the 3k symmetry, whereas PuSb has the 1k configuration.<sup>19</sup> The question is, what happens when we make a compound (U, Pu)Sb where the actinide ions are distributed randomly over the one sublattice of the NaCl structure, and the magnetic anisotropies of U and Pu therefore compete? We find that the anisotropy of the uranium dominates the compounds, and it is not until 75% Pu that unusual effects are observed. This material attempts to transform spontaneously from 3k (as in USb) to  $1\mathbf{k}$  (as in PuSb) as the temperature is lowered (see Figure 6). A magnetic field rapidly stabilizes the 1k state. To establish this phase diagram, we have used a combination of SQUID, neutron diffraction, and resonant x-ray magnetic scattering. The diffraction experiments, especially the high resolution of the x-ray experiments, establish also that the correlation length within these magnetic orderings is relatively short-range. Indeed, the competing

interactions drastically change the magnetic properties.

#### **Future Perspectives**

Much remains to be done. Theory is now actively involved, especially in the pressure experiments on resistivity as well as on the atomic structures. Completely new perspectives have opened up with the production of thin layers in the photoemission effort, not only for basic research, but also in the potential for applications to actinide surface corrosion. New results with the SQUID magnetometer on small samples (less than a milligram) show the complexity of the magnetic interactions in the transuranium compounds, and we shall need all the power of complementary techniques, such as Mössbauer (for Np), neutrons, photons, and muons, to unravel the phase diagrams. In addition, with the completion of the first stage of our "user laboratory," we will have available a facility where outside scientists can come and define their own projects on transuranium materials.

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