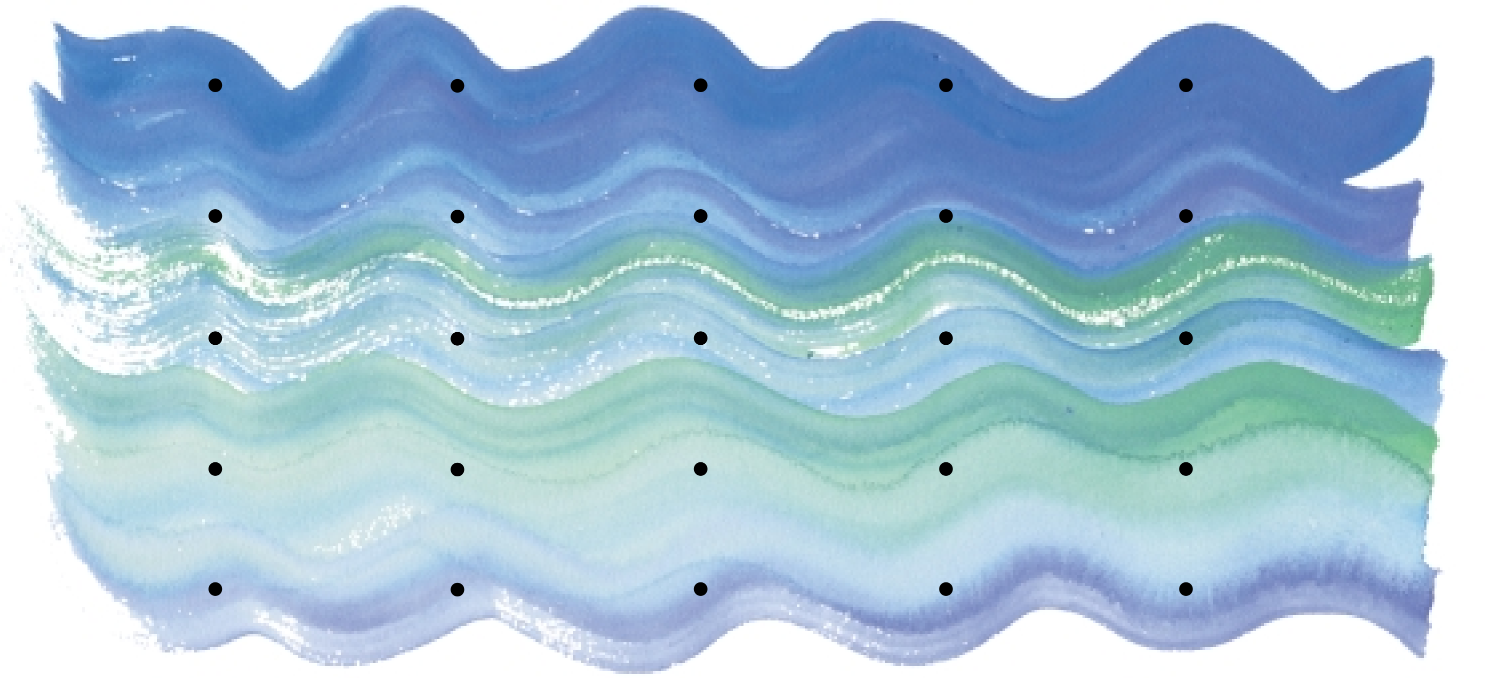


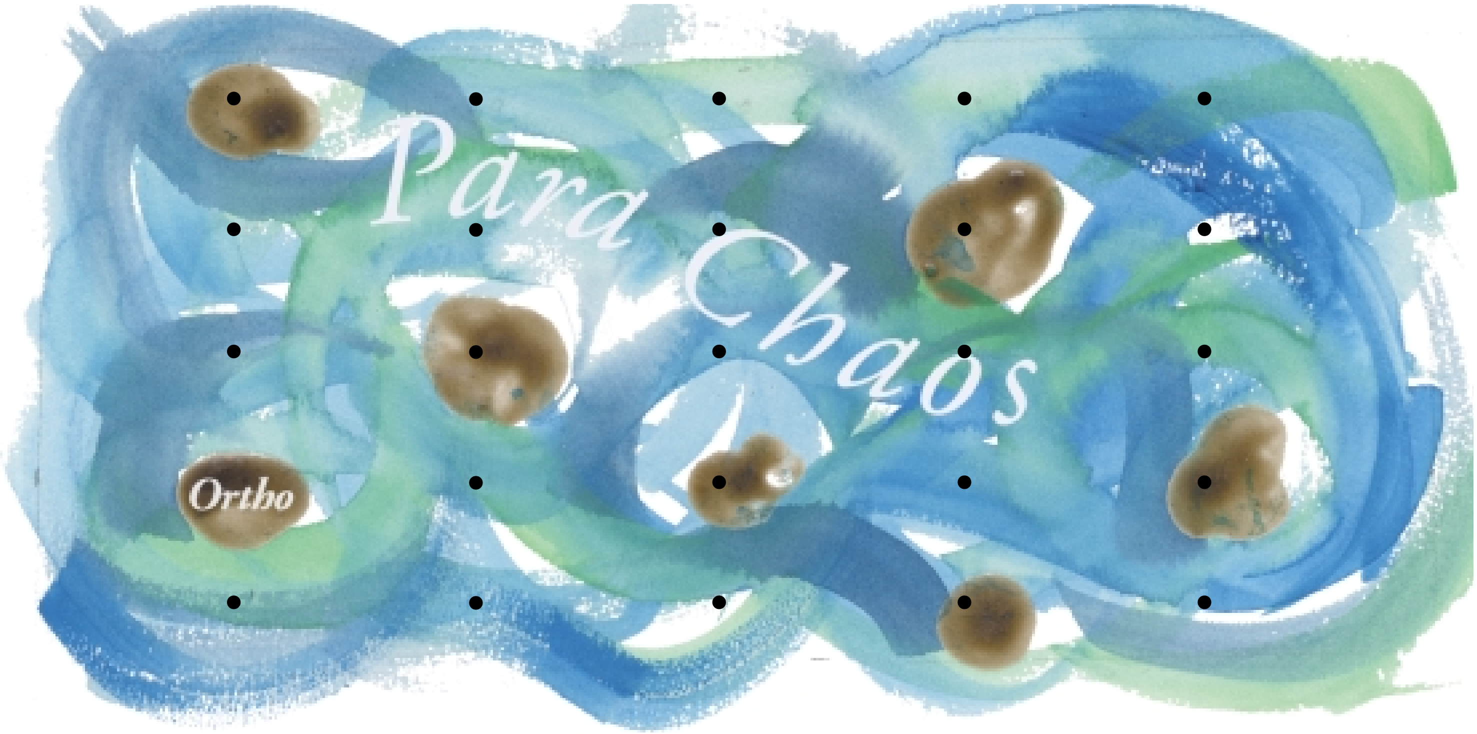
A Possible Model for δ-Plutonium

Self-induced Anderson localization, δ-phase stability, and the melting temperature of plutonium

Bernard R. Cooper

It has been evident for some time that the unusual structural behavior of plutonium in the transition from the α- to the δ-phase is related to the localization mechanism for the 5f electrons. As shown by Donohue (1982), the atomic volume of plutonium expands as the metal goes through the structural sequence alpha (monoclinic at 300 kelvins), beta (monoclinic at 395 kelvins), gamma (orthorhombic at 479 kelvins), and delta (face-centered-cubic, fcc, at 592 kelvins). The δ-phase has a negative thermal expansion; the body-centered-tetragonal δ′-phase (at 724 kelvins) also has negative thermal expansion; and the body-centered-cubic (bcc) ε-phase (at 749 kelvins) expands until melting occurs at the anomalously low temperature of 913 kelvins. In this article, we explain this unusual behavior by a multistep, spatially nonuniform 5f localization process, which is a variant of the disorder-induced localization described by Anderson (1958).

Our localization process involves a disordered array of two types of plutonium on crystallographically equivalent fcc sites that breaks the translational symmetry of the crystal. The sites occupied by the plutonium are of two kinds: the fluctuating para (spin-singlet two-electron state) sites, whose localized f electrons fluctuate between f^4 and f^5 because they hybridize with non-f band electrons, and the localized ortho (spin-triplet two-electron state) sites, whose localized f electrons remain stable at f^5. It is the entropy of mixing between these two types of sites that drives the thermal stepwise transition from plutonium's monoclinic α-phase (ground state) to its fcc δ-phase (Cooper et al. 1999c, Cooper and Lin 1999, Cooper 2000).



This mechanism for f electron localization emerges from the use of two-electron dynamics. The Coulomb exchange interaction (a consequence of electron permutation symmetry) requires that two-electron states have either para singlet or ortho triplet character. As a consequence, not only are there two kinds of 5f electron states (para and ortho), but depending on the relative dominance of exchange vs hybridization in the dynamics, there is a phase transition between a narrow correlated 5f-band-like state that is found in α-plutonium and a homogeneous spatially disordered mixture of the two types of 5f electron states. That is, the localized ortho and fluctuating para states occupy different sites. This is a unique prediction of the two-electron dynamics.

This type of Anderson localization can be self-induced when light-actinide atoms on some sites assume an occupied ortho state (the f electrons at these sites are almost fully localized) and thereby provide sufficiently strong scattering of the itinerant 5f electrons that originate from the para actinide sites. Those itinerant electrons lose their coherent-wave character and return to a localized state, thereby maintaining the para actinide sites in their fluctuating 5f configuration. This spatially disordered mixture of the para and ortho sites, therefore, has overall partial localization. We call this partially localized solid-solution-like phase the randomly localized fluctuating-site (RLFS) phase. In the absence of magnetic ordering, the RLFS phase becomes stable against total localization by maximizing the entropy gain and thereby lowering the free energy. Likewise, the RLFS phase replaces 5f bonding when its free energy is lower than that of the coherent 5f bonding that it destroys. In the absence of magnetic ordering, the entropy of the RLFS phase will be maximized if the sites are equally divided between para and ortho. Which sites are ortho and which are para presumably varies with time, but the mean lifetime of each state is sufficiently long to establish a configurational free energy and, hence, entropy. We show how such a division into two types of plutonium sites can explain the thermal stabilization of fcc plutonium. Figure 1 is an artist's rendition of the change from the f bonding phase of α-plutonium to the RLFS partially localized phase of δ-plutonium.

This partial localization mechanism becomes operative in the light actinides provided the hybridization between the f electrons and non-f band electrons is sufficiently weak (that is, the f band is sufficiently narrow). If magnetic ordering is present, this

Figure 1. Transition of α- into δ-Plutonium by Entropy-Generating Mechanism

(Left) In this rendition, the coherent bonding states of the f electrons in α-plutonium are likened to the serene flow of water in a cold winter stream. (Right) As the system is heated, the serene flow breaks up into a partially localized state as itinerant f electrons from the para sites crash against the localized ortho sites and therefore fluctuate between localization and itinerancy. This localization mechanism drives the stepwise transition with increasing temperature from the α-phase to the β-, γ-, and δ-phases of elemental plutonium.

localization mechanism is enhanced, and it therefore starts at a lower temperature.

A resonant scattering point of view (Coqblin and Schrieffer 1969) is pertinent in the weak hybridization regime. Working from that point of view, we studied the onset of magnetic ordering in certain uranium compounds—the uranium monochalcogenides—as hybridization decreases. Our calculations yielded remarkably accurate absolute ab initio–based predictions (Cooper and Lin 1998, Cooper et al. 1999a, Cooper et al. 1999b) of the Curie temperatures T_C (transition to ferromagnetism) and of the low-temperature ordered moments of these uranium monochalcogenides (Schoenes et al. 1996, Bourdarot et al. 1997, Bourdarot et al. 1999) as they are driven by alloying from ferromagnetic ordering to nonmagnetic behavior. Based on this success, we have since been able to recognize the role of a weakening hybridization and increasing entropy in driving that transition in reverse, that is, from a strongly correlated, extremely narrow band state (sometimes characterized as enhanced-mass or heavy-fermion behavior) to a state of spatially disordered localized magnetism (coupled magnetic ions). The latter ferromagnetic phase is an RLFS solid-solution-like phase with two types of sites, one of which (ortho) has large ordered moments and the other (para) is hybridizing and drives the magnetic coupling between the ortho sites.

In the absence of magnetic ordering, but at sufficiently high temperature, the same weakening hybridization and increasing entropy drive the phase transition between the correlated narrow-band 5f bonding state that stabilizes monoclinic α-plutonium and the RLFS solid-solution-like phase characterizing fcc δ-plutonium. We will discuss how this phase transition comes about and how the fcc δ-phase is stabilized at room temperature and below by the addition of trivalent additives such as gallium. In addition, we will discuss the relationship of this phase transition to the depression of melting temperature in plutonium.

Behavior of 5f Electrons in the Hybridizing Regime

To treat the 5f electron behavior of the light actinides, we focus on the regime in which the 5f electrons are not significantly influenced by direct overlap with 5f electrons from other sites. In this case, the role of the 5f electrons is determined by the hybridization of each such electron with band electrons of non-5f atomic origin, as constrained by the Coulomb exchange interaction with those band electrons and as diminished by the Coulomb repulsion with the other on-site 5f electrons. To treat such a situation, one can derive a model Hamiltonian describing 5f electrons that interact with non-5f band electrons (Sheng and Cooper 1994a). In this Hamiltonian, some of the quantities can be matched to the output of a standard band calculation that uses a linear muffin-tin orbitals (LMTO) method within the local density approximation (LDA). The other quantities can be calculated separately, using the information given by a combination of several LMTO band calculations. In Equations (1a)–(1c), H_0 is the Hamiltonian without interactions between non-f band and f electrons, and H_1 describes the interactions between non-f band and f electrons.

$$H = H_0 + H_1 \ , \tag{1a}$$

$$H_0 = \sum_k \varepsilon_k b_k^\dagger b_k + \sum_{Rm} E_f c_m^\dagger(R) c_m(R) + \frac{U}{2} \sum_{R,m\neq m'} n_m(R) n_{m'}(R) \ , \text{ and} \tag{1b}$$

$$H = H_0 + H_1 \ , \tag{1c}$$

In H_0, Equation (1b), the first term is the non-f band energy and comes directly from the LDA calculation; the second term is the f state energy, which can be calculated indirectly from the LDA; and the third term is the intraatomic f-f Coulomb interaction, a two-electron correlation-energy interaction, which can also be calculated indirectly from the LDA. The first term in H_1 is the LDA hybridization between the non-f band and f electrons; and the second term is the Coulomb exchange interaction between the non-f band and f electrons. Refer to Sheng and Cooper (1994) for the treatment of this two-electron interaction in the almost-atomic-like limit.

Finding the ground state of this Hamiltonian is a truly formidable problem because we have included two two-electron terms—the f-f Coulomb interaction and the non-f band to f electron Coulomb exchange. The on-site f-f Coulomb interaction itself presents great difficulties, but those are increased manyfold if we take into account the two-electron nature of the Coulomb exchange interaction.

Ortho/Para Fine Structure and the Cerium Analogue. To consider the relevance of this physics to the phase transitions of elemental plutonium, we first briefly review the most obvious analogue in the periodic table, the atomic volume collapse from the fcc γ- to the fcc α-phase of elemental cerium on cooling at moderate pressures. That isostructural transition in cerium entails an atomic volume decrease of about 17 percent (Koskenmaki and Gschneider 1978), similar to the atomic volume decrease of about 18.5 percent in the transition between δ- and α-plutonium (Donohue 1982).

In proposing their Kondo volume-collapse model of the cerium transition, Allen and Martin (1982) pointed out the difficulty of explaining the large atomic-volume change involved while at the same time accounting for the atomic-like form factors and other behavior observed experimentally for both cerium phases. In our model for the ground state of either cerium or plutonium, the correlated narrow 5f band in the α-phase has a fine structure of nonmagnetic (para) and magnetic (ortho) subbands imposed by the exchange symmetry of the correlated-electron dynamics. Local probes then see the para or ortho spectral densities (which are atomic-like, or very narrow in energy), but the atomic-volume changes are governed by the cohesive energy associated with the entire 5f spectral width. In both the Kondo model mentioned before and the lattice-periodic Mott transition (Georges et al. 1996), the entropy difference driving the α- to γ-transition in cerium depends on the difference in electronic entropy between an almost-localized and a fully localized lattice-periodic state. In our model, the transition is from a low-temperature coherent (bonding) state to a high-temperature RLFS state, and it is driven by the additional entropy of mixing in a solid-state solution of para and ortho f sites, that is, a perfect mixture with homogeneous lattice disorder. The sum of this entropy[1] of mixing plus the entropy from the individual ortho and para sites is significantly larger than the conventional electronic entropy difference between lattice-periodic states with almost-localized and fully localized behavior.[2]

The existence of the ortho/para fine structure implies a small energy scale associated with thermodynamics and a large energy scale associated with the primary electronic interactions (Fermi energy, occupied 5f spectral width, f-f correlation energy U, and one-electron hybridization potential). The correct small energy scale of the

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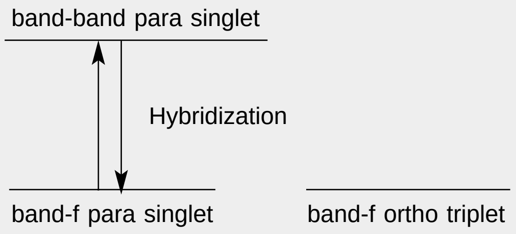
[1] As discussed below, the transition to this solid-solution-like state is driven by Anderson localization which is physically equivalent to Mott localization for a disordered system (Mott 1980, Mott 1990).

[2] Depending on the degree of f localization (for example, cerium versus plutonium vs uranium in the same chemical environment), exchange tends to homogenize the para and ortho behavior, and we anticipate there being considerable homogenization for elemental cerium. We will not discuss elemental cerium further but note that Laegsgaard and Svane (1999) have investigated the Kondo volume-collapse model very thoroughly by a combination of the self-interaction-corrected LDA and the Anderson impurity model. They could explain the α- to γ-transition only by assuming an ad hoc rescaling of the hybridization parameters and concluded that better understanding of the hybridization function is needed.

Hybridization in the RLFS Phase of the Weak Hybridization Regime

As defined in this diagram, the two-electron antisymmetrized states at each site in the lattice are the band-5f para singlet ground state, the band-5f ortho triplet ground state, and the band-band para singlet excited state. (Itinerancy quenches orbital moments, and so there is no band-band ortho state.) The band-f para singlet hybridizes with the band-band para singlet whereas the ortho triplet cannot hybridize with the band-band singlet because hybridization conserves (does not mix) spin. This lattice of two-electron antisymmetrized states is analogous to a lattice of helium atoms in which the atomic-helium ordering of the low-lying energy levels is inverted (the helium-like para ground-state singlet becomes an excited state). The situation shown is for the Hartree-Fock approximation corrected for two-electron correlations to lowest order in band-f hybridization. In this approximation, the hybridization interaction drives the singlet (para) component of the 5f contribution to the two-electron spectral density to fluctuate between configurations differing by one 5f electron. A large-scale calculational scheme, incorporating multiple-scattering effects, which has been designed to predict the Anderson localization will effectively include all orders of hybridization and will yield wave functions more complicated than the simple antisymmetrized products shown.

Energy Levels of RLFS Phase



Properly Antisymmetrized Two-Electron States

Band-f para singlet = $[\mathrm{band}(\mathbf{r}_1)\, f(\mathbf{r}_2) + f(\mathbf{r}_1)\, \mathrm{band}(\mathbf{r}_2)]\, [\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)]$

Band-band para singlet = $[\mathrm{band}(\mathbf{r}_1)\, \mathrm{band}(\mathbf{r}_2) + \mathrm{band}(\mathbf{r}_1)\, \mathrm{band}(\mathbf{r}_2)]\, [\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)]$

Band-f ortho triplet = $[\mathrm{band}(\mathbf{r}_1)\, f(\mathbf{r}_2) - f(\mathbf{r}_1)\, \mathrm{band}(\mathbf{r}_2)] \times \left\{ \begin{array}{l} \uparrow(1)\uparrow(2) \\ \uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2) \\ \downarrow(1)\downarrow(2) \end{array} \right\}$

ortho/para fine structure has been obtained in previous calculations (Wills and Cooper 1987, Wills and Cooper 1990).

Ortho and Para States Defined. The f to non-f band electron hybridization term in Hamiltonian H_1, the first term in Equation (1c), consists of a linear combination of terms that destroy one f electron and create one non-f band electron or vice versa. To treat the correlated dynamics between these two electrons (the exact, instantaneous effects on motion caused by coupling via the interelectronic Coulomb interaction), we must calculate two-electron matrix elements using exchange-symmetrized two-electron wave functions, as one does for the helium atom. Recall that these two-electron wave functions have two possible forms, which we call para and ortho. The first is a product of a symmetric (para) two-electron orbital state and a two-electron spin singlet (which is antisymmetric on exchange of electrons); the second is a product of an antisymmetric (ortho) two-electron orbital state and a two-electron spin triplet (which is symmetric on exchange of electrons). Refer to the box above for the form of such states.

As long as the hybridization is treated as acting between two-electron wave functions that are antisymmetric under exchange, the effects of exchange can be incorporated adequately through the one-electron exchange-correlation potential provided the electrons in the system are not too close to being fully localized. This very substantial simplification allowed us both to develop a calculational technique for the magnetic ordering of a class of uranium compounds and to recognize the mechanisms controlling the phase-transition sequence in elemental plutonium. This development incorporates what was learned from the work of Wills and Cooper (1987) and Sheng and Cooper (1994) on the weakly hybridizing more-atomic-like cerium compounds. Our technique has been very successful in predicting the magnetic ordering behavior of the uranium monochalcogenides, which have sodium chloride crystal structure, under high pressures (to about 20 gigapascals) and under certain uranium-dilution-alloying changes, which are described later. This predictive power led us to apply the same theory and physical picture to elemental plutonium and its stabilization into the fcc structure.

In the weak hybridization regime, the hybridization process can be correctly and usefully pictured if one thinks of a lattice of helium (two-electron) atoms, in which the usual order of the low-lying atomic-energy levels is inverted (see the box on the opposite page). That is, the atomic ground states in this lattice have both s-5f para singlet and s-5f ortho triplet two-electron components, and the excited state is a doubly s-occupied para singlet. The s-like part of these two-electron wave functions comes from the virtual occupation of this state by p and d band electrons that have lost their p and d orbital character through itinerancy (Van Vleck 1932, Kittel 1996).

From Equation (1c), we can see that hybridization conserves spin (does not involve spin) and thus acts only between the excited s-s para singlet and the ground state s-5f para singlet. Thus, to the lowest order, the hybridization interaction drives the singlet (para) component of the 5f contribution to the two-electron spectral density to become itinerant, that is, to fluctuate between configurations differing by one 5f electron. The triplet (ortho) component remains localized—that is, it has a stable configuration (see the box on the opposite page). In fact, this description corresponds to the resonant scattering physics of the Coqblin-Schrieffer (1969) treatment of hybridization.

In the sufficiently weak hybridization regime, the 5f behavior viewed locally at a given site is one of two types: (1) totally localized (ortho) and therefore capable of having a large (free-ion-like) orbital contribution to an ordered magnetic moment (and because of strong spin-orbit coupling, a large spin contribution as well) or (2) fluctuating between f^4 and f^5 (para), and thereby providing an itinerant 5f component that can pass a hybridization-mediated message of orbital magnetic polarization between the localized 5f sites. Thus, magnetic ordering with a large orbital contribution can occur in the weak hybridization regime.

The localized sites are randomly distributed on the lattice, and this disorder supplies a source of entropy, which at sufficiently high temperature stabilizes this RLFS phase. That is, it sufficiently lowers the free energy, $F = U - TS$, to compensate for the loss of 5f bonding energy even in the absence of magnetic ordering. In the RLFS phase, the 5f electronic contribution to the entropy is analogous to the configurational entropy in a random alloy. As the hybridization strengthens or as the temperature drops (especially in the absence of magnetic ordering), the 5f electrons abruptly delocalize to a narrow correlated 5f-band phase because the increase in 5f bonding more than compensates for the loss of the electronic-entropy and possible magnetic-ordering contributions to the free energy.

The RLFS Phase in Uranium Monochalcogenides. This physical picture, which we apply to the structural phase transition and melting behavior of plutonium, was inspired by our remarkably successful predictions of magnetic ordering in a class of uranium compounds. For several years, we realized that there are two subregimes of hybridizing f electron behavior: a very weak regime associated with localized magnetic (ferromagnetic) ordering (Sheng and Cooper 1994, Sheng et al. 1994) and

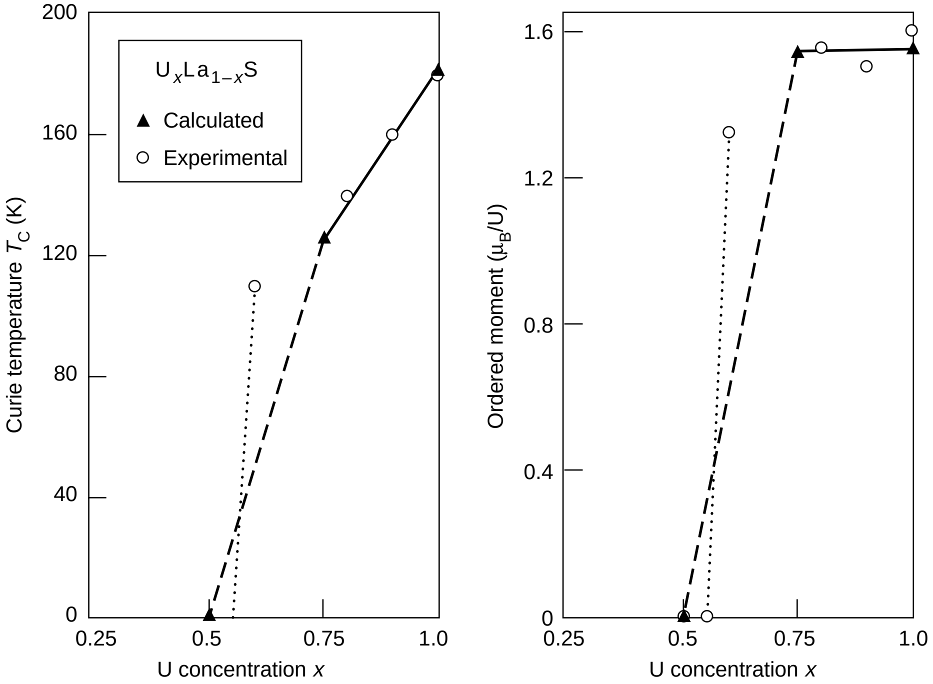


Figure 2. Calculated and Measured Ferromagnetic-Ordering Temperatures and Low-Temperature Ordered Moments of a Uranium Compound with f Dilution Alloying
These plots illustrate the extraordinary absolute agreement between predictions and experiment for the magnetic behavior of the uranium monochalcogenides. In materials such as the uranium-sulfur compound US, both pressure and dilution alloying (substituting a lanthanum for a uranium atom) increase the hybridization of the 5f band with the p/d band, which drives the 5f electrons from the well-localized ortho (stable f configuration) to the itinerant (rapidly fluctuating f configuration) para two-electron states. Lanthanum and yttrium are chemically very similar and close in size to uranium but do not have partially filled f shells. Thus, their substitution for uranium in a system such as $U_xLa_{1-x}S$ increases the hybridization of each of the f electrons in the remaining uranium atoms. The analogy to dissolving a solute (the uranium 5f electrons) in a solvent (the band electrons of non-f atomic parentage) to form a solution may be useful in picturing this situation. In effect, one is decreasing the amount of solute while keeping the amount of solvent the same, and the mixing is provided by the hybridization. This increase of hybridization gives a decrease in the low-temperature ordered moment, and interestingly, we expect a correspondingly enhanced Pauli paramagnetism. That enhancement has been observed (see Figure 4). **(Reproduced with permission from the American Physical Society, J. Schoenes, *Phys. Rev. B*, 53 (22), 1996.)**

a weak regime (Sheng and Cooper 1995) associated with heavy-fermion, or enhanced-mass (narrow-band), behavior. In Figure 3(a), we show the calculated and measured decrease in T_C (the temperature for the transition to ferromagnetism) of the uranium compound $U_xLa_{1-x}S$, as lanthanum is added to the alloy. As explained in the caption, this dilution of uranium by lanthanum increases the f electron hybridization because the number of f electrons, “the solute,” decreases, while the number of non-f band electrons, “the solvent,” remains the same. Figure 3(b) shows the calculated and measured low-temperature ordered moment of $U_xLa_{1-x}S$. Only recently (Cooper et al. 1999) have we realized that, as the lanthanum content decreases below 45 percent, the weakening of f electron hybridization induces the type of Anderson localization described in this article. In this uranium compound, magnetic ordering enhances the localization process, and it drives the system from a narrow-f-band

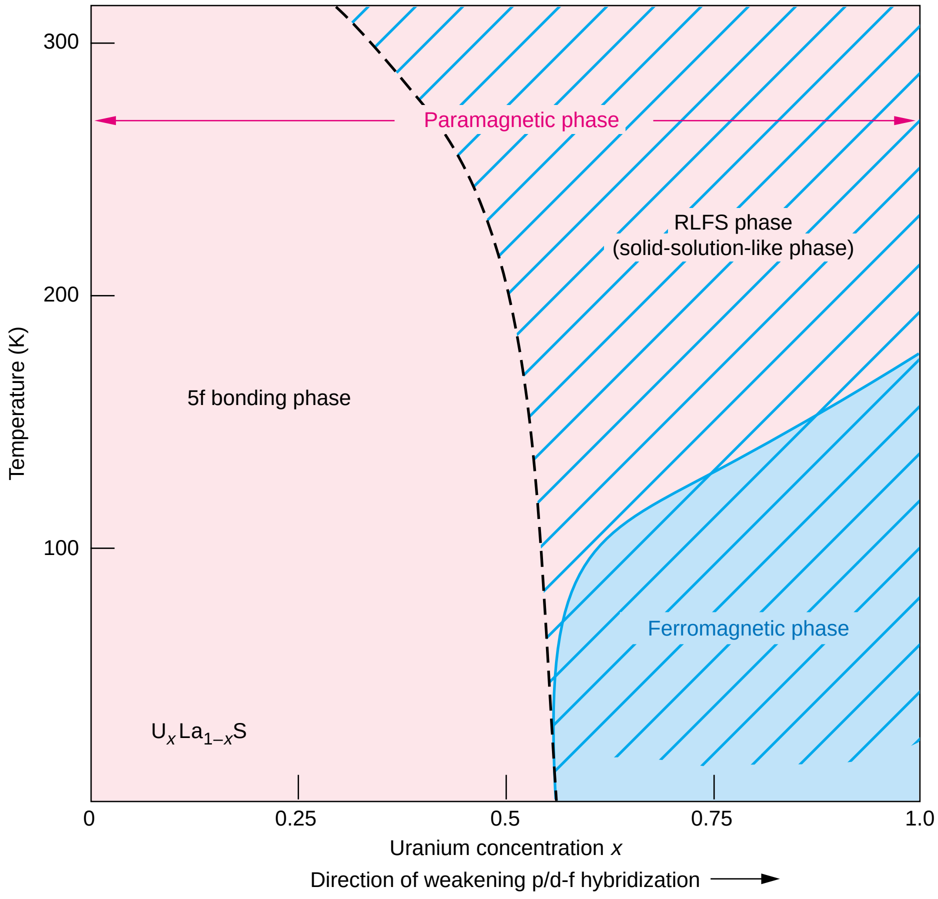


Figure 3. Schematic Representation of the Phase Diagram of $U_xLa_{1-x}S$
The RLFS phase is the hatched area to the right of the dashed curve. The blue curve separates the ferromagnetic phase from the paramagnetic phase. As the uranium concentration increases from left to right, the hybridization of the f electrons decreases, and the system becomes partially localized in an RLFS phase.

paramagnetic bonding phase to a strongly ferromagnetic partially localized (RLFS) phase.

To clarify the analogy between this phase transition and that in plutonium, in Figure 3, we show a schematic representation of the $U_xLa_{1-x}S$ phase transition. We consider the behavior from left to right, that is, as hybridization between the f electrons and the p and/or d band electrons decreases (and uranium concentration increases). At the left, this material is in a 5f bonding phase. As hybridization decreases, this material goes through a magnetic-ordering-enhanced Anderson localization of the 5f electrons to the RLFS solid-solution-like phase. This process can be wholly self-induced, as described below for elemental plutonium.

Once an Anderson localization occurs, it is energetically favorable to develop the maximum entropy. Thus, to have a phase transition at a sufficiently high temperature in the absence of magnetic ordering, there is an abrupt localization at half the lattice sites occupied by the light actinide. If magnetic ordering occurs, this abrupt localization can occur at more than half of these randomly located lattice sites.

Magnetic Susceptibility in the RLFS Phase. The Curie temperature T_C and the ordered-moment behaviors of the uranium monochalcogenides shown in Figures 2(a) and 2(b) are appropriate for the RLFS phase. Those compounds, other magnetically ordered actinide materials, and δ-plutonium (which does not have magnetic ordering) share the experimental signature of the RLFS phase, namely, a high-temperature magnetic susceptibility (χ) that has both Curie-Weiss and enhanced Pauli contributions (Schoenes et al. 1996, Méot-Reymond and Fournier 1996).

$$\chi = \chi_{\mathrm{CW}} + \chi_{\mathrm{Pauli}} \;, \tag{2a}$$

$$\chi_{\mathrm{CW}} = \frac{C}{T - \theta_{\mathrm{p}}} \;, \text{ and} \tag{2b}$$

$$\chi_{\mathrm{Pauli}} = \chi_0 \left\{ 1 - \frac{\pi^2}{12}\left(\frac{k_{\mathrm{B}}T}{E_{\mathrm{F}}}\right)^2 \right\} \;. \tag{2c}$$

Equation (2b) gives the typical inverse temperature dependence of the Curie-Weiss susceptibility, which is due to localized moments. Equation (2c) consists of the typical temperature-independent Pauli susceptibility characteristic of itinerant electrons (delocalized moments) and a T^2 term that depends on the Fermi energy and represents departures from free-electron behavior. (This temperature-dependent Pauli term could arise in our model if the number of para sites increases with temperature.) Figure 4 (reproduced from Schoenes et al. 1996) shows the inverse of the magnetic susceptibility versus temperature for the behavior of $U_{0.15}La_{0.85}S$. That behavior is typical of the susceptibility of magnetically ordered actinide materials, and the best fit to the data indicates an enhanced Pauli term. Figure 5 is a plot of the susceptibility (rather than its inverse) and is reproduced from Méot-Reymond and Fournier 1996. This plot shows a similar behavior for cerium-stabilized δ-plutonium.

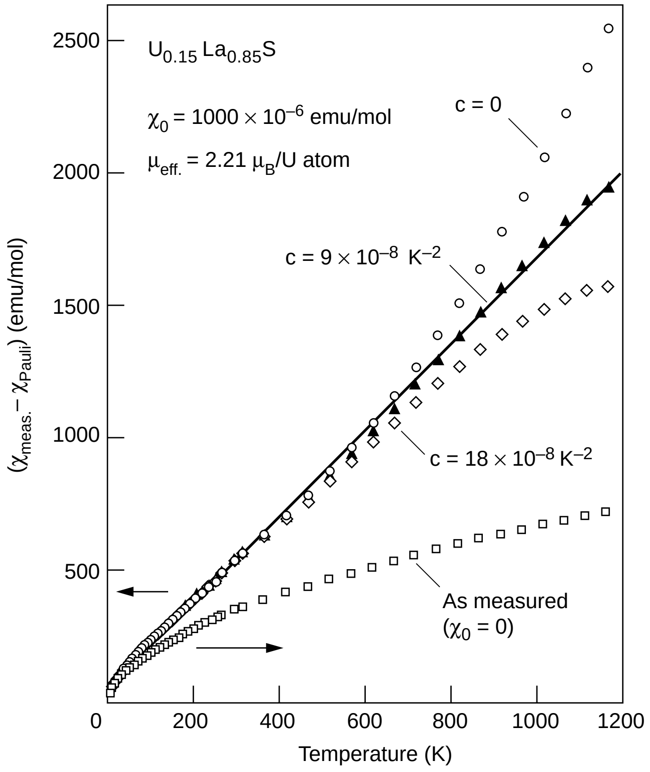


Figure 4. Inverse Susceptibility vs Temperature for $U_{0.15}La_{0.85}S$

A plot of the inverse of the measured susceptibility minus the Pauli susceptibility should yield the straight line characteristic of standard Curie-Weiss behavior. The plot for $U_{0.15}La_{0.85}S$ (reproduced with permission from *Physical Review B*) shows several fits obtained by varying the coefficient of the T^2 term in the Pauli susceptibility, Equation (2c). That coefficient is labeled c in the plot. A nonzero value of c yields the straight line (best) fit, implying an enhanced Pauli contribution to the susceptibility.

For spatially disordered systems, the Anderson and Mott views of the localization process become equivalent. In the Anderson view, if the presence of impurities at random sites of an otherwise perfectly periodic lattice provides sufficiently strong scattering, the integrated intensity of a wave initiated at some starting point becomes localized within some finite distance. In the present context, we can regard the narrow correlated 5f band in the 5f bonding regime as such a wave. If we assume that the 5f electrons become localized on some actinide atoms randomly located on the lattice, the difference in the core (nucleus plus nonvalence electrons) potential caused by the presence of those localized 5f electrons can provide a scattering center for the wave composed of the itinerant 5f electrons. (That is, the departure from a charge density with lattice periodicity scatters the itinerant charge density.) The scattering strength for each such site is diminished by the screening provided by the band electrons of p and/or d atomic origin, and the hybridization of p and/or d band electrons with f electrons is a measure of that screening strength. As the hybridization weakens, the screening does too, and the scattering becomes stronger, favoring the localization, which in turn provides the scattering that causes the localization. In the Mott view of localization, one focuses on the events in the vicinity of one lattice point. As the hybridization and, hence, the screening of the site-centered potential weaken (in effect, the dielectric constant decreases), the site-centered potential becomes more binding. When the hybridization of p/d band electrons with f electrons weakens below a critical value, the 5f states become bound; that is, the 5f electrons localize. Thus, weakening hybridization, whether viewed as providing stronger random scattering of 5f band electrons or weaker screening and hence stronger local binding, ultimately leads to 5f localization at random sites.

It is reasonable to expect that such a situation occurs fairly easily in a narrow-band situation. The banding comes from the hybridization-mediated overlap of orbitals that originate from the periodic array of atomic sites. As disorder develops, it causes the energy levels of the individual atoms to vary randomly from site to site. Atoms with energies near the average-band energy are more likely to have at least some neighbors of similar energy to overlap (bond) with, whereas atoms with energies more toward the band's edges are more likely to be isolated from their neighbors. Thus, the narrowing proceeds toward the band average more and more precipitously as the disorder (and hence the narrowing) increases. Hence, a phase transition occurs. Clearly, starting with a narrower band favors the ease with which localization occurs.

If we go in the opposite direction—from a very weak to a less weak 5f hybridizing subregime—we see that coherent behavior develops and leads to narrow correlated bands. By including two-electron correlations, one imposes a nonmagnetic (singlet) and magnetic (triplet) substructure on the already narrow 5f (or 4f for cerium) bands, but any ordered magnetism will be much weaker than in the RLFS solid-state-solution ("random-alloy") phase. Numerous behaviors are possible, depending on the narrowness of the 5f bands and the singlet or triplet subbands. One extreme is the heavy-fermion regime. As shown in Sheng and Cooper (1995) and Cooper et al. (1997), the characteristic enhanced electronic-specific-heat and Pauli susceptibility behavior in our treatment of this regime occurs with the correct energy (temperature) scale. In addition, as shown in Sheng and Cooper (1995), the division into nonmagnetic and magnetic subbands, which may be overlapping or nonoverlapping, and their placement relative to the Fermi energy (chemical potential) provide a range of Wilson ratio behavior in agreement with experiment for a substantial number of heavy-fermion systems.

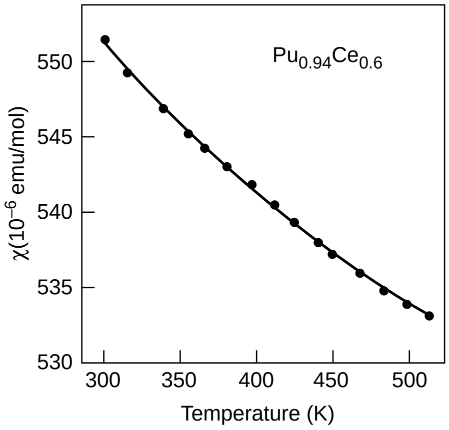


Figure 5. Susceptibility vs Temperature for the Plutonium-Cerium Alloy $Pu_{0.96}Ce_{0.6}$

The fit through the data points, which was calculated with Equation (2), suggests that this plutonium alloy also exhibits an enhanced Pauli paramagnetism.

(This graph is reproduced with permission from the *J. Alloys and Compounds* 123, S. Méot-Reymond, "Localization of 5f Electrons in Delta-Plutonium: Evidence for the Kondo Effect, page 122, Copyright 1996, Elsevier Science.)

In treating thermodynamic behavior for heavy fermions, the extreme narrowness of the magnetic-nonmagnetic subbands means that one must take into account the temperature dependence of the Fermi energy. In elemental plutonium, the 5f band is sufficiently narrow to favor a very low symmetry structure such as the monoclinic α-structure (see the article "Actinide Ground-State Properties" page 128 for details), but the hybridization of the non-f band with the 5f band electrons is sufficiently strong to give a somewhat broader 5f band than is necessary for characteristic heavy-fermion phenomenology.

Entropy Generation and Self-Induced Anderson Localization

If $E_{\text{f bond}}$ denotes the f electron contribution to the bonding energy per atom (measured in millirydbergs, where 1millirydberg = 158 kelvins in temperature equivalent), then the temperature at which we would observe self-induced Anderson localization to the RLFS phase, considering only the entropy change from the site disorder, is given by

$$T_{\text{A loc}} \approx \frac{158 E_{\text{f bond}}}{\ln 2} \approx 228 E_{\text{f bond}} \ . \qquad (3)$$

In other words, at this temperature, the loss of bonding energy per atom would be balanced by the increase in entropy per atom (which is equal to ln 2 for the transition to the RLFS phase because each atom now has two possible states—ortho or para). If magnetic ordering occurred at temperatures above the temperature given in Equation (3), then it would be favorable for localization to occur (the free energy would be minimized) at a lower temperature. That is, magnetic-ordering enhancement of the f electron localization will occur provided the f bonding energy is not too high. In the case of plutonium, it is apparently too high, and therefore the localization temperature will be too high for magnetic ordering and the consequent magnetic-ordering enhancement of the localization.

Stabilization of fcc Plutonium

We are saying that the transition of pure plutonium to the low-density δ-phase at 592 kelvins is due to a self-induced Anderson localization of the 5f electrons driven by the configurational entropy of a random distribution (solid solution) of ortho (stable) f^5 and para (fluctuating between f^5 and f^4) plutonium sites. Equation (3) predicts that this transition at 592 kelvins corresponds to a loss of 2.6 millirydbergs in 5f bonding energy per atom, which falls at the expected value. This value is about 1 percent of the total cohesive energy of 255 millrydbergs per atom of plutonium (Brooks et al. 1984).

It is well known that δ-plutonium becomes stable down to low temperatures by the addition of small amounts of a trivalent IIIB additive such as gallium. (See Figure 6 for a schematic drawing of the phase-transition behavior of plutonium on alloying with small percentages of gallium.) The randomly located additive species atoms presumably provide sufficiently strong scattering (and therefore decreased hybridization) to lower the transition into the RLFS phase to a temperature below room temperature.

A possible way to quantify the distribution between para and ortho plutonium as a function of gallium content is based on the prediction that an increase in hybridization (with a consequent increase in the number of para sites) would lead to a decrease in the low-temperature ordered moment for certain magnetically ordered compounds. That decrease would correspond to an increase in the Pauli paramagnetic component[3] of the paramagnetic susceptibility above T_c (see Figures 4 and 5). This quantitative correspondence between the increase in Pauli susceptibility and the decrease in ordered moment is currently being experimentally validated for a number of magnetically ordered uranium compounds. If it is indeed validated, we will be justified in using measurements of the susceptibility of gallium-stabilized fcc plutonium with varying gallium contents as a way to quantify the distribution between the para and ortho configurations of plutonium. One would expect that the Curie-Weiss component of susceptibility (the number of ortho sites) would increase with gallium content because, as explained next, the hybridization weakens with increasing gallium content.

The effect of alloying in the uranium-sulfur compound US is quite different than that in plutonium because pure US is ferromagnetic. It already has an ortho-para mixture at low temperatures, and the disordered distribution of the ortho 5f sites provides the "imperfections" that prevent the overall propagation of banding 5f waves. Thus, the effect of substituting lanthanum for uranium in US is to dilute the 5f electrons of uranium and, as explained in the caption to Figure 2(a), thereby strengthen hybridization.

In elemental plutonium, the 5f bonding energy is sufficiently high for the transition to the RLFS phase to occur in the absence of magnetic ordering. At zero temperature, all plutonium sites are in the para configuration, and the ground state is the monoclinic α-structure stabilized by 5f bonding. The 5f banding, associated with the 5f bonding, is mediated by hybridization with the plutonium 6d band (valence) electrons originating from other plutonium sites. This process gives rise to a narrow

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[3] The Pauli component can be separated from the Curie-Weiss component by the kind of fitting shown in Figure 4.

5f band with a consequent high density of states at the Fermi energy. Almost invariably in such a narrow band (high density of states—"almost degeneracy" at the Fermi level), the lowering of the free energy will favor some sort of Jahn-Teller distortion in order to break the degeneracy. (In δ-plutonium, elastic forces stabilize the degeneracy inherent in the fcc structure.) However, at $T = 0$, the system still has to choose the most favorable distortion, and that, presumably, in the case of the low-symmetry monoclinic α-plutonium structure reflects the directionality of the weak 5f bonding (Söderlind et al. 1997).

Why Hybridization Decreases when Gallium Is Added to Plutonium. The effect of gallium substituting for plutonium in elemental plutonium is quite different from that of lanthanum or yttrium substituting for uranium in the uranium monochalcogenides. When lanthanum or yttrium substitutes for uranium, the valence d electrons from the lanthanum (5d) or yttrium (4d) simply blend into the hybridizing d band formed from the uranium 6d valence electrons. Thus, one has an essentially unchanged band solvent containing less uranium 5f solute, and the effect is to increase the d band hybridization per 5f electron of uranium, giving 5f delocalization as the dominant effect. On the other hand, for gallium substituted in plutonium, the valence 4p electrons from the gallium compete with the plutonium 5f electrons to hybridize with the band electrons originating from the plutonium 6d electrons. This competition not only effectively decreases the 6d hybridization per 5f electron of plutonium, but it also provides a severe disordered disruption of the 6d-mediated 5f banding. In this way, the 5f electrons become localized. Indeed, the disruption of plutonium-to-plutonium 6d-mediated 5f bonding is sufficiently great for even the vestigial 5f bonding (5f contribution to the cohesive energy) preserved by magnetic ordering not to be present.

Because alloying has a highly nonlinear effect in driving the restructuring of the ground state, the nucleation of localized sites by the addition of gallium is likely to create an avalanche effect, in which stable f^5 (ortho) plutonium sites form at random locations and further break up the f bonding coherency between the fluctuating f^5/f^4 plutonium (para) sites. The extended x-ray absorption fine structure (EXAFS) and x-ray diffraction work of Faure et al. (1996) provides both gallium-plutonium and plutonium-plutonium interatomic distances as the gallium content varies between 1.89 and 10.43 atomic percent (at. %). The gallium-plutonium bond length is always shorter than the plutonium-plutonium bond length, but the difference between them has a minimum near or at 7.7 at. % gallium corresponding to one gallium atom for every 12 plutonium atoms (see Figure 7). Faure and coworkers state that they cannot understand why there is then a substantial increase in bond shortening (that is, a decrease in the gallium-plutonium bond length relative to that of plutonium-plutonium) in going from 7.7 to 10.4 at. % gallium. The avalanche effect might provide an explanation because it reinforces the effect of the gallium nucleation centers in breaking up the plutonium-plutonium bonding. The stabilizing effect per gallium atom depends both on diminishing the hybridization and on breaking up the coherency of the plutonium-plutonium bonding. Thus, as the increase in gallium concentration decreases the coherent hybridization per plutonium atom, a threshold for the spontaneous generation of stable localized f^5 plutonium sites is reached. (At this point, spontaneous, strong magnetic ordering would occur if the gallium sites were not interfering with the magnetic coupling between the plutonium sites.) We suggest that adding gallium beyond 7.7 at. % leads to the formation of the ortho sites and the further stabilization of the system.

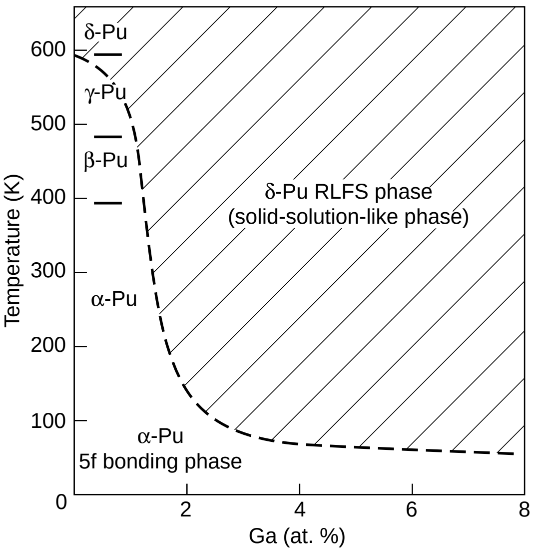

Figure 6. Schematic Representation of the Phase Diagram for Plutonium-Gallium Alloys

As the gallium concentration increases, the hybridization of the f electrons in the narrow f band of α-plutonium decreases. The result is self-induced Anderson localization, producing the partially localized RLFS phase (hatched area) in the higher-temperature phases of plutonium.

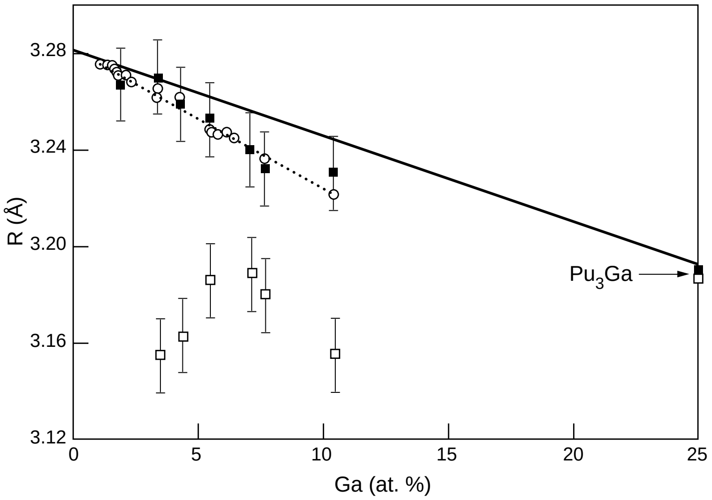

Figure 7. Interatomic Distances for Plutonium-Gallium Alloys in the δ-Phase
These data for plutonium-plutonium and plutonium-gallium bond lengths were obtained with two complementary techniques: x-ray absorption spectroscopy (EXAFS) and x-ray diffraction. The behavior of the ordered compound Pu$_3$Ga is also shown. A Vegard's law linear plot is shown for comparison. The shortening of the plutonium-gallium bond length at gallium concentrations beyond 7.7 at. % may be explained by the formation of ortho sites in an RLFS phase.
(This graph is reproduced with permission from the *Journal of Alloys and Compounds* 123, P. Faure et al., "Lattice Collapse around Gallium in PuGa Alloys as Revealed by X-Ray Absorption Spectroscopy," page 131, copyright 1996, Elsevier Science.)

The Depressed Melting Temperature of Plutonium. How does this physics relate to the anomalous melting behavior of plutonium and neptunium? The melting temperature of plutonium is 913 kelvins and of neptunium, the element immediately preceding plutonium in the periodic table, is 912 kelvins. These temperatures are depressed by 500 to 600 kelvins relative to those of the immediately neighboring uranium and americium. And they are depressed by a significantly larger amount relative to the melting temperatures of the other actinides. Sublimation corresponds to a full debonding—that is, the coherent bonding (delocalization) of the valence and transition-shell electrons in the solid is destroyed. Thus, to the extent that the melting behavior reflects the behavior expected for sublimation, one could think of melting as the phase transition associated with Anderson localization because the heating of a solid generates a sufficient number of imperfections to provide the critical strength of scattering. The RLFS phase transition corresponds to the part of the melting provided by the loss of 5f bonding. Because the temperature for the transition to δ-plutonium corresponds to the configurational entropy gain necessary to counterbalance the 5f bonding, that temperature (592 kelvins) should also correspond rather closely to the depression of the melting temperature. (Having the disorder provided by the ortho-para solid solution means that correspondingly fewer additional thermally induced lattice defects are required for the overall-melting Anderson localization. The transitions to the monoclinic β-phase at 395 kelvins and to the orthorhombic γ-phase at 479 kelvins may be thought of as partial meltings of the 5f bonding.) If one adopts this picture for neptunium, one would have to view the transition from the orthorhombic α-phase to the tetragonal β-phase at 553 kelvins (in that transition, the collapse in the atomic volume is about 6 percent) as corresponding to the 5f melting. Presumably, the immediately neighboring uranium and americium have a much-smaller melting-temperature depression because they are sufficiently closer to full 5f delocalization and coherent 5f localization, respectively. Uranium would perhaps undergo a self-induced RLFS transition sufficiently close to the overall melting temperature so that one lowered phase-transition temperature occurs, rather than two distinctly different ones; and americium is probably in an RLFS phase over much of the temperature range below melting. ■

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