Plutonium Condensed-Matter Physics

A survey of theory and experiment

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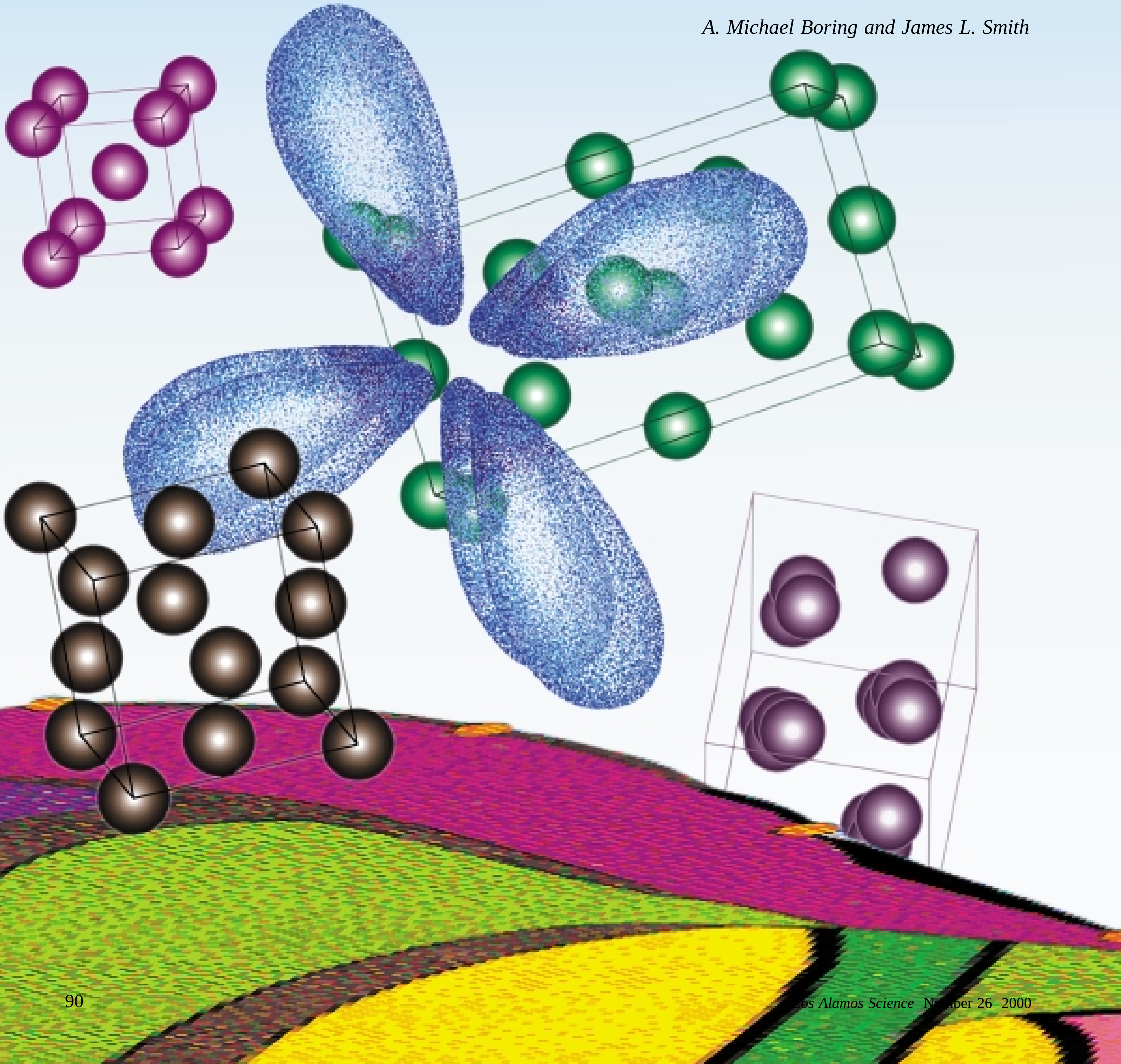
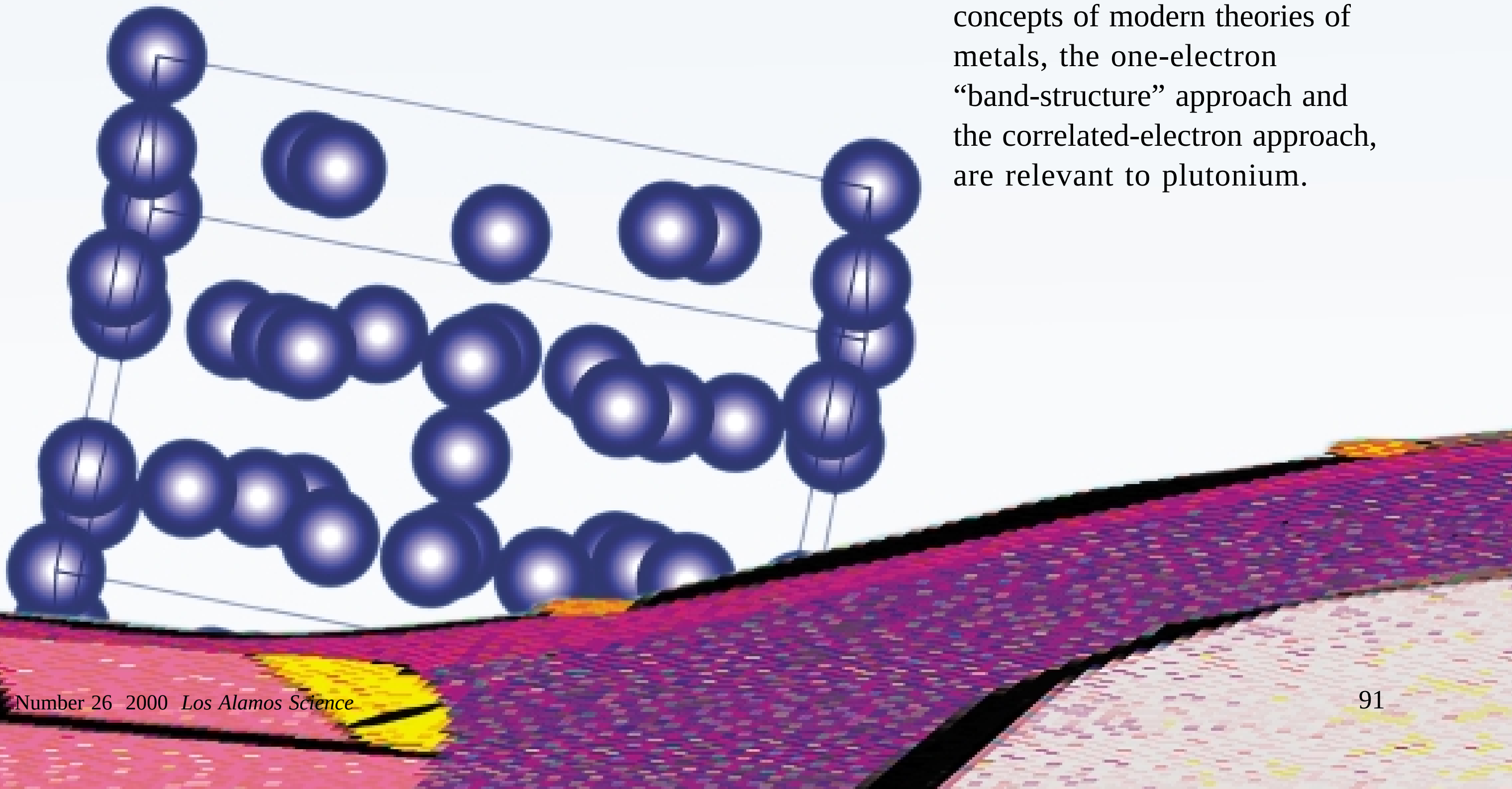


Systems like to be in the lowest-energy state, but plutonium metal has trouble getting there. It has many states close to each other in energy but dramatically different in structure, and so a portion of a sample can change its structure and density in response to minor changes in its surroundings. We probably have yet to see a sample near room temperature that has reached true equilibrium. This metastability and its huge effects are part of the story of the strange properties of plutonium metal, alloys, and metallic compounds, and they are extremely important if we want to leave nuclear weapons untouched for decades.

Here, we will put plutonium metal in perspective by comparing it to the other actinides and to other metals in the periodic table of the elements. Plutonium has many unusual properties. Instead of having the cubic structure found in familiar metals, its ground state has a very low symmetry monoclinic structure with 16 atoms in the unit cell. Its instability is legendary among metallurgists—plutonium goes through six distinct crystallographic phases when heated to its melting point under atmospheric pressure. One of those phases is the face-centered-cubic δ-phase, which can be stabilized down to relatively low temperatures by alloying it with a tiny amount of gallium metal. The δ-phase is itself a tremendous puzzle, having an unusually low density, as well as a negative thermal-expansion coefficient; that is, δ-plutonium contracts when heated. Below room temperature, plutonium continues to display anomalous properties. In particular, it has an unusually high resistivity and an elevated specific heat, suggesting novel interactions and correlations among its electrons. Because they are probably the root for much of plutonium's unusual behavior, we will bring up these unusual electron correlations in connection with both high- and low-temperature phenomena. Figure 1 shows plutonium sitting at the crossover of many properties. As we survey those properties, we will consider the following questions: Is plutonium fundamentally different from other metals? Do we need an entirely new theory to explain its behavior?

Definitive answers must await better and more-complete experimental data leading to a full theory of plutonium and its compounds. We show, however, that the two underlying concepts of modern theories of metals, the one-electron "band-structure" approach and the correlated-electron approach, are relevant to plutonium.



Moreover, many ground-state properties of plutonium can be predicted from modern one-electron band theory. Other problems remain to be solved. As you read this and other papers in this volume, you will learn not only about the successes but also about the ongoing mysteries that place plutonium at a frontier of condensed-matter physics.

The f Electrons and the Role of Narrow Conduction Bands. All metals, including plutonium, are held together by the electronic, or chemical, bonding between the conduction electrons and the positively charged ion cores that constitute the crystal lattice. Conduction electrons are not localized at individual lattice sites. Instead, they are itinerant and travel almost freely through the crystal. They are the "glue" that binds the ions together. We do not think of glue as moving around, so metals are a bit tougher conceptually than other solids. Nevertheless, it is possible to calculate the specific bands of energy levels that are occupied by the conduction electrons. The structure of those bands determines many properties of metals.

In pure plutonium and other light actinides, the conduction electrons include not only the s, p, and d valence electrons, as in the transition metals, but also the valence electrons unique to the actinides, namely, those in the 5f valence shell. Each plutonium atom has five 5f electrons to contribute to bonding. However, the roles of those 5f electrons in the various solid phases of pure plutonium metal and in its metallic compounds and alloys seem to vary. The 5f electrons can be localized (or bound) at lattice sites, in which case they do not contribute to the bonding, or they can occupy a narrow conduction band and contribute to the glue. Pinning down the exact interactions and correlations among the electrons that lead to this variability between localization and itinerancy is currently the subject of intense studies.

For decades, scientists thought that the pointed shape (angular variation) of f-electron atomic orbitals and the likelihood that those orbitals would form directional bonds were the source of the anomalies in plutonium metal. That concept was used for solids because it worked so well for molecules and molecular complexes. In fact, when you read the articles on actinide chemistry, you will see the importance of the shape of f orbitals for those molecular systems. In this article, however, we explain how modern band-structure calculations of plutonium in its low-symmetry ground state (the α-phase) have led to a less atomic-like view of at least some of its properties. Those calculations demonstrate that, for plutonium, as for other metals, it is the energy bands that determine such ground-state ($T = 0$) properties as the cohesive energy, the stability of the crystal structure, and the elastic properties. Furthermore, plutonium's very low symmetry crystal structure in the ground state can be traced to a very particular feature of its energy bands—its dominant conduction band, the one that contributes the most to holding the metal together, is the rather narrow f electron band.

In the latter half of the article, we examine the phase instabilities in pure plutonium, as the metal is heated, and their possible origin in f-electron narrow-band behavior. We then introduce the low-temperature properties that place plutonium among the correlated-electron materials. Finally, we discuss the exotic "heavy-fermion behavior" of cerium and light actinide compounds because, if we can understand these extremely narrow band materials, we may understand plutonium. In general, the low-temperature behavior of correlated-electron materials including plutonium appears to be dominated by as yet unexplained interactions involving their narrow-band electrons. For that reason, the ground states, which in more typical materials are either magnetic or superconducting, are often not well determined and certainly not understood for these materials.

Every few years, condensed-matter physicists find a material with a new ground state that challenges accepted paradigms, and the community turns its attention to this new challenge. But there is also a compelling need to keep working on plutonium: This metal presents some of the most puzzling behaviors of all the elements, and those behaviors bear on the national security mission of the Los Alamos National Laboratory. Although theory can be done anywhere, plutonium cannot be measured at most laboratories, and so we, at Los Alamos, are working on experiment and theory with renewed intensity.

The ideas in our survey of plutonium range in acceptance from firm science to outright speculation. We will try to make clear which is which, but we include both in order to cover our deepest understanding of this complex element efficiently and, we hope, with more interest.

Basic Properties of Metals

For the most part, metals form in a crystalline state. Unlike amorphous or glassy materials, the atoms in a crystal are arranged in a periodic (repeating) array of identical structural units known as unit cells. The repetition in space means that metals have translational symmetry, and this symmetry underlies all metallic behaviors. Most theoretical models of metals are tractable because they exploit the translational symmetry. For example, even with modern computers, one cannot calculate the electronic structure of a piece of wood because it has no underlying symmetry. The translational symmetry of crystalline solids (not just metals) leads to electron wave functions (or Bloch states) that have that same translational symmetry up to a phase factor. These wave functions are macroscopic, extending over the entire crystal lattice, and they serve as the solid-state equivalents of molecular orbitals. That is, just as electrons in molecular orbitals are the glue that bond atoms into a molecule, electrons in Bloch states are the glue that bond atoms into a crystal.

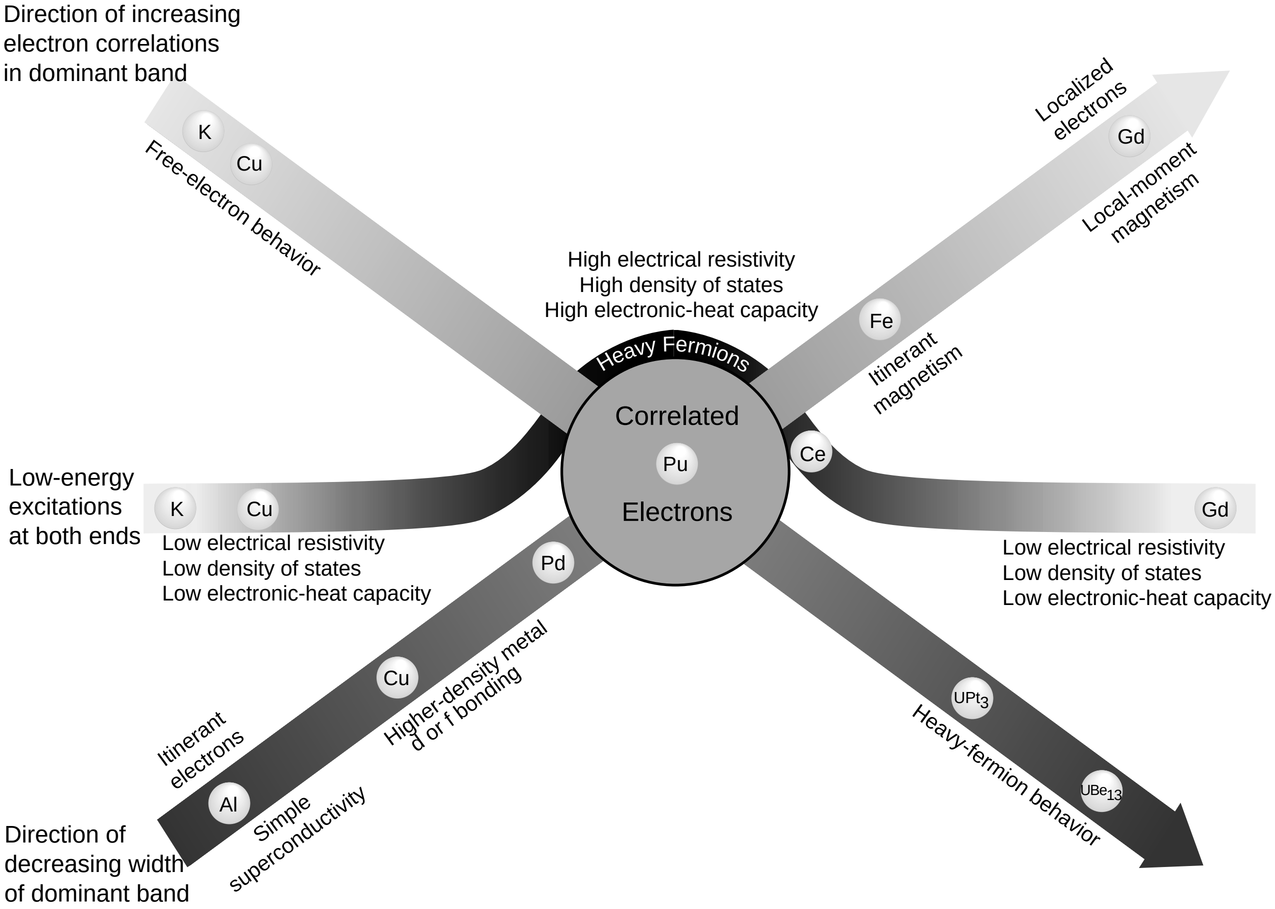


Figure 1. Plutonium at a Crossover in Electronic Properties

This figure summarizes some of the unusual electronic properties of plutonium, stemming from the dominant role of its narrow 5f band. Along one diagonal, plutonium stands midway between simple metals, whose conduction electrons are essentially uncorrelated and exhibit free-electron behavior, and heavy-fermion materials, whose conduction electrons exhibit very strong correlations leading to extremely high effective masses. Along the other diagonal, plutonium stands at the crossover between materials whose itinerant broad-band electrons form superconducting ground states and magnetic materials, whose fully localized electrons (infinitely narrow-band) form local moments and magnetic ground states. Along the horizontal line, plutonium and other correlated-electron narrow-band materials are distinguished from the elements on either side through their high resistivity and specific heat, high density of states at the Fermi energy, and enhanced electronic mass.

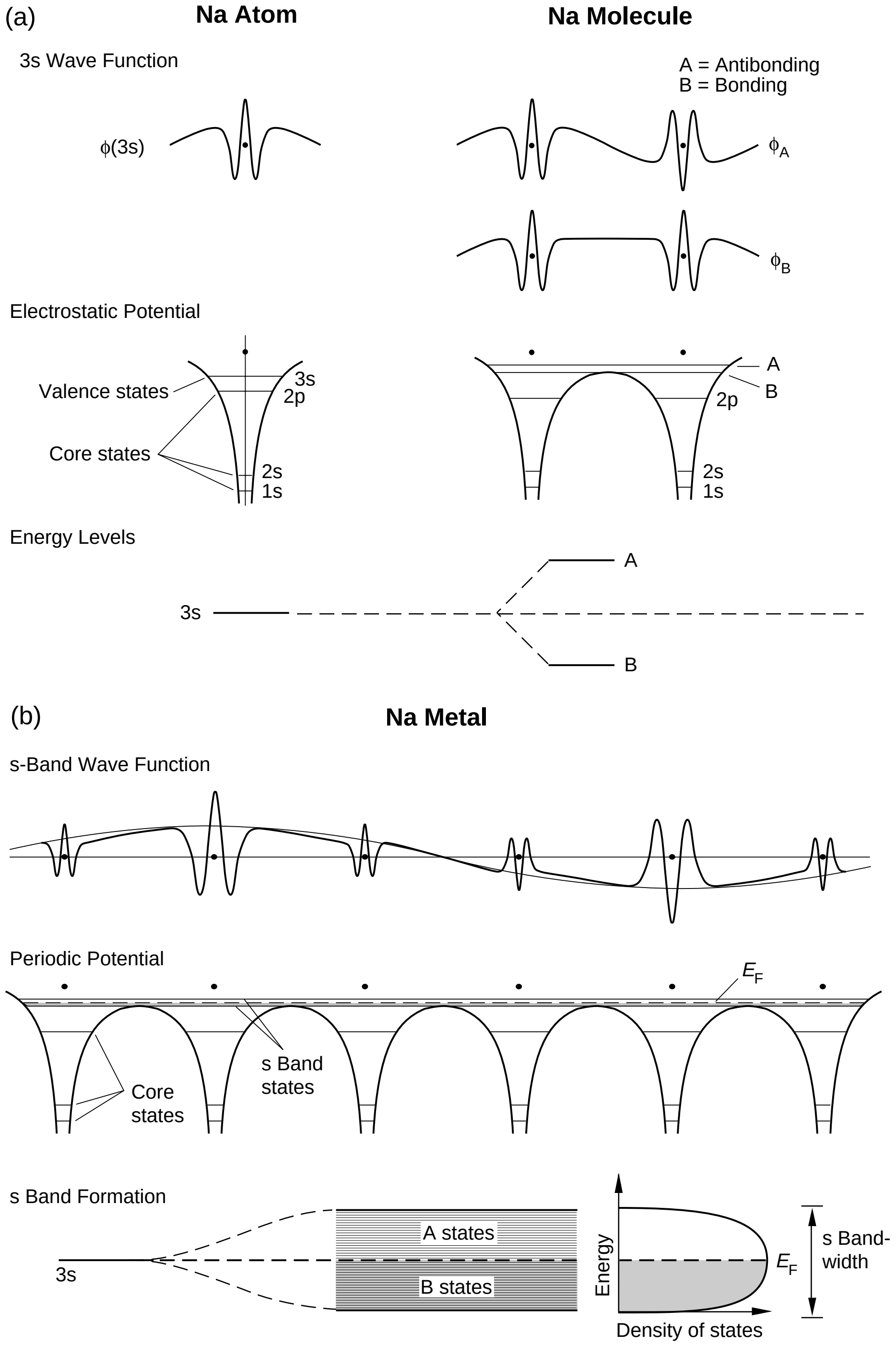
The big difference between molecular orbitals and Bloch states lies in their numbers: In a molecule, there are only a few molecular orbitals, but there are on the order of 10^{23} Bloch states. Therefore, one does not focus on individual Bloch states (it is difficult to choose a particular one) but on averages over these states, such as the density-of-states functions discussed in the next section.

Formation of Energy Bands. When light metallic elements, such as lithium or sodium, condense into the solid state, they typically have cubic structures at room temperature, and the electrons from their atomic valence shells become conduction electrons traveling almost freely through the lattice. That is, these valence electrons occupy one-electron Bloch states, and they are therefore responsible for bonding the solid. The allowed energies of those Bloch states form a broad band of energy levels. In a metal, this energy band is a conduction band because it is only partially filled. Because many empty states are available, the conduction electrons with the highest energies respond to low-energy thermal and electrical excitations as if they were a gas of free particles.

Figure 2 illustrates band formation and the formation of Bloch states in sodium. The top of the figure shows that, when two sodium atoms are brought together, their 3s-electron wave functions (orbitals) overlap, and the valence electrons feel a strong electrostatic pull from both atoms (depicted as the double-well electrostatic potential). The atomic orbitals combine to form molecular orbitals that may bind the two atoms into a diatomic molecule. The single atomic energy level splits into two: one lower in energy, or bonding, and the other higher in energy, or antibonding.

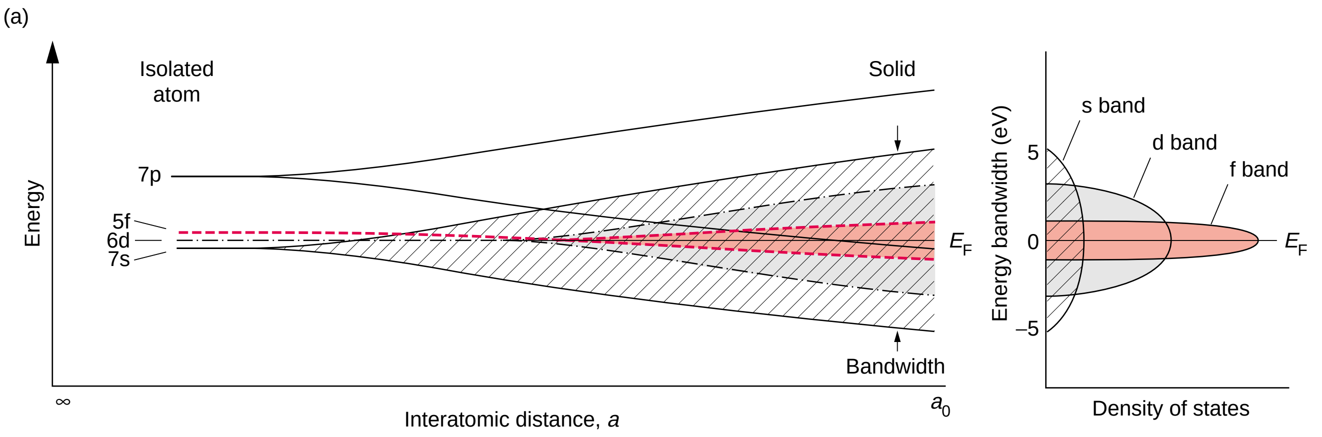
Figure 2. The Formation of an Energy Band in Sodium

The figure shows the transformation of electronic structure when two sodium atoms are brought into close proximity and when numerous atoms condense to form sodium metal. (a) When two sodium atoms are brought together to form a diatomic molecule, the atomic wave function for the 3s valence electron changes into two molecular wave functions—one is bonding (φ_B) and the other antibonding (φ_A)—corresponding to the sum and the difference of the 3s atomic wave functions, respectively. The single potential well of the isolated sodium atom with its 3s-valence energy level and its core energy levels becomes a double-welled potential, with bonding (B) and antibonding (A) molecular energy levels replacing the valence energy level. Finally, the energy level diagram shows the 3s atomic energy level becoming molecular energy levels A and B, which correspond to the molecular wave functions φ_A and φ_B, respectively. (b) When *N* atoms are brought together, the 3s radial wave function becomes a Bloch state made up of a 3s atomic wave function at each atomic site modulated by a plane wave. The single potential well becomes a periodic potential well with core level states at atomic sites and the energy levels of the Bloch (conduction electron) states above the potential wells. The energy level diagram shows the original 3s level becoming a band of *N* very closely spaced energy levels, whose width is approximately equal to the energy difference between levels A and B in the diatomic molecule. That energy difference or bandwidth is proportional to the amount of overlap between atomic wave functions from neighboring sites. In sodium metal, the 3s conduction band is only half full, and the highest occupied state at $T = 0$ is denoted by E_F, the Fermi energy. Also shown is the number of energy levels per unit energy, or the density of states, for this s-electron conduction band.



The energy difference between these two levels is proportional to the amount of overlap of the two s-electron atomic orbitals, and the molecular orbitals (wave functions) corresponding to the bonding and antibonding energy levels are sum and difference, respectively, of the atomic orbitals.

Similarly, when *N* atoms are brought close together to form a perfect crystal (bottom of Figure 2), a single valence electron sees the periodic electrostatic potential due to all *N* atoms. Its wave function (Bloch state) is now a combination of overlapping 3s wave functions from all the atoms and extends over the entire volume occupied by those atoms. As in the molecular case, that wave function can be a bonding state or an antibonding state. The original atomic valence levels generalize to a band of very closely spaced energy levels, half



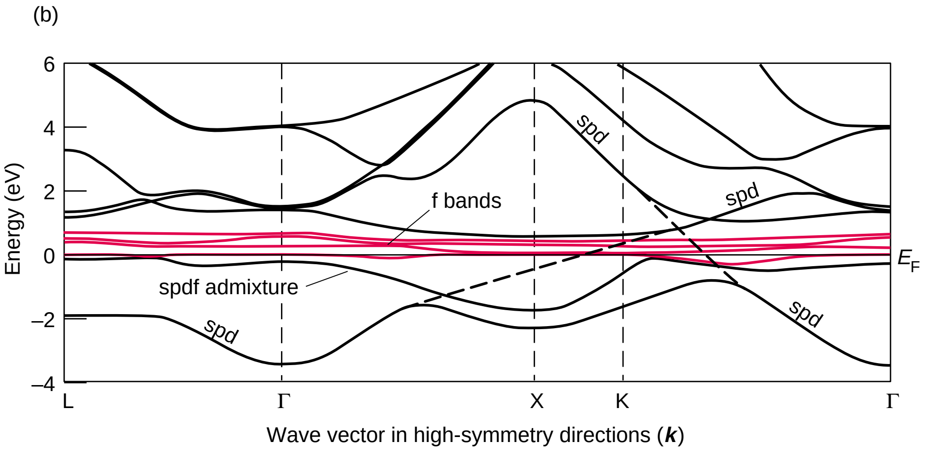


Figure 3. Multiband Formation in the Light Actinides

(a) Illustrated here are the multiple energy bands that form in going from a single actinide atom to a solid. Multiple bands always form when an atom has more than one valence electron. Note that the s and p bands are much wider than the d band, which is much wider than the f band. Also, because the s, p, d, and f states overlap in energy, they can hybridize with each other. That is, any Bloch state with wave vector $\boldsymbol{k}$($\Psi_{\boldsymbol{k}}$) can be a linear combination of states from the different bands with that same wave vector. Finally, the density-of-states functions show that the narrow f band dominates at the Fermi energy because it is so much narrower than the other bands and therefore has many more states at that energy.
(b) The energy bands, one-electron energies as a function of wave vector $\boldsymbol{k}$, are shown for cerium. The very narrow f bands at the Fermi energy are shown in red. The spd bands are broad. States with the same symmetry cannot cross the Fermi energy level. We therefore show by dashed lines how the spd bands would connect if no f bands of like symmetry were present.

of them bonding and half of them antibonding, and the width of the energy band is approximately equal to the energy split between the bonding and antibonding energy levels in the diatomic molecule. This broad band forms whether the crystal is an insulator, a metal, or a semiconductor.

Because in a macroscopic sample the number of levels in the energy band is large (approximately 10^{23}) and the spacing between those levels is small, we can consider the electron energies to be a continuous variable. We describe the number of electron energy levels per unit energy in terms of a density of states that varies with energy. Because each electron must have at least a slightly different energy (the Pauli exclusion principle), electrons fill up the energy levels one by one, in order of increasing energy.

A Bloch state, or the three-dimensional extended wave function of a valence electron in a solid, is represented in Figure 2 in one dimension. In this example, the 3s valence electron wave function of sodium appears at every atomic site along a line of sodium atoms, but its amplitude is modulated by the plane wave $e^{i\boldsymbol{k}\Sigma\boldsymbol{r}}$. As we mentioned before, this general form for a Bloch state in a solid emerges from the requirement of translational invariance. That is, the electron wave function in a given unit cell must obey the Bloch condition $u_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}_n) = u_{\boldsymbol{k}}(\boldsymbol{r})$, where $\boldsymbol{T}_n$ is a set of vectors connecting equivalent points of the repeating unit cells of the solid. It must therefore be of the form $\Psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r})$, where a plane wave with wave vector $\boldsymbol{k}$ modulates the atomic wave function in a solid. The wave vector $\boldsymbol{k}$, or the corresponding crystal momentum $\boldsymbol{p} = \hbar\boldsymbol{k}$, is the quantum number characterizing that Bloch state, and the allowed magnitudes and directions of $\boldsymbol{k}$ reflect the periodic structure of the lattice. Similar Bloch states exist in all crystalline materials, and their occupation by valence electrons is what binds the atoms into a single crystal.

The electronic structure gets more complicated in metals containing more than one type of valence electron. For example, Figure 3 shows that multiple overlapping bands are created when the conduction electrons in a solid originate from, say, the s, p, d, and f valence orbitals of an atom, as in the light actinides. The width of each band increases from left to right, as the interatomic distance decreases and the overlap of the wave functions increases. Also, the s and p bands are always wider (span a wider energy range) than the d band, which in turn is always wider than the f band. The overlapping bands in Figure 3 imply that the Bloch functions with a given quantum number (wave vector) ***k*** could be linear combinations of states originating from the s, d, p, and f atomic orbitals. In other words, the Bloch states could be "hybridized" states containing many angular-momentum components, in contrast to atomic orbitals that contain only one angular-momentum component. Figure 3 also shows the density of states D(ε) resulting from this multiband structure. Note that the f states outnumber all the others at the Fermi energy E_F, which is defined as the highest energy level occupied by a conduction electron at the absolute lowest energy of the metal ($T = 0$). Later, when we discuss cohesion, we will show that these f states dominate the bonding of plutonium in the ground state (or α-phase), primarily because there are five f electrons per atom and only one d electron per atom occupying the Bloch states and participating in bonding. (There are, of course, two electrons in s and p bands but they contribute little to the bonding.) For that reason, we refer to the narrow f band in plutonium as the dominant band. Because narrow bands correspond to small overlaps of wave functions, these f band electrons may be easily pushed toward localization by various effects, in which case they do not contribute to bonding.

If an energy sub-band is filled (electrons occupy all its energy levels), the solid is an insulator. If a band is only partially filled, the solid is a metal. Thus, in a metal there are many empty states close in energy to the occupied states, and so the electrons can easily change their motion (energy) in response to small temperature and electromagnetic perturbations.

The Free-Electron Model and Departures from It. Beyond contributing to bonding, conduction electrons are also thermally excited. In simple broad-band metals such as potassium and copper, the free-electron model describes these low-energy excitations. In that model, the electrons occupying the Bloch states in the conduction band are treated as a gas of identical free particles. That is, the periodic electrostatic potential seen by the conduction electrons and the interactions and correlations among the electrons have no explicit role. However, the model does account for the conduction electrons obeying the Pauli exclusion principle, and therefore at $T = 0$, they fill in the conduction band in order of increasing energy up to the Fermi energy E_F. If we draw the energy states in the three-dimensional space defined by the crystal momentum $\hbar\boldsymbol{k}$, as in Figure 3(b), then E_F traces a surface in momentum space (or ***k***-space) known as the Fermi surface. In the free-electron model, each state corresponds to an electron with crystal momentum $\boldsymbol{p} = \hbar\boldsymbol{k}$ and with kinetic energy given by the free-particle formula, $\varepsilon = (\hbar\boldsymbol{k})^2/2m_e$.

For a gas of free particles heated from absolute zero to a temperature T, classical statistical mechanics would predict that, on the average, the kinetic energy of each particle would increase by an amount k_BT. But because of the exclusion principle, the electrons respond differently. Only those conduction electrons occupying states within k_BT of the Fermi level E_F can be heated (by phonon scattering) because only they can access states not occupied by other electrons (see Figure 4). The number of electrons that participate in properties such as electrical conduction and electronic heat capacity decreases to a fraction T/T_F of the total number of conduction electrons in the metal (here, the temperature at the Fermi surface T_F is defined by the relation $k_BT_F = E_F$). At room temperature, T/T_F is about 1/200 in most metals. Thus, replacing the classical Maxwell-Boltzmann statistics with the Fermi-Dirac quantum statistics implied by the exclusion principle has a profound impact on the electronic properties of metals.

The factor T/T_F shows up explicitly in the low-temperature specific heat of a metal. In general, the specific heat is the sum of a lattice vibrational term (proportional to T^3), which is due to the thermal excitation of the ions, and an electronic term γT, which is due to the thermal excitation of the electrons. The classical coefficient of the electronic term is $\gamma = Nk_B$, but because of the exclusion principle, it becomes $\gamma = Nk_BT/T_F$, and only electrons near the Fermi energy can be heated. Thus, in simple metals obeying the free-electron model, γ is inversely proportional to T_F, or equivalently, E_F, and therefore proportional to the rest mass of the free electron, m_e. Later, when we discuss the low-energy excitations in correlated-electron materials including plutonium, we show that the conduction electrons depart from free-particle behavior. They behave more like the strongly interacting particles of a liquid, more like a Fermi liquid. Because the interactions slow down the electrons, the effective mass of the electrons appears larger, and it shows up as an increase in the value of γ over that predicted by the free-electron model. Thus, low-temperature specific-heat measurements reveal the strength of the electron-electron correlations in a metal and therefore provide a major tool for identifying unusual metals.

Electrical resistivity at low temperatures tells us about the quality of the metal. In a perfect crystal, electrical resistance would be zero at the classical $T = 0$ because the noninteracting conduction electrons, acting as waves, would move through the perfect lattice unimpeded. Above $T = 0$, the thermal excitations of lattice vibrations (phonons) make the lattice imperfect and scatter the electrons. The electrical resistance increases linearly with temperature, as will be shown later in this article. In general, anything that destroys the perfect translational invariance of the crystal lattice will scatter

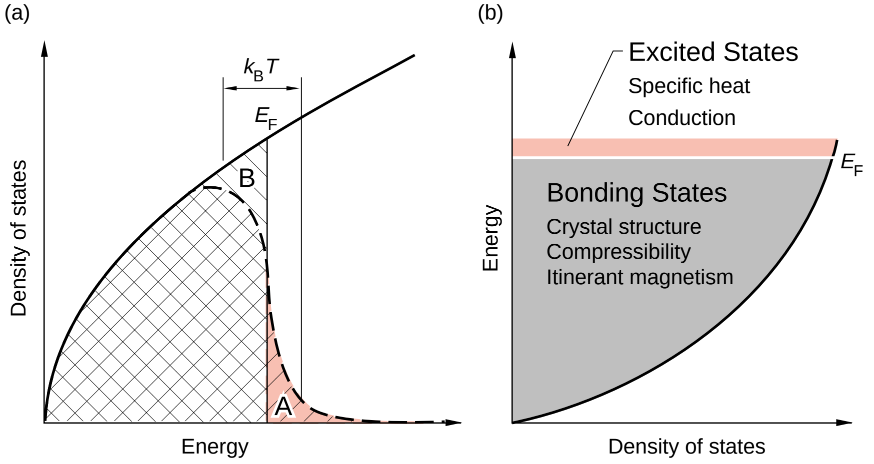


Figure 4. Density of States for a Free-Electron Gas

(a) The solid line is the density of single-particle states for a free-electron gas plotted as a function of one-electron energy ε. At $T = 0$, electrons occupy all the states up to the Fermi energy E_F. The dashed curve shows the density of filled states at a finite temperature T, where k_BT, the average thermal energy per particle, is much less than the Fermi energy. Only electrons within k_BT of the Fermi level can be thermally excited from states below the Fermi energy (region B) to states above that level (region A).
(b) This plot of the density of states emphasizes that all electrons in the conduction band participate in bonding, whereas only those with energies near the Fermi energy contribute to low-energy excitations, such as specific heat, and conduct electricity.

electrons. Foreign atoms, lattice vacancies, more-complicated defects such as stacking faults, and finally, magnetic moments in an array without the full symmetry of the lattice can scatter electrons. Many of these imperfections are temperature independent and lead to a finite limiting resistance as $T = 0$ is approached. Hence, this limit is used as a measure of the quality of metal samples, for which the lowest residual resistance signifies the most perfect sample. We will show that correlated-electron materials often have anomalously high resistivities and very small or zero magnetic moments at low temperatures.

Models of Conduction Electrons

We have suggested that the electrostatic forces holding the metal together can be considered averaged forces between the ions and conduction electrons and that these forces can be modeled by a periodic electrostatic potential. On the other hand, once a metal is formed, its conduction electrons (approximately 10^{23} per cubic centimeter) can act collectively or in a correlated manner, giving rise to what is called quasiparticle or free-electron behavior (not determined by averaged electrostatic forces) and to collective phenomena such as superconductivity and magnetism.

These two seemingly opposing views of conduction electrons and their behavior in solids first appeared in the scientific literature in 1937 and 1957. John Slater (1937) proposed calculating the electronic states—the energy bands in Figures 2 and 3(b)—of solids by the same self-consistent method that had been applied so successfully to describing the electronic states of atoms and molecules. In this method, one treats electrons as independent particles and calculates the average Coulomb forces on a single electron. The other electrons and all the ions in the solid are the source of these Coulomb forces on one electron. This calculation, repeated for all the electrons in the unit cell, leads to a charge distribution from which the electrostatic potential seen by the electrons can be obtained as a solution of Poisson's equation. Using the new electrostatic potential, one then repeats the calculations for each electron until the charge density (distribution of electrons) and the crystal potential (forces on the electrons) have converged to self-consistent values. Slater's approach led to all the modern electronic-band-structure calculations commonly labeled one-electron methods. These one-electron band-structure methods are adaptations of the familiar Hartree-Fock methods that work so well for atoms and molecules. They were put on a more rigorous footing through Walter Kohn's development of density functional theory (DFT). For his achievement, Kohn became one of the recipients of the 1998 Nobel Prize in Chemistry.

Lev Landau (1957) took a different view and argued that the collective motion of electrons in a solid's conduction band was very different from the motion of electrons in atomic or molecular orbitals. He pointed out that particles in the conduction band act as if they were nearly free even though the individual electrons are subject to strong Coulomb forces. Landau's way out of this paradox was to argue that the effect of the electrons' correlated motions from mutual interactions in the solid was to "clothe" themselves, which screens their charge. In heuristic terms, a conduction electron is very much like an onion with many layers. When the electromagnetic force is weak, the interaction penetrates only a few layers, and the electron appears to be clothed. When the force becomes stronger, however (as in the ejection of conduction electrons by photons in photoemission experiments), the interaction penetrates many more layers until the bare electron with its Coulomb force becomes visible, as it does in the one-electron models.

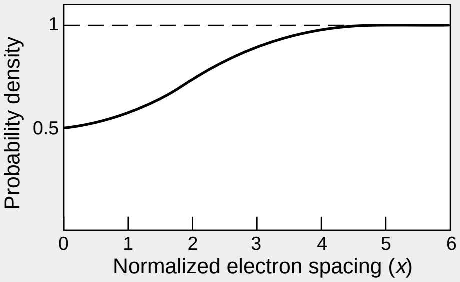
And yet, the conserved quantum numbers characterizing the single-particle states of the clothed electrons—such as spin, momentum, and charge—are unchanged by the

Electron Correlations vs Correlated-Electron Materials

Electron correlations are always mentioned in discussions of electronic structure or excitations, but their physical origin is not always explained. Here, we will give a simple argument for the need to include electron correlations. We will also give some examples of such correlations.

Assume that we have a container of electrons (no ions) that are noninteracting and that we can remove the container and turn on the interactions. At that point, the electron cloud will expand indefinitely because of the Coulomb repulsion between the electrons. No correlations are needed to describe this motion of free electrons. Note that the term free-electron behavior as applied to conduction electrons really means that the electrons act like neutral particles (no charge) that obey Fermi-Dirac statistics—that is, they act like Landau's quasiparticles.

Now suppose that we have a container with an equal number of ions and electrons and that the ions are on closely spaced lattice sites, as in a real solid. Again, we remove the container and turn on the interactions. We assume that our electrons are in random positions and their de Broglie wavelengths are greater than the ion spacings when the interactions are turned on. In this case, the electrons' motion is much more complex because the electrons are simultaneously attracted to the ions and repelled from each other. To minimize the total energy of the system, the electrons must minimize the electron-electron repulsion while maximizing the electron-ion attraction, and the way to minimize the Coulomb repulsion is for them to stay as far from each other as possible. Below, we will demonstrate how electrons are kept apart in real calculations, and the reader will thus get a feel for what we mean by electron correlations.



We will first consider the helium atom, which has two occupied atomic orbitals—one for each electron. Helium was the first many-electron system for which a quantum mechanical calculation was attempted. In developing a model that would predict the observed spectral lines of helium, physicists discovered two unanticipated properties of the electrons. First, the two electrons are indistinguishable—that is, electron 1 can be in orbital A or B, and so can electron 2. Second, the electrons have to obey the Pauli exclusion principle, which means that the total wave function for the two electrons has to be antisymmetric, and that antisymmetry implies that the Hamiltonian must contain an exchange term. This exchange term is what separates the Hartree-Fock calculations of many-electron atoms from the original Hartree calculations of those atoms.

When the exchange term was included in the calculation of an electron gas, it was found that around each electron, there is a "hole," or depression, in the probability of finding another electron close by. The accompanying figure shows the "exchange" hole, which is the probability of finding an electron of the same spin near a given electron. That probability is one-half the value it would have without the exchange term. This exchange hole demonstrates that the electron motion is correlated, in the sense that electrons with the same spin cannot get close to each other. In the 1930s, Wigner performed similar calculations for electrons of opposite spins, which led to a "correlation" hole (very similar to the exchange hole) for the probability of finding an electron of opposite spin near a given electron. The picture of an exchange hole and a correlation hole around each electron is a great visual image of electron correlations in solids. Modern one-electron calculations include these correlations in an average way because these terms can be calculated from the average electron density around a given electron.

Having given a physical basis for the need to include electron correlations, we now refer to the modern usage of the phrase. Any theory that includes interactions beyond the one-electron method is now considered a correlated-electron theory. Likewise, any solid (metal, insulator, and so on) that exhibits behavior not explained by either the free-electron model or the one-electron band model is considered a correlated-electron system. If the properties of a solid deviate strongly from the predictions of free-electron or band models, that solid is called a strongly correlated system. Figure 1 in the main text shows examples of such systems.

Table I. Solid-State Excitations

Excitation	Excitation Energy	Typical Theoretical Method
Photoemission	20–1500 eV	One-electron/many-electron
Band formation	2–10 eV	One-electron
Cohesion	2–10 eV	One-electron
Phase stability	1–25 meV	One-electron
Elastic constants	1–25 meV	One-electron
Magnetic moments (band)	1–25 meV	One-electron
Magnetic moments (local)	1–25 meV	One-electron
dHvA signals	0.1 meV	One-electron/many-electron
Resistivity	0.1 meV	One-electron/many-electron
Specific heat (at low temperature)	0.1 meV	One-electron/many-electron
Magnetic ordering	0.1 meV	Many-electron
Superconductivity	0.01–0.1 meV	Many-electron

interactions. This argument led Landau to propose a one-to-one correspondence between the interacting and noninteracting systems. That is, the number of energy levels in the interacting system (labeled by the conserved quantum numbers of the noninteracting system) and the number of elementary excitations (or clothed particles) in the interacting system would be the same as those in the noninteracting system. The clothed electrons, called quasiparticles, with their physical properties modified, would then interact very weakly and thus have almost-free-particle behavior.

Landau's original argument was meant to explain the nearly-free-electron behavior seen in the conduction electrons in simple metals, in the atoms in liquid helium-3, and in the protons and neutrons in nuclear matter. Later, scientists realized that the same conceptual framework could be applied to small-energy electronic excitations of solids in which the conduction electrons do not exhibit nearly-free-electron behavior but behave more like a liquid. For this reason, the Landau method can be considered a correlated-electron method. Landau's genius was to recognize that these correlations did not have to be calculated directly. Instead, one could assume that the correlations were built into the behavior of the quasiparticles, which could therefore no longer be identified as electrons. The small deviations of those quasiparticles from free-particle behavior were the sign of residual interactions, and the effects of those interactions on the quasiparticle behavior could be determined directly from experimental data. The downside of this theory is that the measurable parameters are not easily derived from first-principles calculations, and so their meaning is not always clear.

Although the one-electron band theories and the correlated-electron theories seem incompatible, we have learned that both are correct and that their relevance depends on the energy and time scale used to view the conduction electrons. We also know that all theories of conduction electrons must include clothing, or correlations. The one-electron methods include averaged correlations, which produce an averaged exchange hole and correlation hole around each electron (these terms are defined in the box "Standard Electron Correlations vs Correlated-Electron Materials"). For higher energies and longer times, such as those involved in bonding, these one-electron methods work well because the averaged correlations dominate the behavior of the electrons. For low-energy excitations, spin and charge fluctuations become more important than averaged values, and the Landau method, which incorporates these fluctuations in the behavior of the quasiparticles, becomes more useful.

Models for Correlated-Electron Materials. Until 1980, we had these two general methods for calculating phenomena involving higher and lower energies, and they worked quite well—except for some isolated systems. But, in the early 1980s, we began finding new metallic materials, the heavy-fermion and mixed-valence materials, whose behavior was as anomalous as that of the light actinides. Resistivities, specific heats, magnetic susceptibilities, electron masses, and other low-energy excitations were different in different materials of the same class and had strange temperature dependencies. Some of these anomalies had been seen before, but they seemed isolated. Almost every new material appeared to exhibit odd behaviors that could not be explained by one-electron models or the Landau treatment.

We now recognize that the central feature of all these materials, including plutonium, is the presence of a dominant, narrow conduction band. We also recognize that the exotic behavior of these materials has a common source: the spin and charge fluctuations associated with the low-energy excitations in those narrow bands. As indicated before, narrow bands mean that the wave functions from different atoms are barely overlapping, and the electrons are thus bordering on being localized. These materials are now collectively called correlated-electron materials, and those with the most extreme behavior are the heavy fermions. (In the late 1980s, another class of materials was discovered, namely, high-temperature superconductors. Although they are complicated and interesting, high-temperature superconductors are not narrow-band materials. Their exotic behavior is therefore unrelated to that of plutonium.)

Along with the discovery of correlated-electron materials came a new class of many-electron models to describe the exotic behaviors of those materials. The Kondo, Hubbard, and Anderson models are among them. These models stand between the one-electron methods and the Landau method in the sense that they can be used to add electron-electron interactions (correlations) to either the semiclothed electrons of one-electron theory or to the quasiparticles of the Landau theory. Originally, the Kondo and Anderson models were invented to solve specific mysteries in materials containing impurities, and they can be generically classed as two-electron "impurity" models. That is, they introduce interactions between pairs of electrons, one localized on an impurity atom and one in a conduction band.

Unfortunately, these impurity models break the translational invariance of the crystal lattice. To become applicable to correlated-electron systems, these models must allow translational invariance to be restored. In the standard approach, the localized (or "almost localized") f electrons become the impurity, and one postulates a lattice of couplings between conduction electrons and the f electrons, which are either located at every lattice site or distributed randomly among the sites. In principle, translational symmetry makes these extended impurity models soluble, but in practice, the models present enormous calculational difficulties, and progress in solving them has been slow.

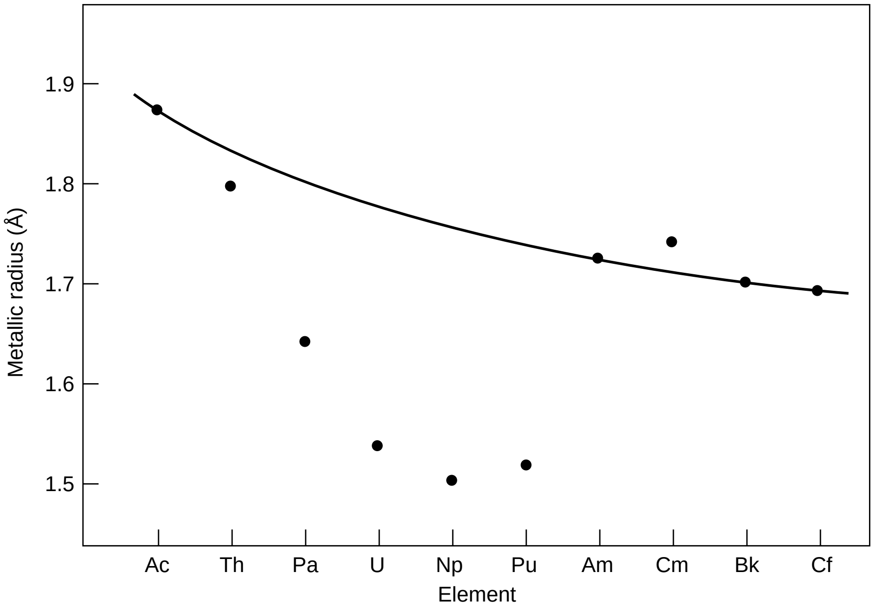


Figure 5. The Metallic Radii of the Actinide Elements in the Ground State
The metallic radius is half the average distance between the atoms in the solid. The line follows the smoothly varying metallic radii of the simple trivalent actinide metals, whose f electrons are localized and therefore nonbonding. The metallic radii of the light actinides—thorium through plutonium—fall on a parabolic curve below the trivalent line, showing the contribution of the f electrons in the bonding, that is, in pulling the atoms closer together.

Energy Scales of Electronic Phenomena. Table I lists solid-state excitations or effects, along with the energy scale and theory most applicable for each effect. Effects for relatively high energies—2 to 10 electron-volts (eV)—include the ground-state crystal structures, as well as the particular bonding energies and stability of those structures. Those properties are modeled with one-electron methods as are the elastic constants, which are among the effects for moderate energies—1 to 25 milli-electron-volts (meV). Low-energy (0.1 meV) excitations and phenomena such as resistivity, magnetic ordering, and specific heat can be described by either one-electron or many-electron models, whereas the very low energy (0.1 to 0.01 meV), collective electronic ground states such as superconductivity and magnetism can only be described by many-electron models.

Not all phenomena in solids, however, can be fully treated by a single approach. For example, the de Haas–van Alphen (dHvA) effect[1], as seen in heavy-fermion materials, requires both. The oscillations can be explained by one-electron theories, whereas the very heavy electron masses are explained only by correlated-electron theories. Another example is provided by the spectra obtained from photoemission experiments, which are performed at relatively high energies but for short times. Photoemission spectra measure the one-electron density of states predicted from one-electron methods, but because of the short time, spin and charge fluctuations may add small features to the overall spectra (see the article "Photoelectron Spectroscopy of α- and δ-Plutonium" on

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[1] The dHvA effect is the oscillation in magnetic susceptibility at low temperatures, as an applied magnetic field changes.

page 168). Clearly, we need both theoretical techniques to explain the properties of metallic plutonium and its compounds.

To convey an overall picture of the actinide metals, we first discuss their bonding properties, for which we use one-electron methods. Later in the article, when we look at phase instabilities and other lower-energy phenomena, we will need arguments and concepts from correlated-electron theories.

Cohesion in the Light Actinides—Similarity with the Transition Metals

Our discussion of the bonding properties in the actinides focuses on the role of the 5f valence electrons. The 5f electrons in the light actinides (thorium through plutonium) are itinerant, just like the 5d electrons in the transition metals, participating in the bonding of the solid and affecting most of the high-energy properties such as cohesion, crystal structure, and elastic properties. In contrast, the heavy-actinide metals (americium through lawrencium) have localized (atomic-like as opposed to itinerant) 5f electrons, and they are thus the true counterpart to the rare-earth metals. (The presence of localized magnetic moments in both the lanthanides and the heavy actinides is a direct sign that f electrons are localized.)

Figure 5 is a plot of the metallic radii of the actinides, and it gives explicit evidence for the bonding behavior of the 5f electron series in the ground state. Notice that the light actinides have smaller metallic radii (therefore, higher densities) than the heavy actinides. The reason is that the f electrons in the light actinides contribute to the bonding. Also, the metallic radius of the light actinides gets smaller with increasing atomic number (Z) because each additional f electron per atom pulls the atoms closer together. This trend stops at americium. The metallic radii of the heavy actinides are all about the same, and that value is larger than that for the radii of the light actinides because the localized 5f electrons have no effect on bonding.

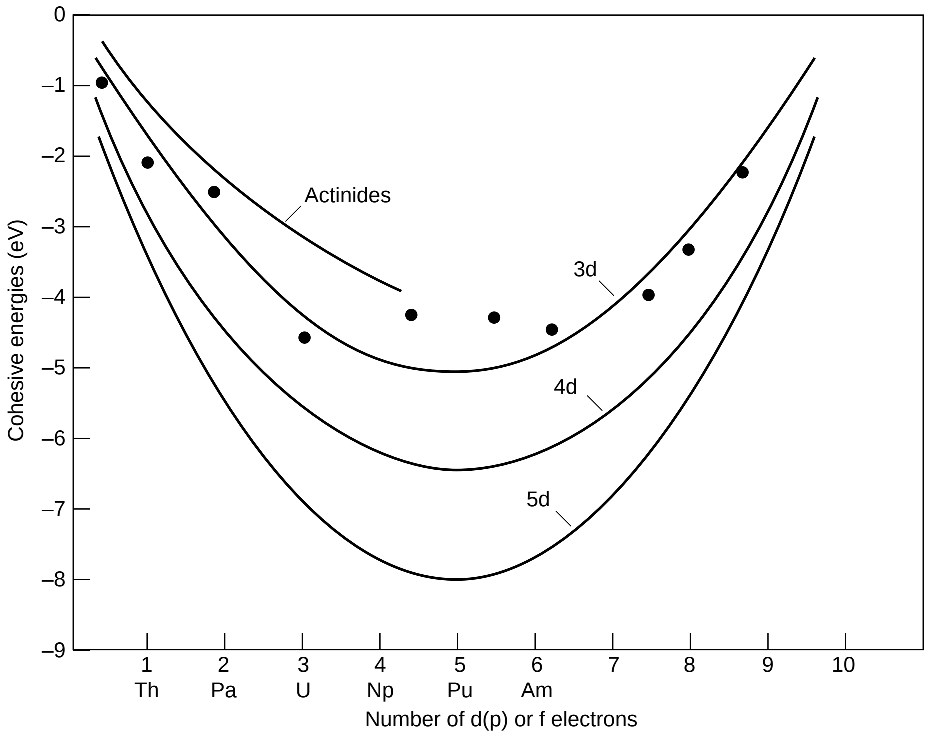

Figure 6. One-Electron and Friedel Model Results for the Cohesive Energies of the d and f Series

The calculated cohesive energies per atom of the 3d metals (dots) are equal to the calculated difference between the binding energy of an isolated atom (excluding atomic valence-electron coupling) and the binding energy of an atom in its solid. For pedagogical reasons, in these LDA one-electron calculations, the metals were assumed to be in the fcc crystal structure. (The cohesion of the other structures differs by up to 10% from that of the fcc phase.) The Friedel model predicts a parabolic curve for the 3d metals. This simplified model of bonding assumes that the density of states in the d band of the transition metals is constant over its width. The model also assumes that the d electrons fill the energy band in order of increasing energy: First the bonding d states are filled, which increase the binding, and then the antibonding d states, which decrease the binding. Thus, maximum stability is reached when the band is half full. (Refer to the article “Actinide Ground-State Properties” on page 128 for a more detailed discussion of this model.) The LDA one-electron results agree with the predictions of the Friedel model. We show only the parabolic curves for the 3d, 4d, and 5d elements and for the light actinides. The cohesive energies of the light actinides look similar to those of the transition metals—that is, they show increased bonding as the f shell is being filled.

Ironically, before the Manhattan Project, when thorium and uranium were the only actinides whose physical properties were known, these metals were thought to belong to a 6d metal series to be placed below hafnium and tungsten in the periodic table of the elements. The similarities between thorium and uranium and the 5d transition metals were the cause for this misconception. After McMillan and Abelson discovered neptunium in 1940 and after the discoveries of plutonium, americium, and curium during the Manhattan Project, measurements of atomic spectra showed that the valence electrons in this ever-lengthening series were filling a 5f shell and not a 6d shell of atomic orbitals. These 5f electrons were expected to be localized in the solid state, like the 4f electrons of the rare earths. Long after the Manhattan Project, the pendulum swung back, as scientists realized that the similarities between the light actinides and the 5d transition-metal elements meant that the 5f electrons in those early actinides did indeed form a conduction band.

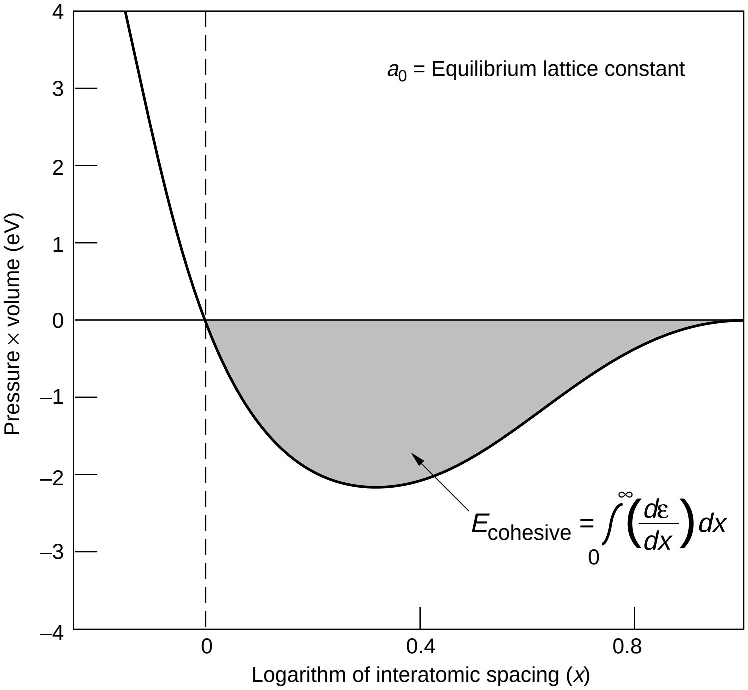

Figure 7. The Bonding Curve for Potassium

The plot shows LDA one-electron calculations of the bonding curve for potassium in the fcc structure, which is the change in cohesive energy per atom, $d\varepsilon/dx$, as isolated potassium atoms at infinite separation are brought together to form a solid. We plot this quantity as $P\Omega$ (pressure times volume or force times length) vs the separation between atoms (or lattice constant a). The shaded area under the bonding curve is the cohesive energy to bond the atom in the solid. To compress the bonding curve, the horizontal axis is a logarithmic scale $x = \ln(a/a_0)$. Equilibrium occurs when $d\varepsilon/dx = P = F/A = 0$, at which point $a = a_0$ and $x = 0$ (the dashed line in the figure). The bulk modulus (average elastic constant) is given by the slope of the curve at equilibrium (that is, at $x = 0$ and $d\varepsilon/dx = 0$). At the minimum in the curve, the attractive forces between the atoms are the greatest. Those forces weaken as the atoms move together until they vanish at the equilibrium separation.

The cohesive energy per atom holding a crystal together is defined as the difference between the electrostatic binding energy per isolated atom (ignoring coupling among electrons) and the total internal (electrostatic binding) energy per atom in a crystal. Both binding energies, and thus the cohesive energy, are calculated self-consistently by one-electron methods. Figure 6 shows the one-electron predictions for the cohesive energy per atom of 3d transition metals in a hypothetical face-centered-cubic (fcc) structure (dots) and the Friedel model predictions for the 3d, 4d, 5d, and 5f elements (parabolic curves). The Friedel Model, a simplified model of bonding, assumes that the d electrons are conducting and are filling an energy band in order of increasing energy: first, the bonding d states, which increase the amount of binding, and then the antibonding d states, which decrease that amount. Note that the Friedel model predictions for the 3d elements fit the results from quantum mechanical one-electron calculations quite well. And the bonding in the 4d and 5d metals is greater than that in the 3d metals because 4d and 5d electronic states have a greater radial extent (more overlap) than 3d states (a feature not obtained from the simple Friedel model). The cohesive energies of the light actinides look similar. That is, they show increased bonding with the filling of the beginning of the 5f shell. However, the parabolic trend in the early actinides ends at americium because the 5f electrons are no longer contributing to bonding.

Similarly, the lattice constants (length of the edge of the basic cubes in a cubic crystal structure) tend to decrease as one goes across the first half of all the d and the 5f series, again indicating that each additional electron increases the bonding or cohesion. Recall that metallic radii also decrease parabolically across the early part of the 5f series, as revealed in Figure 5.

Plutonium and the Universal Bonding Curve of Metals

The parabolic trend in cohesion and lattice constant extends to the bulk modulus, which is the average elastic (or spring) constant of the solid. The bulk modulus thus gives the strength of the restoring forces, or interatomic forces, that bind the solid together as the ion cores vibrate about their equilibrium positions. For most metals, the bulk modulus, the cohesive energy, and the lattice constant can be related to each other through the “universal bonding curve.” We will show next that plutonium fits this curve as well.

First developed as a parameterized equation, the bonding curve is a plot of pressure (cohesive force per unit area) on an atom vs the distance between the atoms. Figure 7 shows the bonding curve for potassium metal calculated from one-electron band-structure calculations in the atomic-sphere approximation (the electrostatic potential around each lattice site is assumed to be spherical). Here, the bonding forces are for atoms arranged in an fcc structure, and they are plotted as a function of *x*, the natural log of the lattice spacing *a* normalized by a_0. At very large interatomic distances, the atoms are isolated, and the pressure on any atom is zero. As the atoms approach each other, their electronic wave functions overlap, and there is an attraction, or pressure, that pulls them together. Finally, they reach equilibrium at the lattice constant a_0, where again the pressure on the atoms is zero. In Figure 7, the cohesive energy is the area between the bonding curve and the line indicating zero pressure; the equilibrium lattice spacing is at $x = 0$ (or $a = a_0$), the value at which the bonding curve crosses the zero pressure line; and the bulk modulus is the slope of the bonding curve at this equilibrium spacing. Remember that this curve represents the forces on an atom in the solid. Therefore, the minimum in the curve is the lattice constant at which the attractive force between the atoms is the greatest. As the atoms move closer together, the attractive force becomes weaker and vanishes at the equilibrium lattice constant a_0.

We will next illustrate that there is only one bonding curve for all metals, including plutonium. We first calculate the bonding curve for molybdenum because, among metals, it has the largest cohesion. We then plot all other metals on this curve, by drawing the zero pressure line for each metal so that the area between that line and the bonding curve is equal to its cohesive energy. The results, shown in Figure 8 for several metals, reveal the following relationships: First, if the cohesion of one metal is greater than that of another, then its lattice constant is smaller. Next, the bonding curve becomes steeper as the interatomic distances get smaller (see the part of the curve to the left of the maximum force point). This means that the tangent to the curve (bulk modulus) becomes larger as one moves up the curve. So, if the cohesion of one metal is larger than that of another, its bulk modulus will be larger. This universal bonding applies to all metals in the periodic table. When considering cohesion and bulk modulus, we can see that plutonium and the other light actinides fit the universal curve just like any other metal. We note that plutonium and the light actinides have relatively small bulk moduli because they have large lattice parameters, which, as we shall see, are due to the electrons in the s and p bands and are consistent with the universal curve.

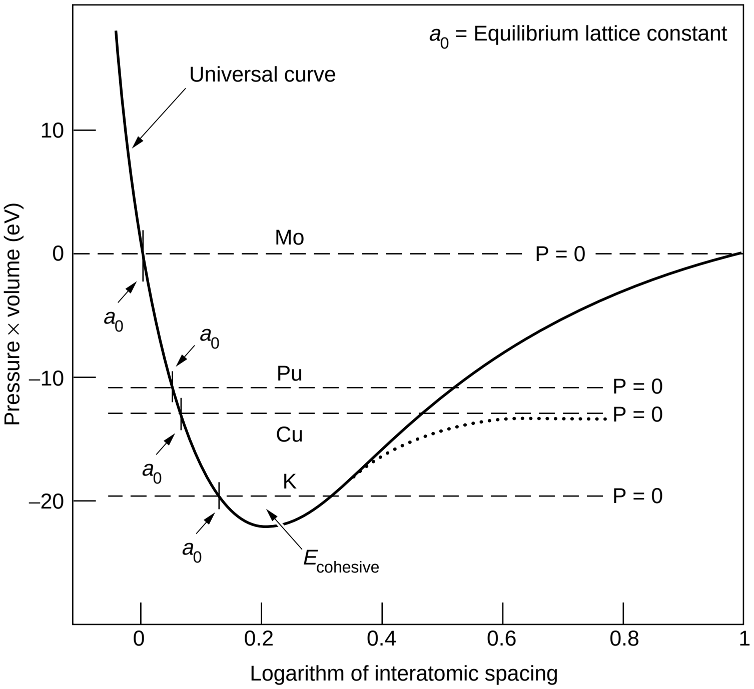

Figure 8. A Universal Bonding Curve

LDA one-electron calculations of the bonding curves for potassium, copper, plutonium, and molybdenum in fcc structures are overlaid on the same curve. The horizontal axis for each metal is placed at zero pressure for that metal, and the area between that axis and the curve gives the correct cohesive energy per atom. (The dotted curve for copper shows that, in this construction, we are ignoring the large distance tails of the bonding curve for each element.) A number of relationships are apparent in this figure. As the cohesive energy increases from one metal to the next, the *P* = 0 axis moves up, and the equilibrium lattice constant a_0 decreases (moves to the left). At the same time that a_0 moves to the left, the force curve at a_0 becomes steeper, and the bulk modulus, which is the tangent to the curve at a_0, increases. So, if the cohesion of one metal is larger than that of another, its lattice constant will be smaller and its bulk modulus will be larger.

More exact calculations of bonding in plutonium are now available and are presented in the article “Actinide Ground-State Properties” (page 128), but a few general remarks are in order. Those modern calculations, as well as the ones we presented above, are based upon the local density approximation (LDA) of the DFT approach to band-structure calculations. But in contrast to our simplified, pedagogical approach, Wills and Eriksson have performed full-potential calculations (that is, no constraints are put on the form of the crystal potential), so that all types of crystal structures can be handled. Their modern calculations are fully relativistic (as were our pedagogical calculations), which is necessary for crystals with high Z-number atoms. For example, a nonrelativistic calculation of the plutonium atom gives a wrong ordering of the s, p, d, and f valence levels.

One of the expected connections between electronic-structure calculations based on one-electron methods and experiment has been provided by the values for the energy levels of the one-electron states, which can be measured by photoemission experiments. In the atomic case, for example, it has been proved that the energy eigenvalues of the one-electron Hartree-Fock equations (see the box on page 98) are equal to the electron-removal, or ionization, energies (Koopman's theorem), which are directly measurable quantities. Unfortunately, when those atomic eigenvalues are calculated with the LDA, they do not have the same physical meaning. Instead, they are equal to the removal energies plus a small calculable correction, and this correction has not been shown to vanish for atomic energy levels nor has it been calculated for the one-electron Bloch (periodic) states of a solid. Therefore, we have to rely on a comparison with experimental data to determine how close the LDA-calculated energies are to the electron removal energies measured from photoemission experiments. Any disagreements do not mean that the theory is wrong.

Finally, we remind the reader that all one-electron methods automatically predict the hybridization between the s, p, d, and f states when those states overlap. The LDA results we reported here agree with experimental data at the 90 percent level, whereas full-potential calculations, such as those in the article "Actinide Ground-State Properties" on page 128, are often in better agreement. However, it is not only the calculated values that are important but also the deeper understanding that LDA calculations enable. Because these calculations are efficient, we can repeat them for many variations of the parameters, thereby uncovering detailed bonding features that determine the structures and bulk properties of all the metals in the periodic table.

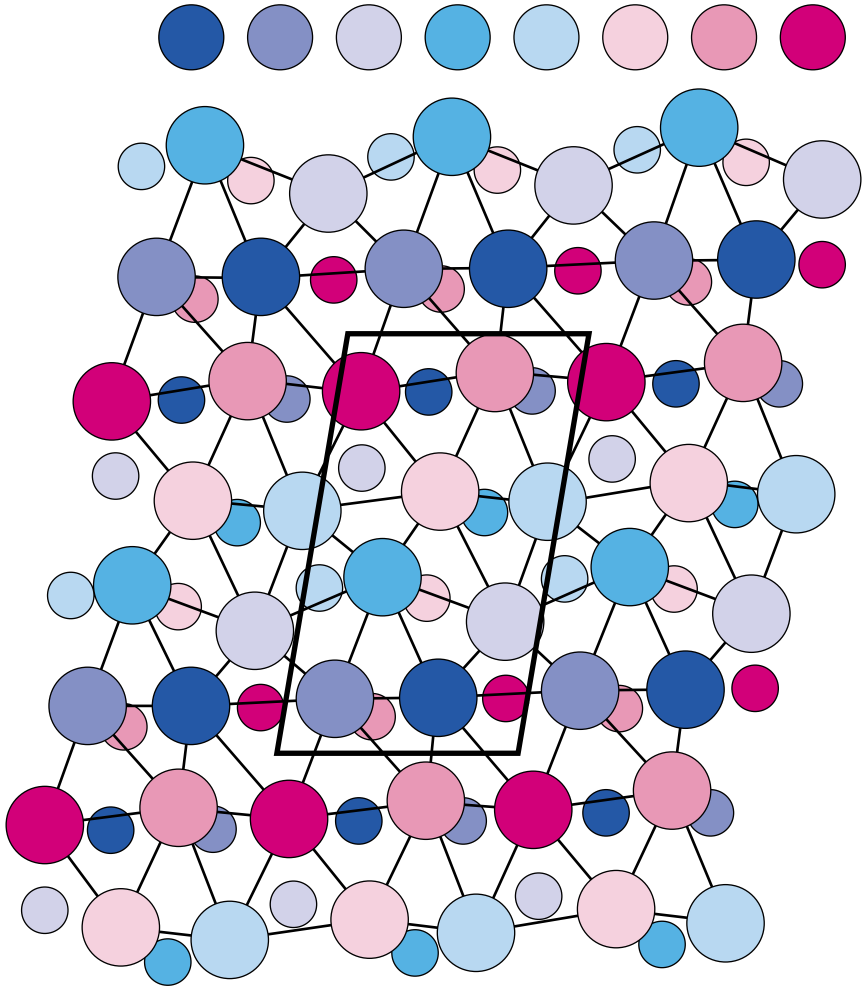

Figure 9. The Crystal Structure of α-Plutonium

The α-phase, the equilibrium phase of pure plutonium at room temperature and below, has a monoclinic crystal structure. The parallelogram outlining the 16-atom unit cell shows 2 flat layers (or planes) of atoms, and 8 distinct atomic sites. The larger numbers label the distinct sites in the top plane of atoms, and the smaller numbers label the equivalent sites in the next layer down into the crystal. The lines between the atoms show that the layers are somewhat similar to a hexagonal structure. For atoms numbered 2 through 7, one side of each atom has only short lengths to its nearest neighbors (2.57–2.78 Å), and the other side has only longer lengths (3.19–3.71 Å). This pattern could be viewed as a strange packing of individual "half dimers," which is what a three-dimensional Peierls distortion might be.

Low-Symmetry Structures from Narrow Bands

One of the striking anomalies of plutonium metal is its very low symmetry crystal structure. In fact, the light actinides exhibit the lowest-symmetry ground states of all elemental metals: from orthorhombic for α-uranium to monoclinic for α-plutonium. Figure 9 shows the room-temperature monoclinic crystal structure of α-plutonium and its departure from a hexagonal structure.

In contrast, the transition metals, despite their relatively complex behavior, form high-symmetry cubic ground states such as bcc (body-centered cubic), fcc, or hcp (a hexagonal close-packed variation of fcc). These high-symmetry structures look like spheres stacked in an

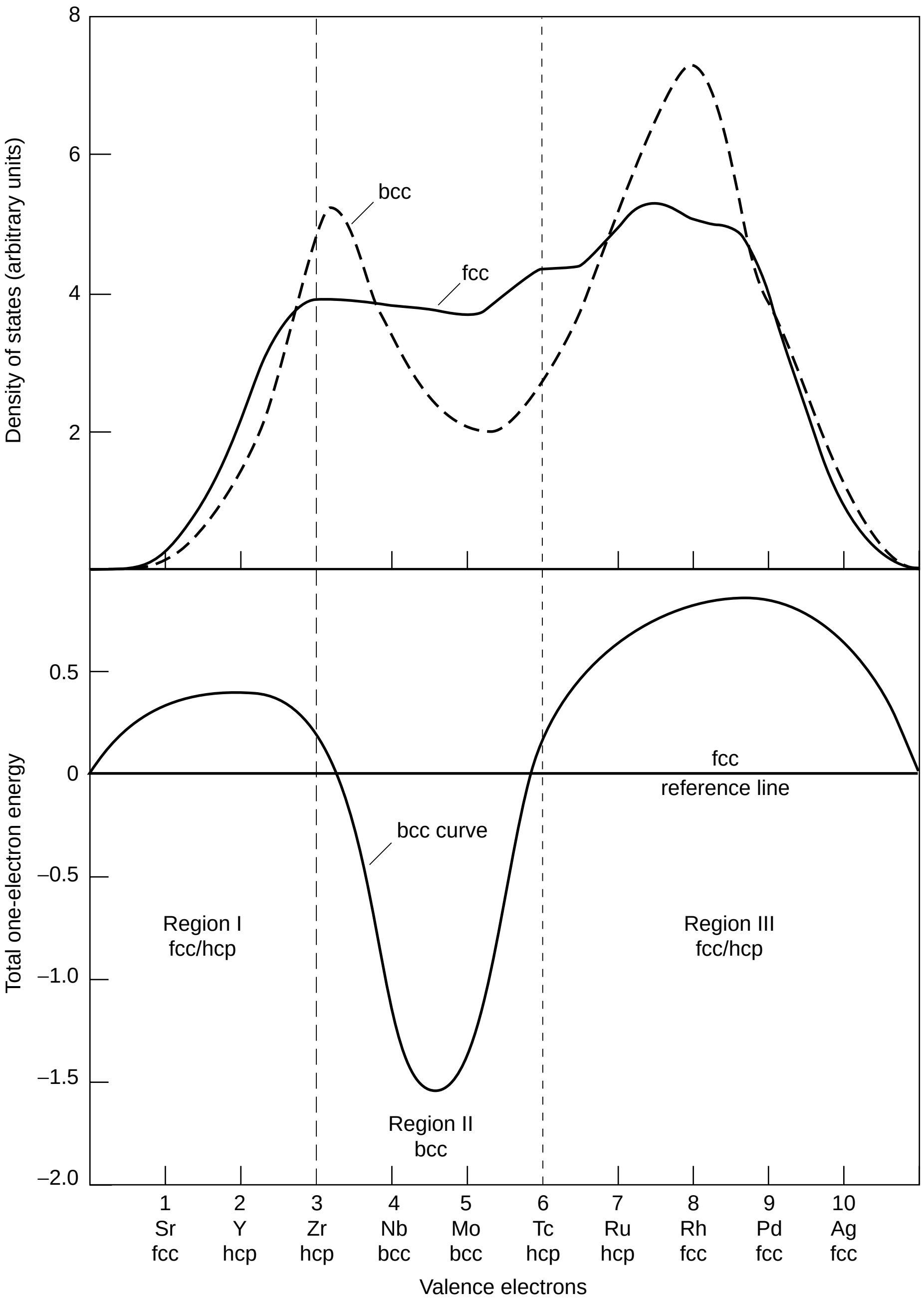

Figure 10. Stability of bcc, fcc, and hcp 4d Transition Metal Structures Determined from the Density of States

(Top) The LDA fcc (hcp) and bcc electronic density of states for the d conduction band of the 4d transition metals are plotted as a function of energy and display their unique signatures. For pedagogical purposes, we ignore the relatively small differences between the fcc and hcp density of states. The d-band density of states is the same for all 4d elements, but the Fermi level, or highest occupied level, for each element (dashed vertical lines shown for Zr and Mo) increases with the number of 4d electrons. (Bottom) The total one-electron energy contributions for each element in both the fcc (hcp) and bcc structures were calculated from the first moment, $\int \varepsilon D(\varepsilon) d\varepsilon$ for that crystal structure, where each ε is a one-electron energy eigenvalue from LDA calculations. The fcc (hcp) results are the reference line, the bcc results are plotted relative to that reference, and the lower value of the two is the prediction of the stable structure for that element. Note that the predicted sequence of structures matches the observed sequence (listed below each element) if we ignore the difference between fcc and hcp. The lines through the top and bottom figures mark the level of band filling (E_F) at which the crystal stability changes from fcc (hcp) to bcc or vice versa. In Region I, the number of 4d electrons per atom contributing to the band increases from 1 to 3. For each element in Region I, the fcc centroid (average value of ε) for the filled states is always lower in energy (farther away from the highest filled level at E_F) than the bcc centroid. Therefore, for those elements, there is more bonding in the fcc (hcp) phase. In Region II, the situation is reversed because the E_F for these elements goes above the first bcc density-of-states peak, and therefore the bcc centroid goes below the fcc (hcp) centroid. Finally, for the elements in Region III, E_F reaches the second bcc peak, the bcc centroid shifts closer to E_F than the fcc centroid, and so the fcc (hcp) phases become more stable again. Thus, the d band filling and the unique signatures of the electronic density of states determine the crystal structures of the 4d transition metals.

efficient space-filling manner with no directional bonding (increased electron density) between the atoms. Once metallurgists know the stacking pattern (or crystal structure), they can predict many of the metallurgical properties. To illustrate the connection between electronic structure and crystal structure, we show how LDA electronic-structure calculations correctly predict the sequence of ground-state crystal structures for all the transition metals.

The LDA calculations predict that the one-electron density-of-states functions for the fcc and hcp transition-metal structures are very similar. For this discussion, we will treat those crystal structures as equivalent and compare the one-electron energy contributions of the bcc structures with those of the fcc (or hcp) structures. The one-electron

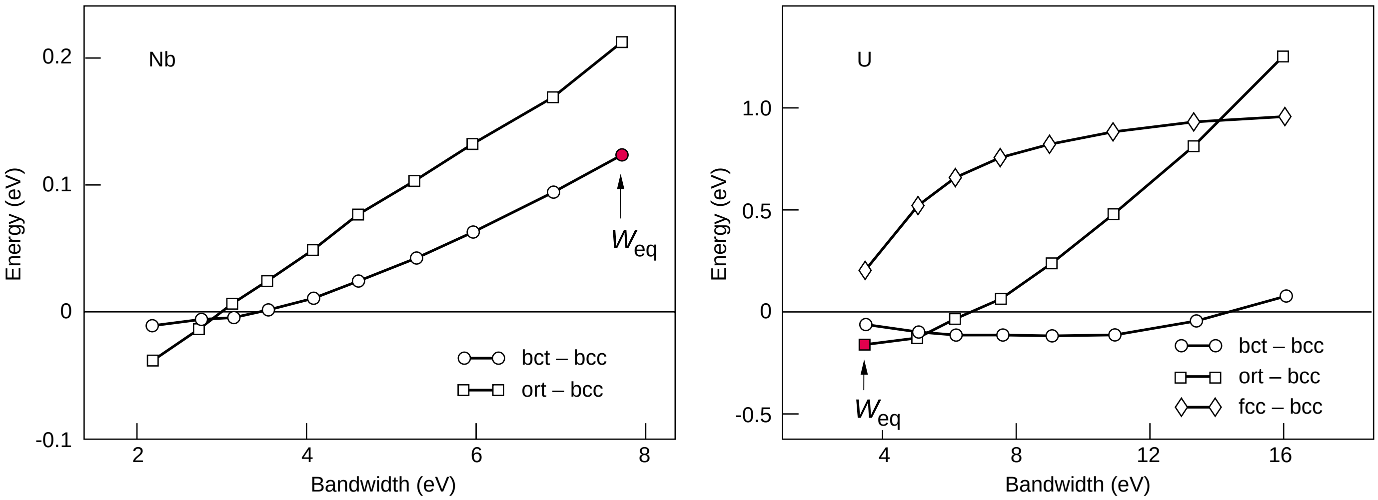

Figure 11. Internal Ground-State Energies as a Function of Bandwidth

DFT results for bonding energy vs bandwidth demonstrate that narrow bands produce low-symmetry ground states and wide bands produce high-symmetry ground states. Results are shown here for niobium (a d-bonded metal), and uranium (an f-bonded metal). The atomic number, crystal structure, and lattice constant (or volume) are inputs to these calculations, and the bandwidth and energy are outputs. The input structures are bcc, bct, and orthorhombic, and in the case of uranium, fcc. The results for the bcc structure are plotted as the horizontal reference line, and those for the other structures are plotted relative to the bcc results.
Thus, a structure is more stable than bcc when its bonding energy appears below the reference line. Note that for niobium, the low-symmetry orthorhombic structure becomes stable when we force the d band to be narrower than 3 eV by decreasing the input volume. Likewise, when we force the f band in uranium to be broader than 7 eV by increasing the input volume, the high-symmetry bcc structure becomes stable. The calculated bandwidth at the experimental equilibrium volume is labeled W_{eq}. The results in the figure suggest that transition metals have broad bandwidths and symmetric structures, whereas the light actinides have narrow bandwidths and low-symmetry structures. (This figure was reproduced courtesy of *Nature*.)

energy contribution for a given element is equal to the one-electron energy ε averaged over the portion of the one-electron density-of-states function $D(\varepsilon)$ that is filled for that particular element ($\int \varepsilon D(\varepsilon) d\varepsilon$). The upper half of Figure 10 shows the approximate forms of $D(\varepsilon)$ for the 4d transition-metal series in the bcc and fcc (or hcp) crystal structures. The lower half of that figure presents the one-electron energy contribution for the 4d series, with the fcc (hcp) results plotted as the horizontal reference line and the bcc results plotted relative to that line. The structure that gives the lower-energy value for each element is the LDA prediction for that element's ground-state structure. In all cases, the LDA prediction agrees with the observed structure. The same methods yield similar agreement between predicted and observed crystal structures for the 3d and 5d metals.

We remind the reader that the total internal energy is equal to this one-electron contribution plus other terms (double counting, exchange, and correlation terms). Our results suggest, however, that the one-electron contribution is the dominant factor in determining the crystal structure. The physical reason for its dominance is that the states at the bottom of the conduction band are the most bonding, so the crystal structure whose average one-electron energy is lowest, or closest to the bottom of the band, should be the most stable.

Figure 10 shows that one-electron theory predicts the right crystal structures for the transition metals, and it also illustrates why crystal structures in the 4d series occur in the sequences observed. In principle, we could perform the same calculations for the low-symmetry structures of the actinide series, but the density-of-states functions for those elements are more complicated, so those calculations would not be as easy to interpret.

Because electronic structure determines crystal structure, we will consider how the electronic structure of the light actinides, of plutonium in particular, differs from that of the transition metals. An obvious difference is the angular character and symmetry of the orbitals associated with their dominant electron bands—that is, d orbitals with even symmetry for the transition metals vs f orbitals with odd symmetry for the light actinides. Perhaps the odd symmetry of the f orbitals causes the ground states to have low symmetry, as do p-bonded metals such as indium, tin, antimony, and tellurium. In these metals, the odd-symmetry p orbitals seem to produce directional covalent-like bonds and low-symmetry noncubic structures. With no way to check this conjecture for plutonium, metallurgists and physicists alike long held on to the notion that directional bonding plays the dominant role in explaining the low symmetry of the light actinides.

Recent LDA electronic-structure calculations of ground-state properties have demonstrated that the narrow width (approximately 2 to 4 eV) of the f bands leads to the low-symmetry ground states of the actinides. The d bands of the transition metals are much broader—approximately 5 to 10 eV. From our discussion of band formation, one intuitively knows that bandwidths are a function of volume. They become narrower for large volumes (the wave functions barely overlap between lattice sites), they turn into a single energy value for fully separated atoms, and they become broader for small volumes. Using the LDA, one can calculate the total bonding energy of a given element in any crystal structure and across a range of volumes (with their concomitant bandwidths) and thereby demonstrate the dependence of energy on bandwidth.

The results of such calculations are plotted in Figure 11. The ground-state (or internal) energy is plotted as a function of bandwidth for niobium and uranium in several structures: the bct (body-centered tetragonal) and ort (orthorhombic) structures for niobium and the bct, ort, and fcc structures for uranium. In both plots, the ground-state energy of the bcc (body-centered cubic) phase is the horizontal reference line. A structure is more stable than bcc when its internal energy goes below the reference line. Figure 11 shows that, when the d band is forced to be narrower than 3 eV because an expanded volume is used as input to the calculation, the low-symmetry orthorhombic structure becomes stable. Likewise, when the f band in uranium is forced to be broader than 7 eV, the high-symmetry bcc structure becomes stable. This is simply a demonstration that narrow bands favor lower-symmetry structures, not that niobium would form in the orthorhombic structure of α-uranium. That particular structure is used only for convenience in the calculations, and we expect that some other low-symmetry structure would be even more stable. Figure 11 also indicates that the true equilibrium bandwidths (W_{eq}) are broad (small volumes) for the transition metals and narrow (larger volumes) for the light actinides.

Lowering the Electronic Energy through a Peierls-like Distortion. In metals, narrow bandwidths (and their high density-of-states functions) lead to low-symmetry structures through a Peierls-like distortion. The original Peierls-distortion model occurs in a one-dimensional lattice: A row of perfectly spaced atoms can lower the total energy by forming pairs (or dimers). The lower periodicity causes the otherwise degenerate electronic-energy levels to split, some becoming lower and others becoming higher in energy. The lowered levels are occupied by electrons, and therefore the distortion increases the bonding and lowers the total energy of the system. In this one-dimensional system, the distortion opens an energy gap at the Fermi level and makes the system an insulator. In the higher dimensional systems, which we will discuss next, the material remains a metal after the distortion because there are other Bloch states that fill this gap.

In real three-dimensional lattices, the energy levels are degenerate along high-symmetry directions. If those levels lie close to E_F, a crystal structure distortion (Peierls-like) would increase the one-electron contribution to bonding, again because the degenerate levels in the band would split, pushing some levels above E_F and others below E_F. This mechanism is very effective if there are many degenerate levels near E_F—that is, if the energy bands are narrow and therefore the density of states is large. Materials with broad bands (wider than 4 eV), gain less energy from level splitting because there are fewer levels near E_F, and therefore symmetry-lowering distortions are rare in these materials.

Stabilizing Wide Bands into High-Symmetry Structures. Besides the one-electron contribution, there is another important contribution to the ground-state energy, namely, the electrostatic Madelung energy. This term is generated because the conduction electrons do not completely shield the ions on the lattice sites. The unshielded positive charge leads to a long-range attractive force on the conduction electrons that lowers their energy. This negative Madelung energy is largest for high-symmetry crystals, opposing the Peierls-like term. So, for the broad s-p[2] and d band metals with few degenerate levels near E_F, the Madelung term dominates the effects of the Peierls-like distortion, and these metals are stabilized in high-symmetry structures. Although the Madelung term stabilizes these high-symmetry structures, remember from our discussion of crystal structures that the one-electron contribution determines which structure (fcc, hcp, or bcc) will be stable. For the light actinides with their narrow 5f bands and a very high density of states near E_F, the Peierls distortion wins out, and these metals form low-symmetry structures. A closer look at Figure 9, for example, shows that six of the eight different atoms in the α-plutonium unit cell have neighboring atoms that fall into near distances on one side and far distances on the other. It is as if one hemisphere around the atom were smaller and the other larger, and it is difficult to imagine how to pack such objects efficiently. But this type of problem is just what one might expect to solve with the three-dimensional version of the Peierls distortion.

Why Are the 5f Bands Narrow? By considering the contribution of each energy band (s, p, d, and f) to the bonding curve of the universal bonding picture, we can understand why the 5f bands are narrow at the ground-state equilibria of the light actinides.

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[2] The broad s and p bands often mix strongly and are therefore referred to as the s-p band.

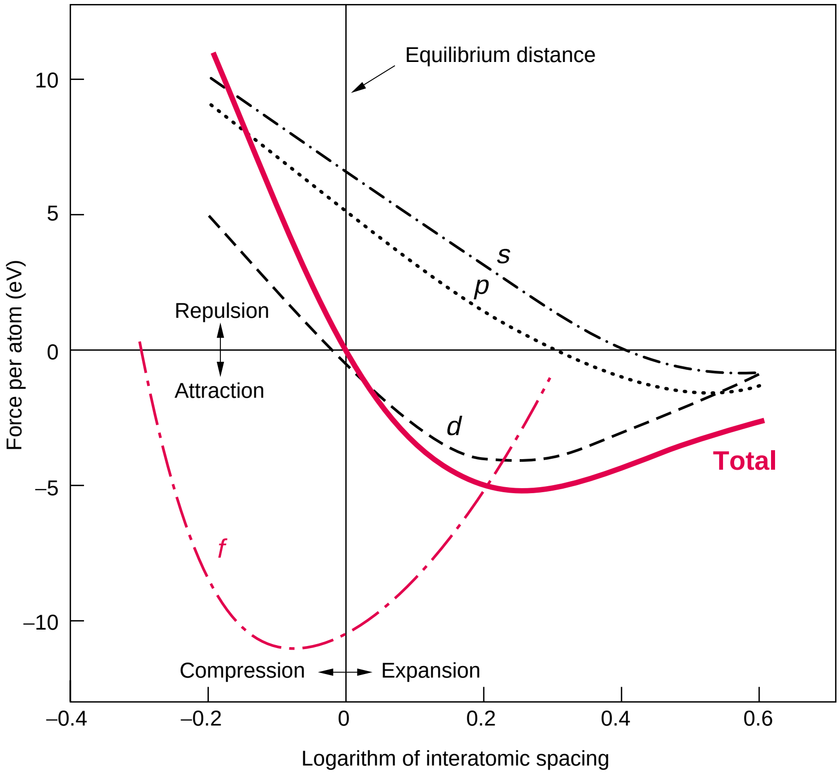

Figure 12. Contributions of Different Electrons to δ-Pu Bonding

LDA predictions for the bonding curves of δ-Pu (fcc structure) are plotted as a function of the interatomic spacing $x = \ln(a/a_0)$. The figure includes the curve for the total cohesive energy per atom, as well as the individual contributions from the s, p, d, and f energy bands. Note that, if the bonding came from the f band alone, the equilibrium lattice constant of Pu would correspond to the value of x at which the f band contribution crosses the horizontal axis; that is, the lattice constant would be well below a_0. At this smaller volume, the f band would be wider, and Pu would stabilize in a high-symmetry crystal structure. In the true equilibrium represented by the vertical line at $x = 0$, the s-p bands contribute a repulsive term and therefore help stabilize Pu at the larger volume. The f band is narrow at that larger volume, and the narrowness leads to the low-symmetry ground-state crystal structure of δ-Pu. It may seem strange that the s-p bands are not bonding at equilibrium, but we must remember that they are also not bonding in d-electron transition metals, which form the bulk of metals in the periodic table.

We used the atomic-sphere approximation to calculate the contributions from individual bands, and for simplicity, we performed those calculations in the fcc phase. Figure 12 shows the results for plutonium. To understand this figure, consider that, if the metal had only one energy band, the lattice constant in the ground state would be given by the point at which the bonding curve for that band crossed the zero pressure line. From Figure 12, you can see that, if plutonium had only an f band contribution, its equilibrium lattice constant would be smaller than it actually is, its f band would be wider, and this metal would stabilize in a high-symmetry crystal structure. In reality, the contribution from the s-p band (a repulsive term at true equilibrium) helps to stabilize plutonium at a larger volume; the f band is narrow at that larger volume, and the narrowness leads to the low-symmetry crystal structure. This argument is universal for multiband metals. In the transition metals, the s-p band is repulsive at equilibrium and leads to slightly larger volumes than would be the case if these metals had only d bands.

We conclude that the width of the dominant band determines the symmetry of the ground state, and one does not need to invoke directional bonding to obtain low-symmetry structures. When Willie Zachariasen and Finley Ellinger first identified the crystal structure of α-plutonium in 1957, they called it a covalent structure, suggestive of directional bonds, but they never repeated that name. (We note that this was one of the most difficult structure identifications ever done because single crystals were not available, the x-ray pattern had many lines, other phases in the samples contributed to the pattern, and the x-ray lines were terribly broadened by strain.) In recent years, John Wills and collaborators (see the article “Actinide Ground-State Properties” on page 128) have been able to calculate the charge density for several actinides using the full-potential DFT method. They find no dominant directional 5f bonds and, most important, no charge buildup between atoms. Instead, the calculated ground-state properties of α-plutonium indicate that this metal is quite average.

We already have hinted, however, that plutonium may not be so average. The strong competition between the repulsive s-p band contribution and the attractive f band term in Figure 12 is the first sign of instability near the ground state. The second sign is the fact that the density-of-states functions for different low-symmetry crystal structures are very similar. Thus, the total energies for different low-symmetry crystal structures are likely to be very close to each other—that is, many states lie close to the ground state.

The Landscape of Actinide Phases

Knowing that the ground states of the light actinides are in a very shallow minimum of energy, we might expect these metals to change phase as they

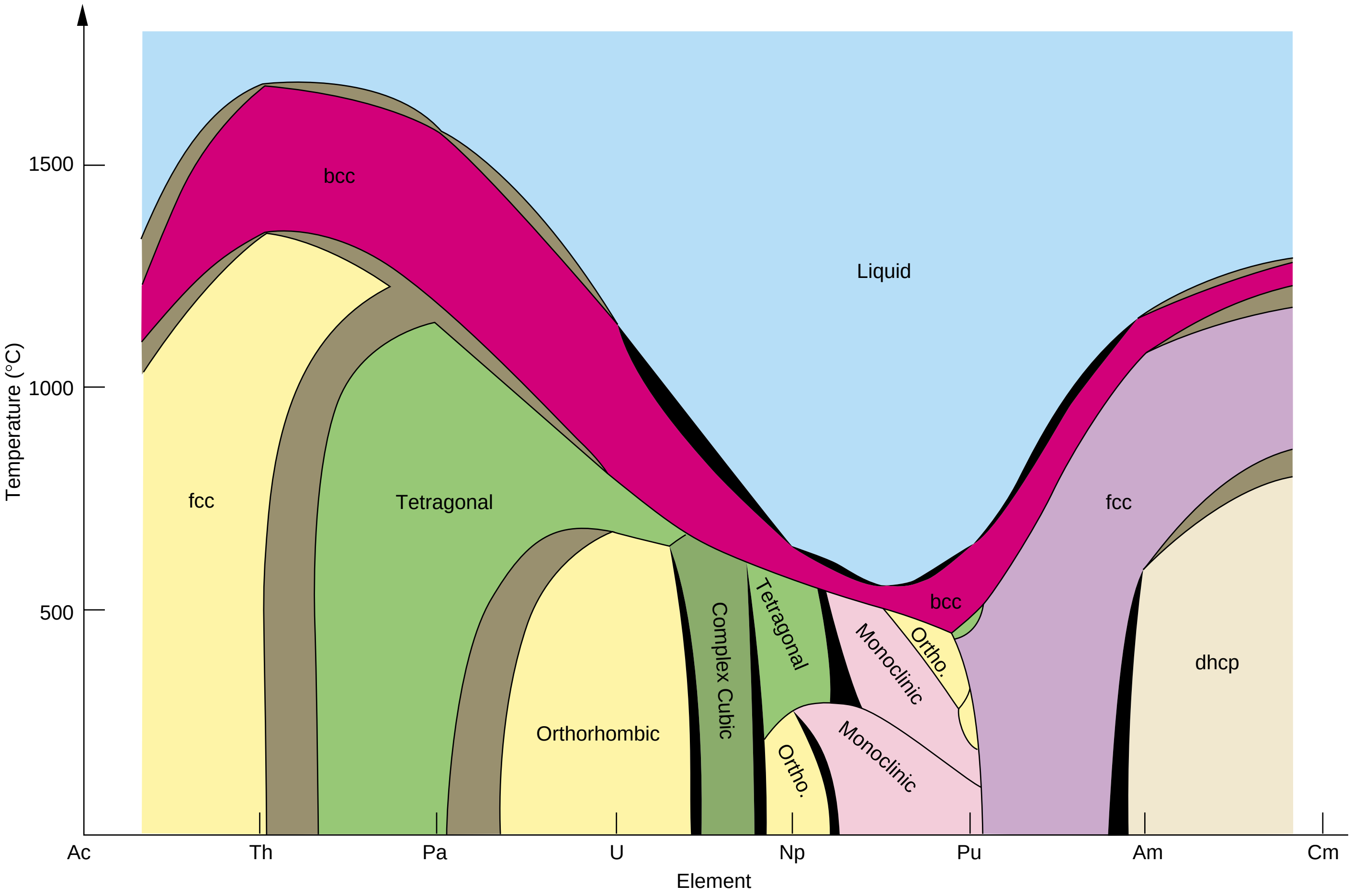

Figure 13. Schematic Phase Diagram of the Light Actinides

This phase diagram connects individual binary alloy diagrams of the light actinide series. The black areas are two-phase regions; the brown are regions where the details are unknown. Whereas the trend in phases is rather ordinary at either end of this series, the phase variation in the middle (at neptunium and plutonium) is very complex (also revealed by the opening illustration to "Atomic Vibrations and Melting in Plutonium" on page 190). In these two elements, the 5f electrons play a major role in bonding because they are so numerous. This widely reproduced and compelling figure shows nature in action, and we have yet to match it with an equally appealing theory.

are perturbed by heating or alloying. An atomic argument leads to the same conclusion. In the actinides, two or three different shells of electrons in an atom are partially filled, producing more states to compete with the lowest-energy ground state. Also, the heavier the atom (or the higher the value for Z), the smaller the energy difference between the last few valence electrons in different shells, and hence the greater the chance for metamorphosis.

A composite phase diagram for the entire actinide series is drawn in Figure 13. This plot was constructed from individual-alloy phase diagrams for the actinide neighboring-element pairs. Each original diagram showed the change in phase as the temperature and the binary composition were varied. In Figure 13, these diagrams have been simplified and drawn side by side. The gray areas represent guesses for unidentified details. The resulting "landscape" of the actinides has been reprinted widely since Smith and Kmetko drew it in 1980 because anything with such a pretty pattern was something the actinide community needed to understand.

Phase Instability and the f-f Interaction. One striking feature of Figure 13 is the large number of allotropes, or solid-state phases. In fact, the actinides have the largest number of allotropes of any series in the periodic table. Note also that most of the allotropes occur at neptunium and plutonium, the elements having the highest number of bonding f electrons. Figure 14, a replotting of the actinide metallic radii in Figure 5 that now includes some of the allotropes, emphasizes the effects of the f electrons on bonding. The f electron bonding begins at thorium, with a fraction of an f electron in the energy bands, and increases all the way to plutonium, which has the highest phase instability. Thus, in the ground-state phases of the early actinides, each additional f electron increases the bonding and decreases the interatomic distance. At americium, the f electrons localize completely and become nonbonding

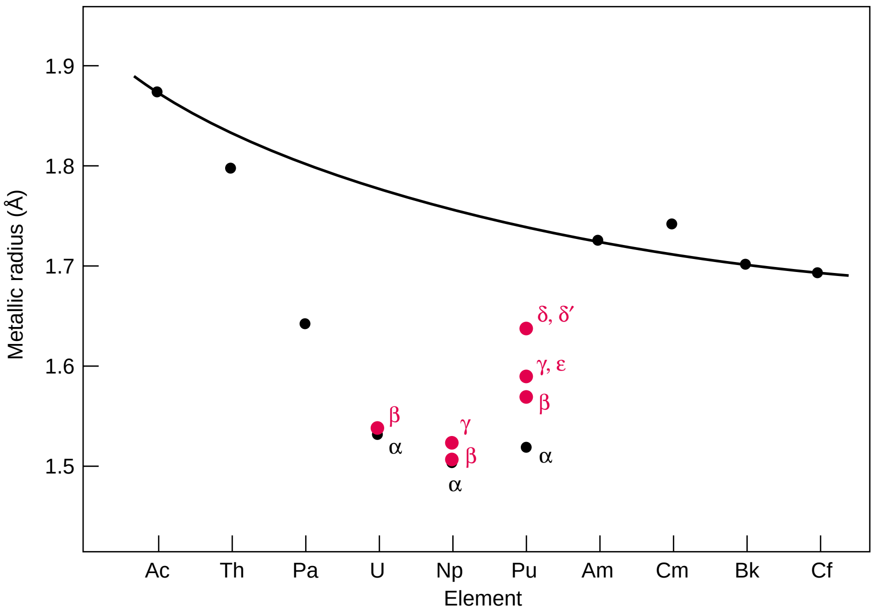

Figure 14. Metallic Radii of Actinide Allotropes

Here, we have replotted Figure 5 to include additional allotropes (red) of the actinides. As in Figure 5, the metallic radius is half the average distance between the atoms in the solid, and the line represents simple trivalent metals with nonbonding f electrons. The points falling below the line show the involvement of the f electrons in the bonding, which pulls the atoms closer together. Notice that the various allotropes of uranium and neptunium have similar metallic radii. In contrast, the radii of the phases from α- to δ-plutonium increase monotonically. The δ-phase still departs from the trivalent line but is much larger than the α-phase, indicating that the f electrons are not completely localized and therefore still contribute to bonding.

because Coulomb forces have at last become strong enough to pull the f electrons inside the valence shell, leaving only the three (or sometimes two) valence electrons in the s-p and d bands to form the glue that holds the atoms together for the rest of the actinides. The metallic radii increase at this crossover to localization, and as shown in Figure 14, the low-temperature phases of the heavier actinides (beginning with americium) form close-packed or bcc structures.

The upper (high-temperature) part of Figure 13 shows the liquid phase, and the melting curve separating the liquid from the solid state goes through a minimum between neptunium and plutonium, at which point the crystal structures are least stable. In its broadest features, the pattern shows the light actinides forming low-symmetry ground states but melting out of high-symmetry structures as the heavy actinides and most other metals do. This observation is striking, but the really difficult aspect to explain is that the transition from low symmetry to high symmetry occurs over an extremely small temperature range, small enough that the f band remains narrow. What property of narrow bands (or, specifically, narrow f bands) enables them to stabilize high-symmetry structures at modest temperatures?

We know from standard Wigner-Seitz rules that, for electrons in narrow bands, the radial portion of the electronic wave function measured from a given lattice site must change rapidly as a function of energy. These rules also tell us that the electrons in the upper half of a band are less bonding, so we can use the molecular concept of bonding and antibonding orbitals to understand the Bloch states of solids.[3] Also, the electronic wave functions of atoms on different lattice sites overlap less for narrow bands than for wide bands. Cerium, the only 4f metal with a narrow f band, is a good example. The f-electron wave functions overlap only the nearest-neighbor sites, whereas the s-p and d wave functions, which are associated with wide bands, overlap sites that are far from a given site. In other words, narrow f bands imply a short-range, rapidly changing interaction among the f electrons. This means less overlap between f electrons on different sites and also weaker hybridization of electrons in f orbitals with electrons in s, p, and d orbitals.

The many phase transformations in the center of the actinide landscape suggest that the f-f interaction varies dramatically with very small changes in the interatomic distances, such as those produced by lattice vibrations or heating. Also, electron-phonon coupling appears to be very strong in these narrow bands. We would even suggest that the variation with temperature in the f-f interaction (and f-spd interactions) might cause some of the f orbitals to become localized as plutonium transforms from the α- to the δ-phase. The situation is complicated by several different interatomic distances in the low-symmetry structures of the light actinides (see the crystal structure of plutonium in Figure 9). Unlike the phase transformations in the transition metals, which follow simple, well-understood routes, such as the Bain path (fcc↔bcc) or the fcc↔hcp path, the individual transformations in plutonium (say, α↔β or β↔γ) are difficult to characterize. And the whole path from the α- to the δ-phase is even more difficult to characterize. We need more detailed analysis and many more calculations to work out the details of these phase transformations. But we do know

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[3] According to the Wigner-Seitz rules, the radial part of the wave function at the top of the band is zero at the Wigner-Seitz radius (a radius that is roughly half the interatomic distance). At the bottom of the band, the derivative of that radial part is zero at that same radius.

that the short-range nature of the f-f interaction in the light actinides and the partial transition from bonding (itinerancy) to localization (rather than directional bonding) are key ingredients for a better understanding of plutonium.

The Role of Entropy in Phase Stability. To understand fully the stability of these different phases as a function of temperature, we must go beyond the one-electron methods. Remember that those methods determine only the internal energies of solids (they describe the system at $T = 0$), whereas phase stability depends on the free energy, which is the internal energy plus the entropy of the system. So far, theorists have not been able to calculate the free energy from first principles. Nevertheless, we can make some general comments about the role of entropy.

For the low-symmetry structures of the light actinides, which have similar density-of-states functions and therefore similar internal energies, the internal-energy path between different low-symmetry phases is very shallow. That is, the lower-energy phase sits in a relatively flat potential well connecting it to the higher-energy phase. For that reason, it often has very soft (low-frequency) vibrational modes in its phonon spectrum. Low-frequency modes imply large numbers of phonons per mode and therefore lots of entropy. For example, entropy is a driver in the first three solid-to-solid phase transformations in plutonium (α to β, β to γ, and γ to δ), in which low-symmetry structures are involved. (A recent measurement on phonons in uranium gave the entropies for uranium. See the article “Vibrational Softening in α-Uranium” on page 202).

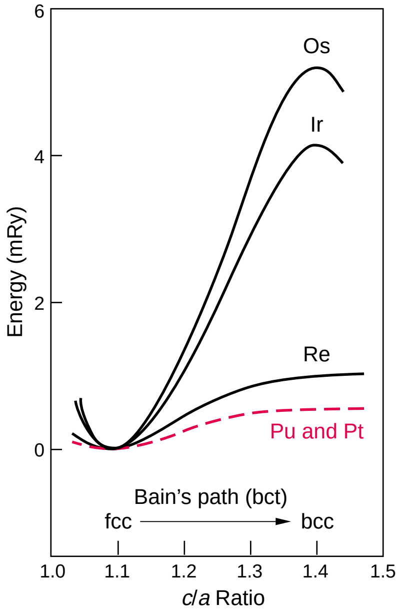


Figure 15. The Bain Paths for Typical Transition Metals and for the δ- to ε-Plutonium Transformation
We performed these calculations by varying the *c/a* ratio in the bct structure to go from the fcc to the bcc phase. The calculated internal energy as a function of the *c/a* ratio yields the path the solid must follow to get from the fcc to the bcc phase. As shown, the Bain’s paths for typical transition metals (5d), such as osmium and iridium, are steep. The platinum path is very shallow, and we use it as our model for the plutonium path (red dotted lines). The shallow well in the fcc phase for platinum and plutonium leads to soft modes and large entropy. The observation that plutonium goes through the δ′-phase (bct) in going from δ- to ε-phase implies that the Bain’s path for plutonium is flat enough to make the δ′-phase metastable at least at some value of *c/a*.

The δ- to ε-phase transformation in plutonium is between two high-symmetry structures, following the standard Bain’s path (fcc↔bcc) seen in most transition metals. Typically, the internal-energy path between cubic structures is not shallow. However, experimental data indicate that this path is shallow in plutonium. In Figure 15, we show the Bain’s path for a few typical transition metals and the postulated path for the δ- to ε-phase in plutonium. When the internal-energy path between phases is shallow and the entropy is large, the range of stability of a phase can be small. And that is exactly what is seen in the δ- to ε-phase transformation. The δ-phase remains stable for only 160°C, whereas in a typical transition metal, the fcc phase remains stable for around 1000°C before becoming bcc. (See the article “Elasticity, Entropy, and the Phase Stability of Plutonium” on page 208 for a discussion of how to estimate the vibrational entropy through measurements of elastic constants.)

The actinides are not unique in having shallow internal-energy paths between them. The same is true of some transition metals (see Figure 15) and even simple metals such as lithium. In all these metals, entropy plays a big a role. We emphasize, however, that in all the actinides, and particularly in plutonium, the initial instabilities (leading to high entropy and frequent phase changes) are due to the role of the f electrons and the existence of many internal-energy states whose energy values are very close.

Low Melting Temperatures and Electron-Phonon Coupling. The last remarkable feature of Figure 13 that we will comment on is the pronounced dip in the melting curve at neptunium and plutonium. We suggest that two effects may lead to this reduction in melting temperature: the strong electron-phonon coupling in narrow-band materials (which in a one-electron theory would be seen as the large variation of the f-f interaction with temperature) and the instability of the phases due to the large entropy term. Strong electron-phonon coupling implies that small temperature changes lead to larger-than-usual electronic changes. As a result, the effective temperature is larger than the actual one, and therefore the material melts at a relatively low temperature. Evidence for strong electron-phonon coupling is seen in the strong temperature dependence of the elastic constants of gallium-stabilized δ-plutonium deduced from neutron diffraction measurements (see the article “Atomic Vibrations and Melting in Plutonium” on page 190). Strong electron-phonon coupling is also implied by the high resistivity of pure plutonium just below room temperature.

The large entropies (soft vibrational modes) in these materials also imply that relatively small temperature changes produce relatively large changes in free energy. As a result, the average temperature change between phases in plutonium is 85°C, whereas in typical transition metals, it is around 1000°C. In other words, a free-energy change large enough to cause melting requires only a small temperature change—that is, the melting temperature is relatively low. These general insights notwithstanding, Migliori is right to emphasize that much more work is needed to quantify the vibrational energy and entropy contributions to the free energy and phase stability. We now return to the problem of how electronic structure affects the phase stability of plutonium, especially its δ-phase.

Delta Plutonium, f Electron Localization, and Plutonium Metallurgy

Delta-phase plutonium is of special interest because its fcc structure allows plutonium to be formed into shapes as easily as aluminum. Used in building nuclear weapons, this phase is most important to understand from first principles. Ironically, although electronic-structure calculations of plutonium have improved, the δ-phase has been the toughest one to get right in spite of its simple cubic structure because its f electron behavior does not fit the usual categories. The plot of metallic radii in Figure 14 indicates the dramatic increase in the metallic radius (decrease in density) of the δ-phase, suggesting that f electron bonding decreases markedly from the α- to the δ-phase. On the other hand, f electron localization is not complete because the interatomic distance for δ-plutonium is still below the trivalent line defined by actinium and the heavier actinides, whose f electrons are fully localized. (The side a_0 of the cube of the unit cell is 4.637 angstroms in δ-plutonium and 4.894 angstroms in cubic americium.) Thus, the f electrons in δ-plutonium are in limbo between localization and itinerancy, a state that has yet to be modeled in any convincing way. Plutonium can easily change its crystal structure and density in response to its surroundings, and the δ-phase is the most sensitive.

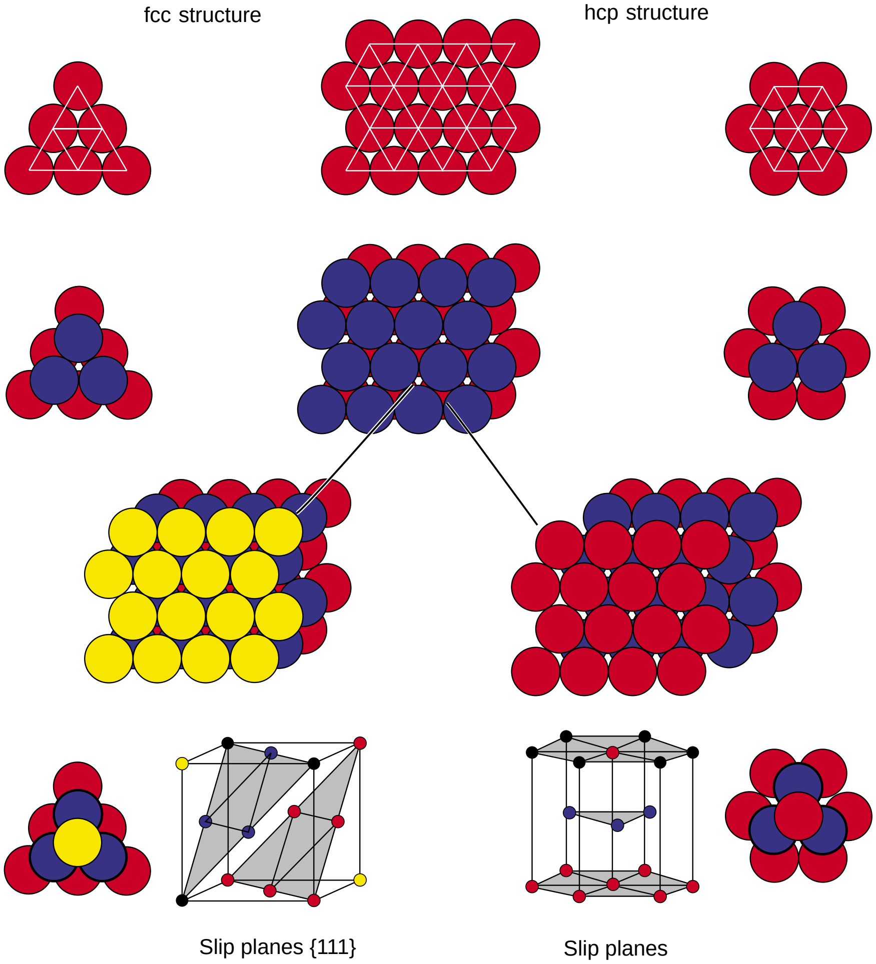
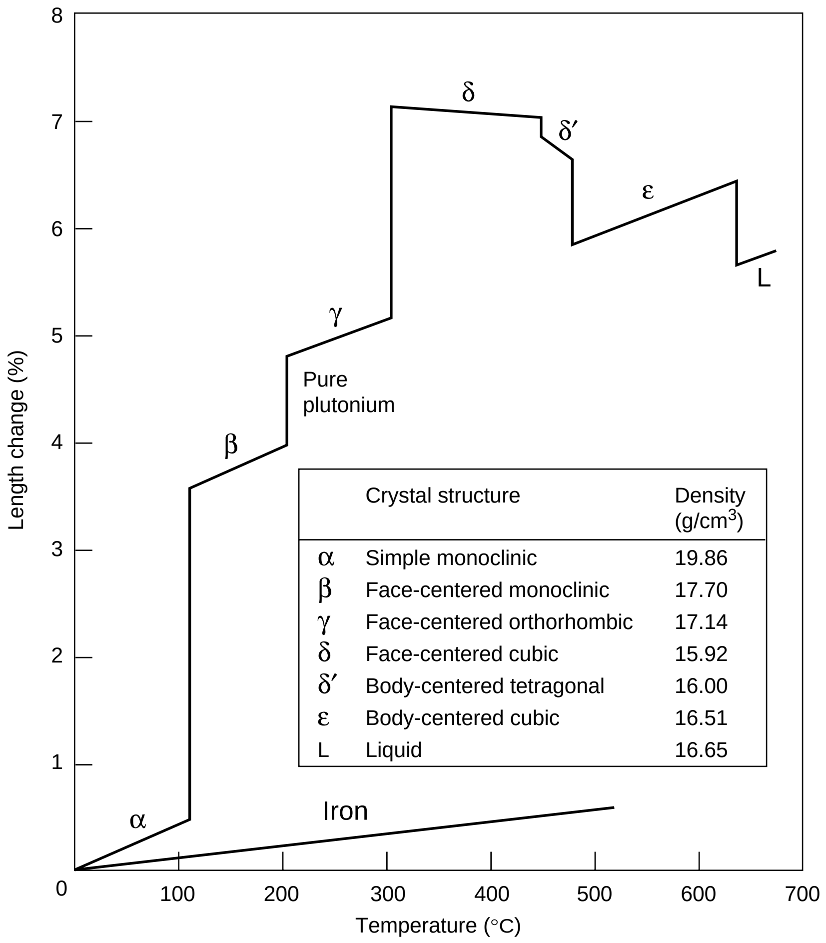


Figure 16. Stacking Close-Packed Crystal Structures

The red and blue layers of the fcc and hcp crystal structures are stacked identically. In the fcc structure, the third layer (yellow) is in a new position; in the hcp structure, it is perfectly aligned with the first layer (both are red). The ability of one plane to slide (slip) over another leads to the ductility of fcc metals. It takes a bit of practice to visualize the close-packed planes (shaded) within the fcc unit cell. The many slip systems in fcc metals are discussed in the box "Atomic Packing and Slip Systems in Metals" on page 308.

The only other transformation that comes close to producing the 26 percent volume expansion seen in the transformation from α- to δ-plutonium is the isostructural expansion from the fcc α-phase to the fcc γ-phase of cerium. This transition produces a 20 percent volume expansion. Before f bands were known to exist, the reverse transition in cerium—the collapse from the fcc γ-phase to the denser fcc α-phase near room temperature and under pressure—was attributed to a change of an f electron (localized) to a d electron (itinerant), which would explain the volume change and the magnetic properties. However, accumulating data showed no change in the number of f electrons through the change in volume. In 1974, Börje Johansson suggested that the collapse in cerium involved a Mott transition. Mott had described how the localization of conducting electrons turned conductors into insulators, and delocalization did the reverse. Johansson saw that cerium's fcc isostructural expansion involved localization and its collapse involved delocalization just as in the Mott metal-insulator transition, but for cerium, only the f electrons were involved. The s-p and d electrons remain conducting in both fcc phases, and thus this Mott-like transformation is between two metallic phases of cerium. Many theorists believe that a similar localization mechanism is probably responsible for the series of phase transitions from α- to δ-plutonium, except that the net result falls short of the more complete transformation to localization seen in the transformation from α- to γ-cerium because five, instead of one, f electrons are involved (see the article "A Possible Model for δ-Plutonium" on page 154).



	Crystal structure	Density (g/cm^3)
α	Simple monoclinic	19.86
β	Face-centered monoclinic	17.70
γ	Face-centered orthorhombic	17.14
δ	Face-centered cubic	15.92
δ′	Body-centered tetragonal	16.00
ε	Body-centered cubic	16.51
L	Liquid	16.65

Figure 17. Thermal Expansion of Plutonium

The percentages by which the lengths of plutonium and iron have changed are shown as a function of temperature for 0°C to 660°C. Abrupt changes in the curve for plutonium denote phase transitions, and each of the smooth segments is in the labeled structures. The crystal structures and densities of each phase are also listed. Note that plutonium's thermal expansion is very large, the material goes through six solid-state phases before melting, the δ-phase contracts as it is heated, and plutonium contracts as it melts. These features are in stark contrast to the small linear expansion of iron and most metals.

Despite its weird electronic state, δ-plutonium signals the return of the actinides to the typical metallic close-packed crystal structures. That is, it forms the tip of the "iceberg" of the fcc phases at the right in Figure 13. The fcc structure is what makes metals such as copper, aluminum, stainless steel, and δ-plutonium very useful. It is a high-symmetry, close-packed structure that one can easily construct by stacking marbles, as in Figure 16. The first layer of marbles (red) forms hexagons made of triangles. The second layer (blue) falls naturally into a set of first-layer depressions. The marbles in the third layer can be either directly above those in the first layer (red) or in a third set of positions not found in the layers below (yellow). The hcp structure is formed if the third layer is on top of the first one; the fcc structure, if the third layer is in the third position. Notice that, in all cases, it would be fairly easy to slide one layer across the next one because the marbles do not have to move up and down too much in order to land into the next set of holes. Sliding them across some other plane would not work as well because there are fewer atoms in all other nonequivalent planes and the wells are deeper. It is precisely because one plane can easily slide across the next one that fcc metals are ductile and therefore easy to shape.

Ductility, a remarkable feature of metals, is not necessarily long lasting. As a plane of atoms slides, some of the atoms may not move uniformly. And as more and more planes "misslide" in this way, the misfits accumulate, and the metal gets stronger—that is, it takes greater force to deform it or to make it fail. This process is called work hardening. Alpha plutonium is an example of a naturally brittle and strong material. From the α-plutonium structure shown in Figure 9, it is easy to see that sliding planes across each other in any direction would be extremely difficult because the atoms would no longer fit. In contrast, the planes of δ-plutonium slide very easily, like those of aluminum.

On the other hand, new single crystals of very pure α-uranium were shown to bend easily when squeezed by hand. Single crystals are expected to be easier to bend because there are no grain boundaries and dislocations to pin the sliding. However, these uranium crystals seem softer than expected. We do know that uranium deforms by making twins, which are structures that look like mirror images of each other separated by planar boundaries. In general, low-symmetry structures have more planes across which twins can form, and this may mean that, if we had single crystals of very pure α-plutonium, they would be far softer than any crystals we have ever seen. For a more complete description of these metallurgical properties, see the article "Plutonium and Its Alloys" on page 290.

Unfortunately, δ-plutonium is not very stable. It takes only about 1 kilobar of pressure to transform δ-plutonium into a lower-symmetry phase such as α-plutonium. A fascinating reversal of this transformation was seen during the fracture of α-plutonium and is described in "Plutonium and Its Alloys." The surface of fractured typical-purity α-plutonium appears jagged and broken, as would be expected for a brittle monoclinic metal. However, under a scanning electron microscope, the surface looks covered by ductile dimples, like a peanut butter sandwich that has been pulled apart. Such dimples are never seen in brittle materials because the plastic flow needed to make them does not occur. So, where did the dimples come from? Although the following explanation has not been proved so far, it is believed that a region of hydrostatic expansion preceding the tip of the crack is created during the fracture of α-plutonium. The expansion, or effective negative pressure, in this region instantaneously transforms the α- into the δ-phase. After the fracture has propagated through the region, the material relaxes and returns to the α-phase. These fracture results show that plutonium easily moves back and forth from the α- to the δ-phase and that spreading out the atoms (during hydrostatic expansion) stabilizes the fcc phase, as one would guess. Yet, this quick transformation to the δ-phase increases the volume by 26 percent.

Plutonium in the Liquid State

Plutonium must be happier (have lower energy) in the liquid because it has a higher density than the phase from which it melts. It seems likely that plutonium forms clusters in the liquid (as water does) because it has the highest viscosity of any molten metal and because it forms complexes, as discussed in the article "The Complex Chemistry of Plutonium" on page 364. We note that the bcc crystal structure has its second-nearest neighbor atoms almost as close as the closest neighbor atoms and has little shear strength; that is, it is the most liquidlike crystal structure and the highest-temperature solid phase for most metals. That is why bcc sodium cuts with a butter knife. Because water and plutonium are both good solvents, it may be fair to draw a comparison between the polar molecules of water and the atomic misfits of plutonium. To find the nature of liquid plutonium, we therefore need to use neutrons or some other probe. We remind the reader that, if plutonium were not such a good solvent, we would have more usable containers in which to put it while we make measurements at high temperatures.

Figure 17 shows the complex pattern of length changes produced by heating plutonium metal. Plutonium goes through six solid phases before it reaches its melting point, with the δ-phase having the lowest density (and the most-localized f electrons) of all the phases including the liquid state. These changes in volume are not only challenging for physicists to explain but also extremely troublesome to metallurgists. For example, when castings are made from plutonium in the liquid state, the metal expands as it solidifies (see the box "Plutonium in the Liquid State") and thus helps fill a mold. During subsequent cooling, however, the many changes in volume lead to the formation of voids, which reduce the structural integrity of cast plutonium.

Another surprising feature is that δ-plutonium contracts when heated, as revealed in Figure 17. Remember that thermal expansion is an anharmonic effect and therefore not predicted by the usual harmonic models of a solid. In harmonic models, a solid is described as a set of masses held together by springs. That is, the potential energy as a function of distance between neighboring atoms is a parabola, and the forces are linear in the displacement from equilibrium, as they are for springs. In these models, the coefficient of thermal expansion is always zero, and this is true for all even powers of the potential energy as a function of interatomic spacing.

So, the common belief that atoms vibrate more at higher temperatures and therefore take up more room is not correct. Instead, when atomic excursions become large enough to run into the "hard core" of the filled-shell electrons of the neighboring ions, the interatomic potential becomes steeper than a parabola, and this anharmonicity, or increase in pressure, leads to an expansion in volume with increasing temperature. Conversely, a potential that increases more slowly than a parabola (including higher even powers) at large atomic excursions yields a contraction in volume with increasing temperature and reflects a change in electronic structure. We will return to this topic when we discuss magnetism. For the moment, we can say that a negative thermal-expansion coefficient may be due to a conversion of magnetic into bonding energy as in Invar (see the box "Itinerant Magnetism, Invar, and δ-Plutonium" on page 120).

New Models for Delta Plutonium

As yet, there has been no established model for the unusual features of the fcc δ-phase. Here, we suggest that both the unusual thermal properties and

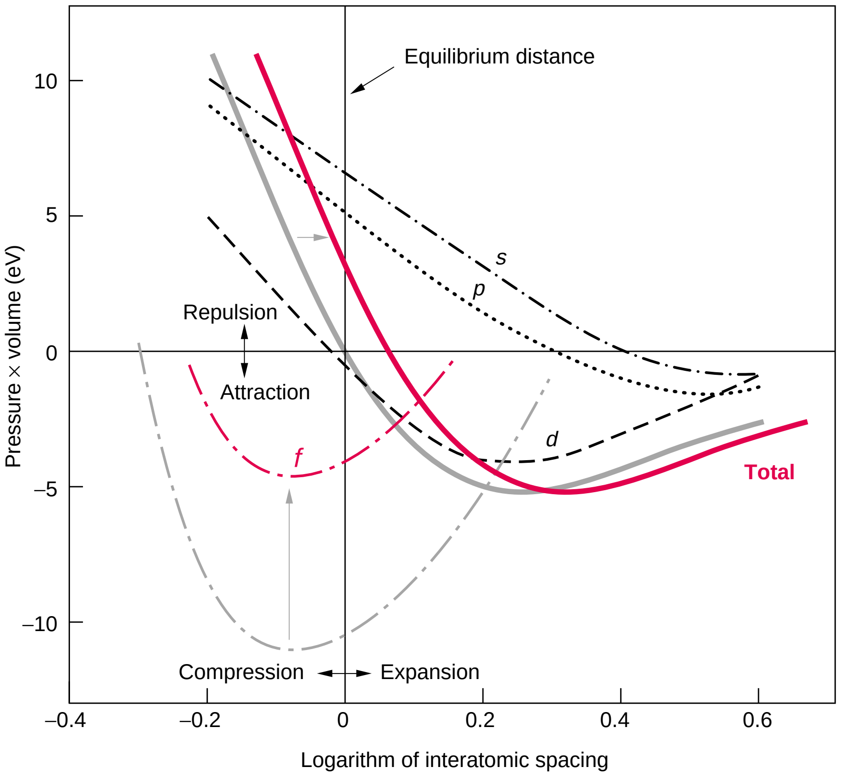


Figure 18. Modified Bonding in Plutonium with Fewer 5f Bonding Electrons

In this figure, we show how the bonding would change if only one 5f electron is in the conduction band instead of the usual five, and the other four are localized at lattice sites. We illustrate the effect of this localization by artificially reducing the f band contribution to bonding by roughly 80% relative to the results plotted in Figure 12. In this case, the s-p repulsion term is not balanced by the f bonding term, and the lattice must expand to reach a new equilibrium.

the absence of measured magnetism in δ-plutonium may be related to the delicate balance of forces between the repulsive s-p bands and the attractive f band (and the sensitivity of the f-f interactions) shown in Figure 12. First principles ground-state calculations have shown that all five 5f electrons are bonding in the α-phase. Because it has never been demonstrated that plutonium has less than five 5f electrons in its atoms, molecules, and solids, we must assume that the δ-phase also has five.

In the δ-phase, some or all of these electrons may be localized, a fact consistent with Figure 12. Localization would reduce the contribution of the five 5f electrons to pressure, and the lattice would expand. If their number were reduced from five to, say, one, then the three electrons in the spd broad bands would become more important in determining the crystal structure (see Figure 18). And because broad bands favor cubic structures, the δ-phase is a reasonable outcome of localization. The real problem, however, is to determine a mechanism for such localization in the f shell.

Wills and Eriksson (see the article “Actinide Ground-State Properties” on page 128) have used one-electron calculations to show that localizing four of the five 5f electrons leads to a correct prediction of the δ-phase volume. Through a separate atomic calculation, they show that the energy gain from localizing those four electrons yields the lowest-energy state at the δ-phase volume. However, those calculations provide no mechanism for the localization.

In “A Possible Model for δ-Plutonium” (page 154), Cooper presents the self-induced Anderson localization model, a two-electron impurity-like model. According to this model, all the 5f electrons on some plutonium sites become localized. The strong scattering from these “impurity sites” can disrupt the coherence of the 5f band states and drive the whole system toward localized 5f states. The Anderson Hamiltonian, as used by Cooper, has both the Hubbard repulsive Coulomb term and a Kondo-like two-electron term (originally invented to treat the spin-spin interaction between an electron on an impurity atom and a conduction electron). The Hubbard term keeps the 5f electrons localized, and the two-electron term leads to a partial localization of the conduction electrons. This model has therefore all the right ingredients for yielding localization in going from the α- to the δ-phase, but it may take years before it could be used for realistic calculations. Moreover, to start the calculation, one must have some impurity sites. In effect, this prerequisite helps avoid the question of how the five 5f electrons become localized.

Can we obtain a translationally invariant solution for fcc plutonium in which the five 5f electrons are localized by starting from a calculable Hamiltonian? The usual one-electron calculation (translationally invariant) at the δ-phase density predicts itinerant 5f electrons. So, we must modify the Hamiltonian to predict localization. In the Anderson model, the Hubbard term prevents the f electrons on other sites from hopping onto a given site. This is the impurity view, but as we have pointed out, it is almost impossible to obtain translationally invariant solutions from impurity models. Instead, let us find out what will keep the 5f electrons from leaving a site. Clearly, we need to add an attractive Coulomb term. We therefore propose a model with a small attractive Coulomb term added (in the f states only) to the band Hamiltonian in a one-electron calculation. Such a calculation would have to be performed self-consistently so that the hybridization of the f states with the non-f states could change in value as the 5f electrons become more localized. We believe such a calculation is feasible within the standard codes of electronic-structure calculations. Having such a solution, we could then apply the two-electron model to obtain the dynamics of partial localization.

A feasible approach closer to the impurity models would be an electronic-structure calculation of an alloy, in which there are two plutonium sites: One has an added attractive Coulomb term, and the other does not. Such a self-consistent calculation would demonstrate whether random sites with localized f states could drive all the f states to localization on all sites. The physical basis for an attractive term may be the poor screening of the nuclear charge by the 5f states, as it is by the 4f states in the case of the lanthanide contraction. As we are looking at new models for the δ-phase, we must also consider the alloy-stabilized δ-phase.

Gallium-Stabilized δ-Plutonium. Although no one understands the electronic structure of δ-plutonium, people in the nuclear weapons program work with this phase all the time. In fact, the secret to stabilizing this phase down to room temperature dates back to the Manhattan Project. At room temperature, pure plutonium would be in the very brittle α-phase, but as luck would have it, one of the very first "high-purity" samples made by Manhattan Project workers had enough impurities to become ductile. Those pioneers knew therefore from the start that they could deform the new metal into a required shape. They soon figured out that it was the addition of a few percent of a trivalent metal at high temperature that held plutonium in the δ-phase down to room temperature.

But why should the addition of those small atoms stabilize a phase with a dramatically low density and the desired malleability? The answer is not known yet, so we can only make suggestions. The impurity picture suggests that atoms at random lattice sites create strong scattering, thereby blurring the periodicity of the lattice and killing the coherence of band states. Applying this mechanism to plutonium, we would say that the addition of impurity atoms containing no f electrons would destroy the coherence of the f band. Without its narrow f band, plutonium could no longer lower its energy by lowering its symmetry through a Peierls-like distortion into the α-phase; it would therefore remain in the δ-phase. Another view is that plutonium atoms relax and move toward the smaller non-f atoms, thereby reducing the f-f interactions that stabilize the α-phase. So, the solid remains stable in the high-symmetry fcc phase even as the temperature is lowered. In this cubic structure, only 3 atomic percent aluminum or gallium dissolved in plutonium (the replacement of one plutonium atom by a gallium atom in every three-atom-sided cube) is enough to hold the fcc structure down to room temperature. Roughly, any atoms that are soluble in pure δ-plutonium at its elevated temperatures and that have no f electrons should stabilize the δ-phase to lower temperatures. (Like plutonium, cerium and americium have f electrons, but they also stabilize the δ-plutonium. Understanding how their more-localized f electrons interact with the itinerant f electrons in plutonium, however, is best left to band or alloy calculations that can include some of these effects.)

Our discussion of the plutonium δ-phase and other phases highlights the complexity of the 5f bonding in plutonium and its impact on metallurgical properties. We believe that improved one-electron methods, along with new measurements conducted with modern techniques, will clarify our understanding of bonding in all plutonium phases. One might also have to go beyond the average electron correlations inherent in one-electron methods to include specific spin interactions and specific interactions between more-localized and less-localized electrons, as in the two-electron dynamics described in the article by Cooper.

We now leave the topic of phase instabilities, the least understood aspect of the light actinides, and turn to the low-temperature properties of the light actinides. Recently, these properties have been recognized as similar to the low-temperature properties of other correlated-electron materials.

A Revised View of the Periodic Table

Plutonium is not alone in having its electrons precariously balanced between bonding and localized states although it exhibits this property better than any other element. If the periodic table is arranged to show only the d and f electron series, and the f series are put on top and squeezed together to fit as in Figure 19, then the elements highlighted by the white diagonal stripe are the rough dividing line between localized (local moment magnetism) and itinerant (superconductivity) long-range collective behavior. This is a good indication that the f and d electrons of the diagonal elements may be balanced between being localized and itinerant, and their behavior is therefore interesting. We will discuss the "normal metals" off the diagonal before we consider the diagonal elements.

Normal Behavior off the Diagonal: Magnetism vs Superconductivity. Figure 19 indicates that the f and d electron metals away from the diagonal divide neatly into two categories. In one category, the f and d electrons are itinerant and fully bonding, and they tend to form a superconducting ground state at very low temperatures. In the other category, the f and d electrons are fully localized, usually forming local magnetic moments and ordering into a magnetic ground state at some temperature.

This association of localized electrons with local magnetic moments and of shared electrons with bonding is familiar to chemists. When chemists make a new insulator or organic compound containing an f or d electron atom, they can

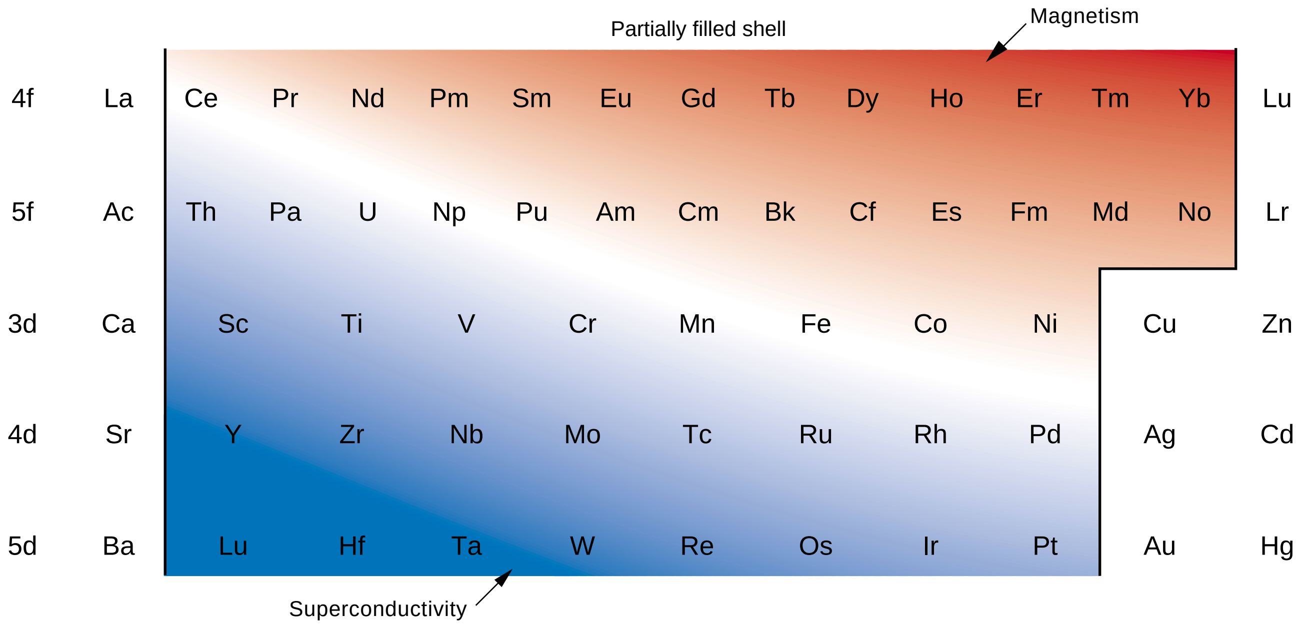


Figure 19. A Revised Periodic Table of the f and d Series

The periodic table is rearranged with the rare-earth, or lanthanide, elements in the top row, the actinides in the second row, and the d-electron transition elements below them. Most metals have predictable ground states and become superconducting (blue) or magnetic (red) as the temperature is lowered. But the low-temperature metallic properties of the elements along the diagonal are difficult to explain because, in the solid-state, their f or d valence electrons are poised between localization and itinerancy.

deduce the valence state of that atom by measuring the magnetic moment of the compound. The measured value tells them the number of electrons contributing to the moment and therefore the number of electrons localized on the atom. The remaining f or d electrons are participating in bonding, and their count gives the valence. Usually, metals are not so simple, but it is useful to think of electrons as magnetic or bonding.

So, how do we know if there are local magnetic moments in a material? Magnetic susceptibility χ measures the internal response of a material to an applied magnetic field. That is, $M = \chi B$, where M is the magnetization of the material and B is the magnetic field intensity. In 1845, Michael Faraday showed that some materials were drawn to the high-field region of his magnet and others were repelled. He called the former behavior paramagnetic with a positive susceptibility and the latter diamagnetic with a negative susceptibility. Most common metals have no magnetic moments and are weakly paramagnetic or diamagnetic. As shown in Figure 20, these nonmagnetic metals have low susceptibilities, which are roughly temperature independent. Magnetic materials have positive, much larger susceptibilities, and because thermal motion counters the tendency for moments to align with the applied field, this positive susceptibility is inversely proportional to temperature, as shown in Figure 21. We can extract the size of the magnetic moment in a magnetic material from the slope of χ vs T.

In the solid state of metals or insulators, local moments at lattice sites tend to line up at some temperature as the material is cooled, producing a state of long-range order called magnetism. (Following Hund's rules, the local magnetic moments at each lattice site are proportional to a vector sum of the total spin and total orbital angular momentum of the localized electrons.) In particular, each magnetic material has a critical temperature, at which the free energy of the system is lowered through an alignment of the local moments. If the moments line up parallel to each other, forming a ferromagnetic state, the transition temperature is called the Curie point T_C. If the moments line up antiparallel, forming an antiferromagnetic state, the temperature is called the Néel temperature T_N. Magnetic transition temperatures range from close to absolute zero to about 1000 kelvins, and a ferromagnetic material whose T_C is above room temperature is called a permanent magnet. Figure 21, a generic plot of the inverse susceptibility vs temperature, shows how the temperature intercept can indicate whether a material will be a ferromagnet or an antiferromagnet at lower temperatures. If the intercept is at a positive temperature, the material should be ferromagnetic, and if it is at a negative temperature, antiferromagnetic.

Local moments in one of these magnetic ground states in a metal are arranged following the symmetry of the lattice, and they do not scatter the conduction electrons well. As a crystal is heated above T_C or T_N, the magnetic ordering disappears, the local moments point in random directions, and those

Figure 20. Magnetic Susceptibility of Plutonium and Other Materials

The susceptibility of most metals is close to zero on this plot, but that of UBe_{13} is very large as though this heavy-fermion compound had local moments. It was therefore conjectured that UBe_{13} would become an antiferromagnet at low temperatures. Instead, however, UBe_{13} becomes a superconductor at low temperatures, and the reason for its high susceptibility is not well understood. The susceptibilities of plutonium's various phases are also higher than those of most metals, but they are lower than those of materials with local moments. The blowup of the plutonium curve (see inset) displays more clearly the variation in susceptibility as plutonium changes phase. Although essentially temperature independent, the susceptibility of plutonium appears to increase slightly as the temperature decreases. It is fair to say that plutonium behaves as if it were almost magnetic.

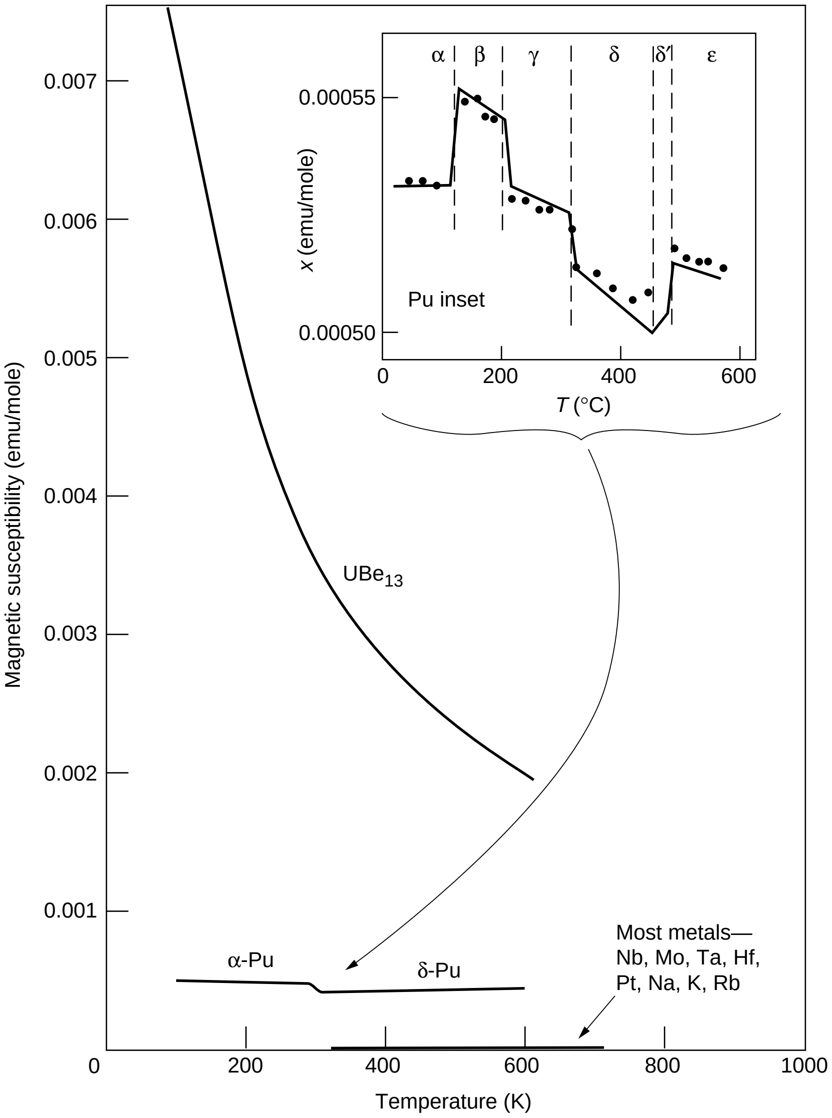
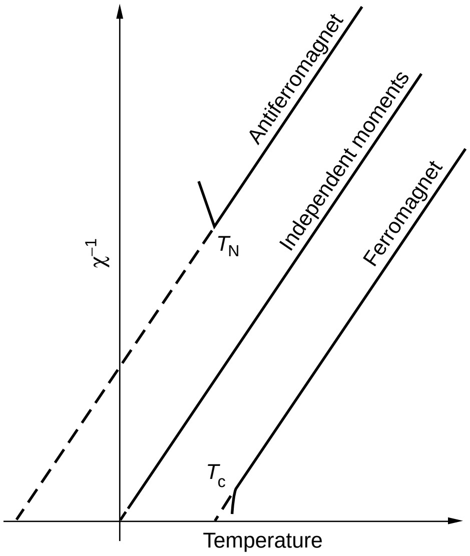


Figure 21. Curie-Weiss Plots of Inverse Magnetic Susceptibility

The magnetic susceptibility due to local moments follows the Curie-Weiss law: It is inversely proportional to temperature because thermal motion tends to wash out the natural alignment of local moments as temperature increases. The inverse susceptibility is plotted for several cases. If there is no interaction among local moments, the inverse susceptibility extrapolates to zero at $T = 0$. If there is a ferromagnetic interaction among the local moments, it extrapolates to zero at a positive temperature intercept, and if there is an antiferromagnetic interaction, it extrapolates to a negative intercept. The absolute value of the intercept tends to correlate with the magnetic ordering temperatures.



moments can now scatter the conduction electrons. The scattering occurs through a magnetic interaction that can flip the spins of the conduction electrons. We shall see that plutonium scatters the conduction electrons very well although it does not have local moments.

Superconductivity is a state of truly perfect conductivity that can exist in an electrical conductor at low temperatures. In general, materials with magnetic moments do not become superconductors at low temperatures because magnetism in any form is inimical to superconductivity. The typical superconducting state forms at temperatures of a few kelvins and consists of pairs of conduction electrons with opposite spins and momenta that are bound together through their interaction with the crystal lattice. These pairs act like a Bose condensate and travel through the lattice with no resistance whatsoever. This low-energy collective state was explained in the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity (1957). However, if a material has ordered moments, a net magnetization, or spins from random impurities, the magnetic field resulting from any of these sources would tend to flip one of the two opposing spins in the pair and prevent the pairs from forming. Thus, elements with localized d or f electrons typically have magnetic ground states, and those with conducting d or f electrons typically have superconducting ground states.

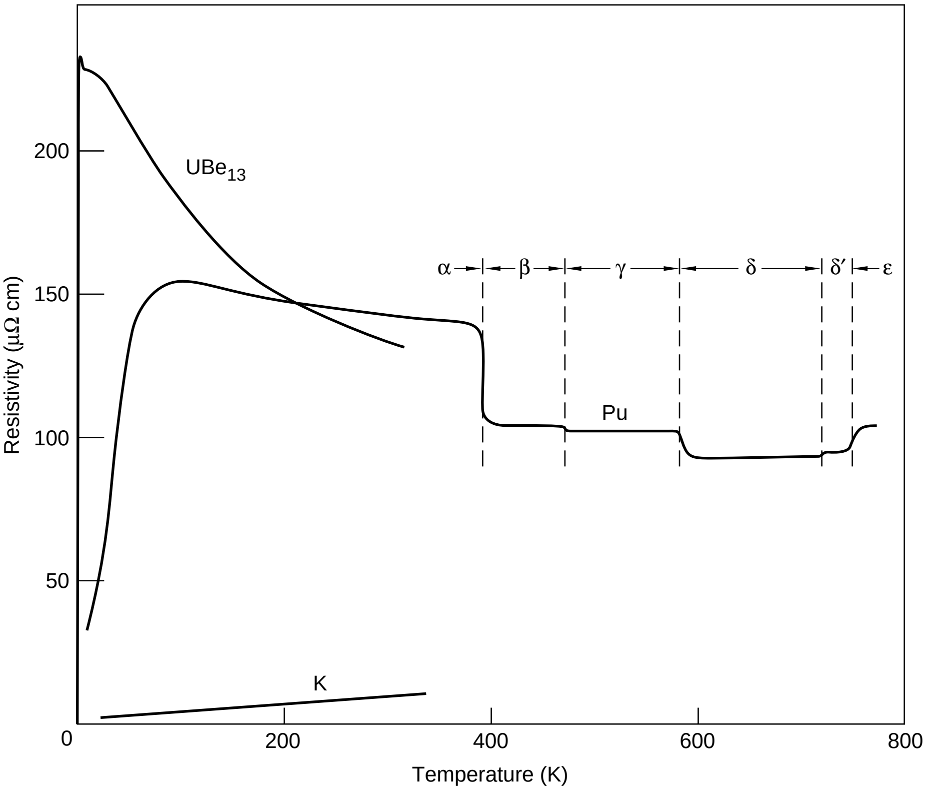


Figure 22. Resistivity of UBe$_{13}$, Plutonium, and Potassium
Electrical resistance in most metals increases linearly with temperature because electrons are scattered by phonons, as shown for potassium. Imperfections such as foreign atoms, lattice vacancies, and more-complicated defects, which are temperature independent, also scatter electrons and lead to a finite limiting resistance as *T* = 0. Plutonium has much higher resistivity values at all temperatures, showing enhanced scattering of the conduction electrons. The electron scattering comes from electron correlations. The compound UBe$_{13}$ yields one of the most extreme examples of electron scattering in a metal.

Anomalous Properties of Elements on the Diagonal. Now, we turn our attention to the elements on the diagonal in Figure 19. On the atomic level, these elements are like plutonium because they have two or more incompletely filled atomic shells that are close in energy. The electrons can therefore shift between shells relatively easily. As a result, these elements show giant resonances in their atomic optical spectra, reflecting their many close-lying energy levels.

These energy levels in the atom translate into a multiband system with one relatively narrow band and a high density of states at the Fermi energy in the metal. This description is true of the transition metals on the diagonal, even though their d bands are not quite as narrow as the f bands in elements along the diagonal. Narrow bands tend to mix or hybridize with other close-lying bands (a phenomenon that is predicted by one-electron band calculations). Moreover, weakening or strengthening the hybridization can push the d or f electrons in these narrow bands toward greater localization or greater itinerancy, respectively. Thus, the electrons in these narrow bands are highly sensitive to small perturbations. This sensitivity can lead to many allotropic crystal structures in the same element and to catalytic activity. It can also lead to the metal's ability to absorb hydrogen easily and to spark when struck. Catalytic activity and hydrogen absorption occur when perturbations can modify the chemical state, and the diagonal is the place to look for those behaviors.

First, let us consider a metal's ability to make sparks. All metals shower off burning pieces when put to a grinding wheel because the wheel heats the pieces as they break off, and most hot, finely divided metals burn. However, steel, cerium, uranium, neptunium, and plutonium make sparks under far more gentle conditions. For example, it is the cerium

Itinerant Magnetism, Invar, and δ-Plutonium

In some magnetic materials such as iron, conduction electrons rather than localized electrons produce ferromagnetic ground states. In these “itinerant magnets,” the conduction band splits into two distinct bands, one composed of spin-up states and the other of spin-down states. Although those two sets of states exist in all materials, in most they remain degenerate, except in the presence of an applied magnetic field. In iron, for example, the somewhat narrow d band splits spontaneously (without an applied magnetic field) into spin-up and spin-down bands. As in the Peierls distortion described in the main text, the separation of degenerate states into two bands lowers the total energy of the filled states. (Note that itinerant magnetism does not follow Hund’s rules because the orbital angular momentum of conduction electrons is quenched.) Itinerant magnets are less robust than local-moment magnets because the split conduction bands remain close to each other in energy and various perturbations can easily overwhelm the energy advantage from the split. The ferromagnetic state of iron, for example, disappears when iron is alloyed with other elements to make stainless steel.

We note the little-appreciated correlation between corrosion and magnetism. Most stainless steels are nonmagnetic and, of course, do not corrode. After welding or deformation, they sometimes rust in exactly those spots that have converted to a magnetic form of iron, martensite. Why? We suggest that any electrons that are not fully participating in bonding, including localized electrons or conducting electrons that are magnetically ordered, are more available for chemical reaction and thus for corrosion. We also note that, if the electrons in an itinerant magnet become less bonding and more magnetic, the lattice becomes bigger and vice versa. It is this effect that made Invar possible. Invar, as well as being an itinerant magnet, is an alloy with a zero coefficient of thermal expansion around room temperature. Accurate pocket watches were made of Invar a century ago. As an itinerant magnet is heated, thermal motion interferes with the spin alignment of electrons in the narrow bands, and this decrease in magnetic ordering makes those electrons a little more bonding (van Schilfgaarde et al. 1999), thus countering the normal thermal expansion. By choosing the correct combination of elements, one can make an alloy that maintains its size over some temperature range because these competing effects exactly balance out over that temperature range. It is now clear that Invar watches had to be kept out of magnetic fields because those fields could have bent the parts. We will not discuss the Invar effect in detail but will give a simple example that illustrates the electronic-structure changes leading to this effect.

The energy contained in the magnetic field of a permanent magnet can become noticeable on the scale of the cohesive energy. When dropped, modern neodymium-iron-boron permanent magnets break not because the metal is weak but because the huge magnetic energy decreases dramatically .

Consider the itinerant magnets iron, cobalt, and nickel. By one-electron calculations, we can determine the volumes of the true ferromagnetic state and of the hypothetical paramagnetic state. We calculate the ferromagnetic state by including spin, and thus we have spin-up and spin-down bands as mentioned before. In the paramagnetic calculation, we do not include spin, and the spin-up and spin-down bands are degenerate. In all cases, the calculated volume of the paramagnetic state is smaller than that of the ferromagnetic state. In other words, if the itinerant electrons contribute to magnetism, their contribution to bonding is reduced. Can this tradeoff be related to the contraction upon heating that is seen in the δ-phase of pure plutonium?

Although plutonium has no local magnetic moments, one might ask whether its conduction electrons could make it an itinerant magnet, like iron. There is little evidence now for magnetism in pure plutonium, but many plutonium compounds are magnetic and tend to be itinerant magnets. Simply dissolving hydrogen in plutonium is enough to make the electrons localize and the system ferromagnetic. Also, a comparison of the light actinides with the transition metals indicates that the light actinides should be superconductors unless they have local moments. So, the fact that plutonium is not a superconductor may indicate that plutonium is an incipient, weak itinerant magnet and that the loss of magnetic ordering with heating plays a role in the contraction of the δ-phase.

in a lighter flint that makes the sparks for lighting fires. We argue without proof that the high density of states near the Fermi surface causes the transfer of electrons to or from a tiny piece of highly deformed metal as it breaks off from a large piece, no matter how gently the breaking occurs. The resulting voltage difference produces a tiny electrical discharge across the gap, which then ignites the shard. Lanthanum, which is mechanically similar to cerium and is far more chemically active, does not make sparks because it has no f electrons and its density of states is low. The uranium-manganese compound UMn_2, which is made of two narrow-band elements from the diagonal in Figure 19, sparks so readily that its powder burns as soon as it is poured in air.

The most-common anomalous property, and the simplest one to measure, is the departure from the usual linear relation between electrical resistivity and temperature that occurs below room temperature. In Figure 22, we compare the resistivities of potassium and plutonium. Over the temperature range shown, potassium's resistivity increases linearly with temperature, as expected from the interaction of conduction electrons with lattice vibrations (phonons). Instead of following this simple linear increase, plutonium's resistivity bulges high above linearity at temperatures below room temperature and remains extremely high above room temperature, where it shows off its many phase transitions. The resistivity of plutonium at the bulge is of the order of 150 micro-ohm centimeters (μΩ cm), which means, microscopically, that an electron is scattered by roughly every atom in the lattice. This type of scattering is considered the highest possible simple resistance that can be seen in a metal and is called the unitary limit. Many correlated-electron metals show higher resistivities, which can only be explained by correlated-electron models such as the Kondo and Anderson models for extended systems. These models add electron interactions and correlations beyond those included in one-electron methods.

This puzzling enhanced electrical resistivity upon cooling began receiving attention thirty-five years ago, when it was noticed that a small amount of iron dissolved in gold showed an increasing electrical resistance as it was cooled at temperatures of a few kelvins. At the same time, the iron atoms had no magnetic moments. (The increase in the resistance of plutonium from room temperature down had already been measured, but this curve was neither as reproducible as the curve for the iron-gold alloy nor as easy for everyone to check.)

Jun Kondo was the first scientist to have come up with an explanation for the increase in the gold alloy's resistivity: The missing magnetic moment in iron was responsible for it. Kondo then made a model in which the spins of conduction electrons could flip the spins of the electrons on the iron atoms and thereby cancel the magnetic moment within the small volume around each iron atom impurity. This model predicted the desired increase in resistivity with decreasing temperature. In time, theories with a characteristic Kondo temperature were used for explaining not only the increase in resistivity upon cooling but also the leveling off in magnetic susceptibility upon further cooling, once a high value had been reached. They could also explain why magnetic moments were missing in so many materials. So, the Kondo impurity model was expanded to a Kondo lattice model, an extended system, in which crystallographically ordered moments could again be made to disappear, even though there seemed not to be enough conduction electrons to do the job. The most extreme example are the "Kondo insulators," in which no conduction electrons are present, but their spins are assumed to make magnetic moments vanish. We believe that these are examples of overworking a model simply because it fits the data. Such situations would not occur if we had a comprehensive theory for these phenomena. We note that the disappearance of the iron moment in the gold alloy should have come as no surprise because that moment is also known to disappear when iron is alloyed to make stainless steel. Indeed, it has been well known since the 1930s that the magnetism of iron is not robust (see the box "Itinerant Magnetism, Invar, and δ-Plutonium" on page 120). However, we are so used to calling iron a permanent magnet that even today many people believe iron is an archetypal example of a magnetic atom or metal.

Correlated-Electron Materials. Despite exaggerated claims, the Kondo model and all its offshoots have shown the condensed-matter physics community that there are very interesting anomalies going on in metallic systems, especially the metals on the diagonal in Figure 19, and this group includes plutonium. Although we do not have a simple predictive model to explain the origin of high resistivities, the materials exhibiting these conundrums are now lumped under the single category of correlated-electron materials. As shown in Figure 1, apart from high resistivities, these materials exhibit high magnetic susceptibilities, and they have no local moments at low temperatures. Other anomalies include tiny magnetic moments (as much as 1000 times smaller than expected), higher-than-expected magnetic ordering temperatures, failure to follow the quadratic temperature dependence of resistivity predicted by the Fermi-liquid model, and high specific heats indicating enhanced electron masses. All the signatures of correlated-electron materials are believed to result from strong electron-electron correlations involving spin and charge interactions.

Plutonium is probably the clearest example of a pure element in the correlated-electron category. Figure 22 shows its anomalous resistivity. Plutonium also has the most enhanced low-temperature specific heat of any pure element. The specific heat shown in Figure 23 indicates that the electron effective mass of plutonium is 10 times larger than that of most metals. Finally, plutonium has a relatively large magnetic susceptibility in all its solid-state phases, as seen in the inset on Figure 20.

The relatively large paramagnetic susceptibilities of the various phases of plutonium suggest that phases with magnetic moments or itinerant magnetism must have similar internal energies. Perhaps all the phases in pure plutonium above the α-phase have magnetic moments, but because the temperature range of each phase is so narrow, we have not been able to demonstrate them by magnetic susceptibility or neutron diffraction measurements. Correlated-electron materials usually show increases in susceptibility as they cool, but that susceptibility levels out within a few kelvins of absolute zero. Our best chance of finding out whether plutonium has local moments is to do synchrotron x-ray and neutron-scattering experiments on single crystals. Those measurements would be adequately sensitive to magnetic moments. We note that Méot-Raymond and Fournier (1996) claim to have found the signature of local moments on top of a huge paramagnetic background in δ-plutonium. Although the presence of local moments is consistent with the model of δ-plutonium described in Cooper's article, we

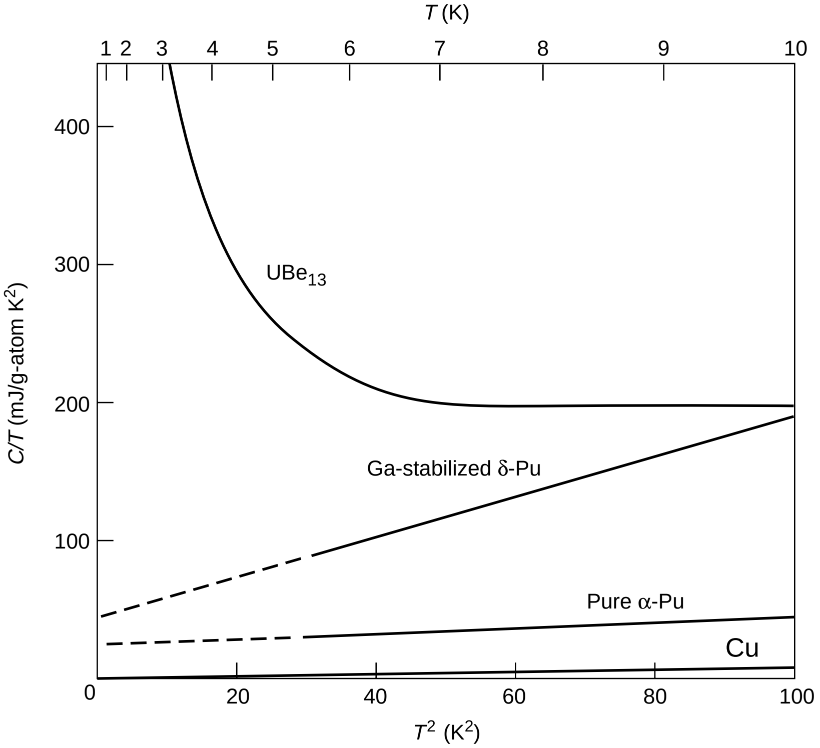


Figure 23. The Specific Heat of Plutonium and Other Metals

The low-temperature specific heat of a metal is the sum of a lattice term proportional to T^3 and an electronic term γT; that is, $C_V = \gamma T + AT^3$. Hence, when we plot C_V divided by T vs T^2, we get a straight line that has an intercept equal to γ at $T = 0$ and a slope equal to A. That slope yields the Debye temperature Θ_D via the relation $\Theta_D{}^3 = 1944\ A^{-1}\ J{\cdot}mol^{-1}\cdot K^{-1}$. As we explained in the section on the free-electron model, the specific-heat coefficient γ is proportional to T/T_F, and T_F is inversely proportional to the mass of the electron. So, γ is proportional to the electron mass. In this figure, the line for copper represents the behavior of most metals whereas the lines for α- and δ-plutonium have the highest values of γ (intercept values) of any pure element, indicating that conduction electrons have an enhanced effective mass. The compound UBe_{13} has an extremely high electronic specific heat, which continues to increase until it is cut off by the compound's transition to superconductivity just below 1 K (not shown). The superconductivity of UBe_{13} proves that its large heat capacity must be associated with the conduction electrons rather than the local moments and that the anomalously large values of γ are enhanced electron masses, or heavy-fermion masses, m^*.

remain somewhat skeptical of this data interpretation because so many correlated-electron systems show the same type of susceptibility even when they do not have local moments.

Magnetism and local moments do become manifest in plutonium if we spread out the plutonium atoms. As mentioned in the box "Itinerant Magnetism, Invar, and δ-Plutonium," plutonium hydride is ferromagnetic because the increased separation between plutonium atoms causes the f electrons to localize and pushes their behavior across the diagonal limit in Figure 19 and into the magnetic regime. This last statement leads us into a discussion of actinide compounds that exhibit localized 5f states or whose ground states become superconducting.

Hill Plots and Actinide Compounds

The crossover from itinerant to localized electrons can clearly be achieved if the atoms are spread out. Before 1970, investigators could not guess or understand whether cerium and uranium compounds would be superconducting or magnetic. In 1970, at Los Alamos, Hunter Hill explained under what conditions metallic compounds containing f electron elements would be superconducting or magnetic. Until then, the light-actinide and lanthanide compounds seemed to show these two collective ground states in an unpredictable manner.

Hill realized that in cerium and light-actinide compounds, the distance between the f electron elements determined whether their ground states were superconducting or magnetic, usually quite independently of which atoms containing non-f electrons were separating them. Figure 24 shows what is now called a Hill plot for uranium compounds. Superconducting or magnetic transition temperatures are plotted vertically, and the spacing between the f electron elements is plotted horizontally. In Hill's original plot, the known behaviors fell into two of the four quadrants—large spacing correlated with magnetism and short spacing with superconductivity.

At the time, it was quite strange to think that superconductivity did not depend on the intervening atoms containing non-f electrons. Energy band calculations were just beginning to show that the f electrons would be in bands, but those calculations were limited to the simplest structures. Hill conjectured that the f electrons could hybridize only with f electrons at other sites and that the intervening non-f electron atoms were just spacers to change the degree of overlap between the f-electron wave functions. In this way, Hill's plot became a major step toward understanding the light actinides. This picture is far more general in Figure 19, where we see that elements on or near the diagonal can have their properties easily modified.

Figure 24 shows many more materials than were plotted in Hill's original version, including two superconducting compounds that, based on the relatively large distance between two f-electron atoms, should have been magnetic. These two, namely, the uranium-platinum and

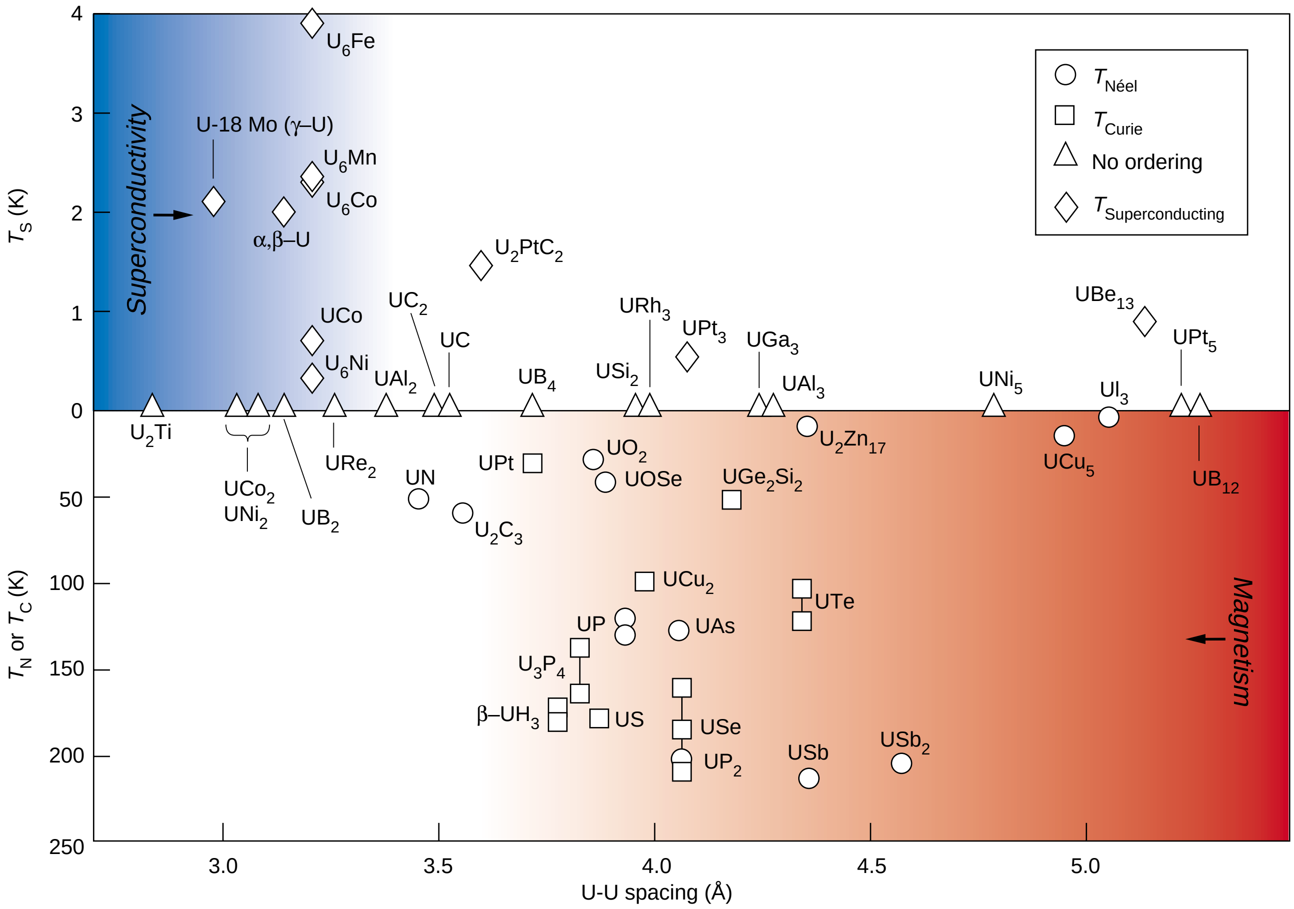


Figure 24. Hill Plot for Uranium Compounds

The Hill plot shows the superconducting or magnetic transition temperatures vs interatomic spacing separating the f electron atoms. We augmented the original Hill plot for uranium compounds to include more data—in particular, the transition temperatures of the two superconducting heavy-fermion compounds UPt_3 and UBe_{13}. Hill conjectured that the overlap of the f-electron wave functions between the uranium atoms determines whether the f electrons are localized (magnetic) or itinerant (superconducting) independent of the intervening atoms. Most compounds behaved as Hill expected. The superconducting compounds occurred at short f-electron spacings (blue quadrant), and the magnetic compounds at large f-electron spacings. The heavy-fermion superconducting compounds are exceptions. Although the spacing between the uranium atoms in those compounds is fairly large, the f electrons are still not fully localized and can condense into a superconducting state.

uranium-beryllium compounds UPt_3 and UBe_{13}, are examples of heavy-fermion superconductors.

Heavy-Fermion Materials

Many compounds and alloys containing elements near the diagonal in Figure 19 are called heavy-fermion materials, which means that their conduction electrons behave as if they had extremely heavy masses. The very high heat capacity of UBe_{13} shown in Figure 23 indicates that the electrons have an effective mass hundreds of times larger than that of conduction electrons in normal metals. Heavy-fermion materials also show very strange magnetic and superconducting ground states. All these materials are narrow-band metallic systems. So, their unusual collective ground states arise from very strong electron correlations involving the electrons in their narrow bands. Also, their low-energy excitations are associated with the spin and charge fluctuations in that narrow band. One difference between these materials and the light actinides is that the former do not exhibit crystal structure instabilities because their narrow bands are not the dominant bonding bands. This feature can be seen in UPt_3, whose wide d band has roughly 27 electrons (9 electrons for each platinum atom) and its narrow f band has only 3 electrons. So, it is the low-energy excitations (mostly at low temperatures) that make the heavy-fermion materials resemble the light actinides. We will discuss the discovery of the heavy-fermion materials and the significant role played by the Los Alamos scientists, as well as the exotic properties of these materials.

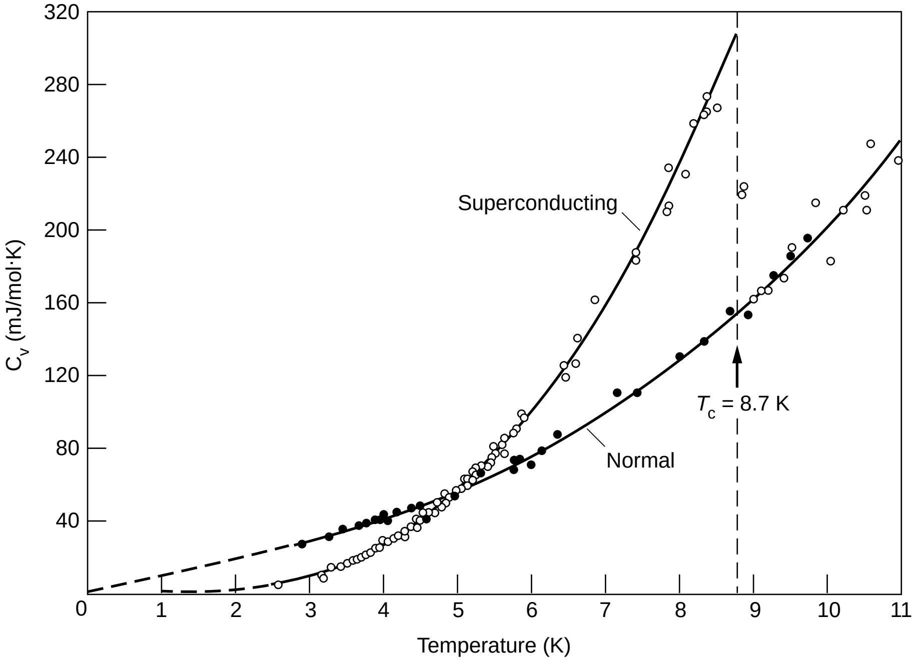


Figure 25. Specific Heat Signature of the Superconducting Transition in Niobium

Common superconductors, such as niobium, show a drop in specific heat as the superconducting transition temperature is reached because a gap opens in the spectrum of possible electronic energies. It is this energy gap that makes the resistance of the material vanish. That is, once in the superconducting state, conduction electrons cannot be scattered as they move through the material because the scattering would cause them to have energies within the energy gap. If an external magnetic field is applied to the material, the superconducting transition will be suppressed, and the specific heat will vary with temperature as in a normal metal. Note that this plot is not a straight line because *C*, rather than *C*/*T*, is plotted on the vertical axis. The same specific-heat signatures of superconducting transitions occur in heavy-fermion compounds such as $CeCu_2Si_2$ and UBe_{13} but at temperatures that are 10 times lower and with changes in specific heat that are 10 times larger.

In the late 1970s, in Cologne, Germany, Frank Steglich and coworkers were the first scientists to observe an anomalous superconducting ground state. They were measuring the low-temperature properties of the cerium-copper-silicon compound $CeCu_2Si_2$. The behavior of this compound at temperatures above 100 kelvins suggested that, at very low temperatures, $CeCu_2Si_2$ would become an antiferromagnet. That is, this compound showed the standard inverse temperature dependence of the magnetic susceptibility, as shown in Figure 21, with a negative intercept on the temperature axis. It also had a huge heat capacity at low temperatures, of the order of joules per mole-kelvin, the size associated with localized magnetic moments.[4] On the other hand, the magnetic susceptibility of $CeCu_2Si_2$ became temperature independent at low temperatures, implying that magnetic ordering never took place. The real surprise was a large jump in the specific heat, as the compound went superconducting just below 1 kelvin. The specific heat of a superconductor at its transition point is shown in Figure 25.

The opening of a large gap in the midst of the huge heat capacity of $CeCu_2Si_2$ meant that the electrons that presumably were localized and associated with large magnetic moments had become superconducting. But that conclusion simply did not make sense. Localized electrons cannot even conduct electricity, much less be superconducting. These properties were considered so unlikely that they were discounted as artifacts of bad samples, but Steglich defended his results.

Then, in the early 1980s, Los Alamos scientists found that the compounds UBe_{13} and UPt_3 have the same properties: very large heat capacities and a superconducting transition at low temperatures. The Los Alamos results made clear that a new ground state of matter existed, one in which electron interactions were so highly correlated that only an extreme quasiparticle picture could cause that behavior. That is, the electrons were so heavily clothed by interactions that they acted as if their masses were 1000 times larger than the mass of a free electron. A heat capacity that should typically belong to magnetic moments belonged, in this case, to the electrons moving through the metal.

The existence of this new ground state blurred forever the distinction between localized and itinerant electrons. Fully localized electrons, with their definite energy levels, can be thought of as belonging to an infinitely narrow band. Because no energy levels are near by, those electrons act as if they had infinite mass—that is, they cannot move at all. By analogy, the f electrons in heavy-fermion materials occupy such a narrow energy band that the electrons act as if they had a huge mass—that is, as if they were almost localized.

Zachary Fisk, Hans Ott, Al Giorgi, Greg Stewart, Joe Thompson, Jeff Willis, and other Los Alamos scientists went on to identify more compounds that had the same heavy-fermion, or

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[4] The electronic heat capacity of a magnetic material is much larger than that of a normal metal because the moments on all the atoms contribute to the former whereas only T/TF of the conduction electrons contribute to the latter. The low-temperature electronic specific heat of normal metals is of the order of 1–10 millijoules per mole-kelvin.

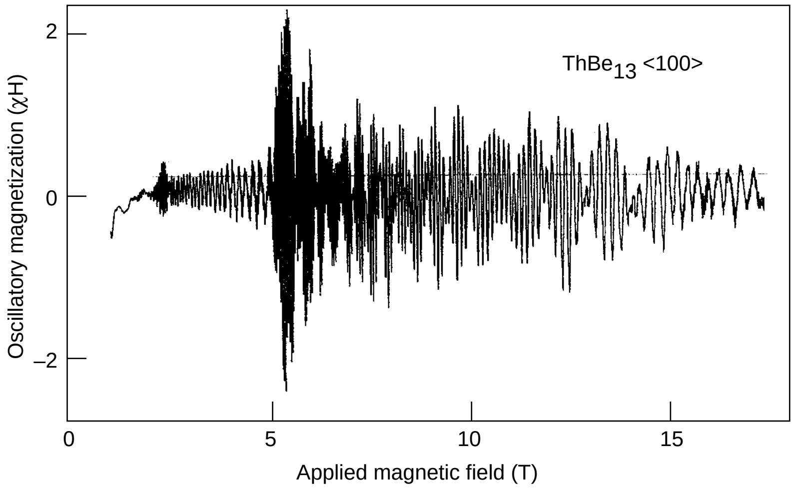

Figure 26. The de Haas–van Alphen (dHvA) Effect

At low temperature and in a high magnetic field, the susceptibility of a metal oscillates with a period that is inversely proportional to the field. This oscillation occurs because the field imposes a quantization condition on the allowed levels of the electrons. The Fermi surface can be extracted in this way. Illustrated here are the oscillations for the $ThBe_{13}$ compound, which is a noncorrelated-electron counterpart of UBe.

enhanced-mass, behavior but did not become superconductors. Some of these heavy-fermion materials became antiferromagnetic and others, as measured then, had neither magnetic ordering nor superconducting ground states. Heavy-fermion compounds had been seen earlier, but until some were seen to be superconducting, there was no way to distinguish them from the magnetic materials, which have large heat capacities. Indeed, in the mid 1970s, Jim Trainor[5] and coworkers noticed that the antiferromagnetism of the neptunium-tin compound $NpSn_3$ showed, at its magnetic ordering temperature, a heat capacity anomaly in the shape of a superconducting anomaly, similar to the one shown in Figure 25 for a superconductor. Because they could fit the shape of a magnetic anomaly with that of a superconducting one, the scientists knew that something quite unusual was occurring. However, no one was listening then, and the puzzling result went unnoticed.

Several many-body theory groups have tried to understand the unusual metallic properties of the heavy-fermion compounds by developing Fermi-liquid descriptions. In the mid 1990s at Los Alamos, Kevin Bedell and his coworkers Gerry Brown, David Meltzer, Chris Pethick, David Pines, Khandker Quader, and Carlos Sanchez-Castro carried out the most detailed theoretical study of this kind**.** They developed very simplified one- and two-band Fermi-liquid models of heavy-fermion compounds such as UPt3. The surprise was that these simplified models yielded quantitative results in agreement with the low-energy and low-temperature physics of these materials. Again, like the Kondo model, the Fermi-liquid quasiparticle turns out to be a far more useful model than originally expected. Lev Landau's principle of one-to-one correspondence between electron and quasiparticle states continues to be correct and to yield profound insights into systems of strongly interacting particles.

The series of discoveries on heavy-fermion materials established Los Alamos as an institution for leading-edge research into condensed-matter physics and turned the attention of theorists and experimentalists worldwide to the actinide elements. High interest in these materials continues today.

High Magnetic Fields for Measuring Enhanced Masses. In the early 1930s, W. J. de Haas and P. M. van Alphen were measuring the magnetic susceptibility of a bismuth crystal and observed oscillations in susceptibility as they varied the field. The period of the oscillations varied as the inverse of the applied magnetic field. The explanation is now simple. Placing a metal in a large magnetic field at low temperatures triggers a new quantization condition. The continuum of energy levels in the conduction band becomes a new set of discrete Landau levels with a splitting between levels given by $\hbar eH/2\pi mc$. For most experiments, the number of these levels ranges from 1 to 10^{10}. This new set of available states affects all the properties of the metal, provided the applied field is very large and the temperature very low. As the magnetic field increases, one discrete level at a time rises above the Fermi energy and causes the fixed number of electrons (or quasiparticles) to be redistributed on the remaining levels. This electron redistribution is seen as an oscillation in all metallic properties. By measuring the periodicity of the oscillations in different crystallographic directions, we can map the shape of a metal's Fermi surface. And by measuring the temperature dependence of the oscillations, we can determine the effective masses of the electrons on the Fermi surface. Figure 26 shows the dHvA oscillations in $ThBe_{13}$.

This dHvA effect was used in the 1950s and 1960s to show that Fermi surfaces existed and to measure their shape for simple metals. Later, however, scientists stopped using this technique because most pure metals had been measured. And then, in the late 1980s, the dHvA effect became fashionable again because verifying

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[5] At that time, Trainor was a postdoctoral fellow at Argonne National Laboratory.

the heavy-fermion masses in cerium and uranium compounds was of interest and the higher magnetic fields necessary for that work became available at the National High Magnetic Field Laboratory in Tallahassee, Gainesville, and at Los Alamos. It was thus immediately clear that dHvA methods would allow measuring the heavy-electron masses in heavy-fermion compounds. In the early 1990s, at the Cavendish Laboratory in Cambridge, England, Gil Lonzarich, Stephen Julian, and Louis Taillefer resurrected the 20-year-old technique and used high magnetic fields (up to 20 tesla) and the very low temperatures of a dilution refrigerator (down to 10 millikelvins). After much work, they saw effective electron masses as high as 210 in UPt_3. This mass is so large that the highest oscillations visible at a temperature of 10 millikelvins were gone by 30 millikelvins. This means that the highest fields, lowest temperatures, and highest-quality samples are a must. Although many groups have looked for similar oscillations in UBe_{13}, such oscillations have never been reported in credible work because UBe_{13} masses are much larger than UPt_3 masses, and the oscillations are already gone at the lowest temperature attainable at this time.

In 1998, Jason Detwiler, George Schmeideshoff, and Neil Harrison observed dHvA oscillations in the praseodymium-beryllium and thorium-beryllium compounds $PrBe_{13}$ and $ThBe_{13}$ by working with a 70-tesla pulsed magnet at the National High-Magnet Laboratory at Los Alamos. These compounds do not have the heavy electrons of UBe_{13}, and so the scientists focused on measuring the Fermi surface and showed that their results agreed with one-electron calculations. Then, to try and sneak up on UBe_{13}, they next tried the thorium-uranium-beryllium compound $Th_{0.95}U_{0.05}Be_{13}$ and saw nothing. They did, however, see oscillations in $Th_{0.995}U_{0.005}Be_{13}$, but much work lies ahead before the masses of UBe_{13} can be seen. We will have to create the following mandatory conditions: very low temperatures, very high fields, and samples of even higher quality. Because the one-electron behavior of $PrBe_{13}$ and $ThBe_{13}$ has already been confirmed, the natural next step is to measure the clothed masses in UBe_{13}.

Future Steps

If researchers think of narrow-band phenomena when thinking of plutonium, we have succeeded in making our point. The narrow 5f bands lead to all the unusual behaviors of plutonium at all energy scales. At higher energies, the narrow bands predicted by one-electron DFT calculations lead to low-symmetry crystal structures but normal elastic properties. At low temperatures and energies, strong spin and charge fluctuations connected to the excitations from those narrow bands lead to all the anomalous heavy-fermion-like behaviors. The strong electron-phonon coupling of narrow-band electrons may lead to higher effective temperatures, which form a depressed melting curve in the light actinides. The instability of these band states (due to the small radial overlap of the f-electron wave functions and the many states with similar energies) leads to the many-phase transitions in these materials. This instability most likely leads to the partial localization of these 5f states suspected to exist in δ-plutonium.

For the past 40 years, we focused on the difference between the angular character of d and f wave functions as the key to understanding the light actinides although, for most of that time, we knew that the 5f electrons go from being itinerant in plutonium to being localized in americium. That change to localization occurs only because of a change in the radial part of the wave function. We have also known for almost 10 years that the low-symmetry crystal structures are less related to the angular character than to the narrow bonding bands in these metals. Therefore, we need to study other features, such as the short-range nature of the f-f interactions in Bloch states. How can we construct states with partial localization, that is, with two kinds of 5f electrons (localized and itinerant) in the same metal?

Over the next few years, improved one-electron theories will better describe the short-range nature of the 5f interactions. To determine the range of the f-f interactions, these theories might involve some Slater-Koster fitting of the f bands. Such a scheme could also be used in determining the variation of the f-f interaction as a function of volume. Some calculations of this nature have been performed, but details of the f-f interactions have not yet been extracted. Also, the modern electronic-structure calculations have only demonstrated that the angular character of the single-atom orbitals is not a main factor in determining crystal structures. Indeed, it appears to be washed out when a large number of states build up to form bands, and for that reason little or no charge buildup is seen between atoms in the actinide metals. However, improved calculations may show some small charge buildup, and then we would have to reconsider this feature. Models of localization of the 5f states need to be developed.

Many low-energy properties are still so poorly understood that existing correlated-electron theories need to be improved and new theories might have to be developed. Theorists are still unable to predict the collective ground states in many of these materials. Also, we cannot explain why neptunium and plutonium are the only f electron elements that do not develop a collective magnetic or superconducting state. After examining heavy-fermion materials more closely, we now believe that all may have a magnetic ground state. By using the most-modern experimental tools, we now can try and measure magnetic moments that are 1000 times smaller than they should be. From this work, we hope that new insights into plutonium will emerge.

But right now, the most-modern experimental techniques cannot be applied to plutonium because they require large single crystals, and those are not yet available for plutonium. Learning how to grow such crystals in a repeatable fashion would be a real break-through in plutonium studies. One could then use the crystals in neutron-scattering experiments to measure the entire phonon spectrum of plutonium and in photoemission experiments to measure its energy bands as a function of crystal momentum. Photoemission (photon in and electron out) is now sufficiently accurate to determine the widths and structure of the narrow 5f bands in materials such as plutonium. In all the earlier photoemission experiments, the instrument resolution for x-rays was so poor and the surface contamination for ultraviolet rays so high that the result was merely featureless spectra. Now, with some of the new photoemission machines and improved surface-cleaning techniques, we should obtain actinide spectra that show the structure predicted by the electronic-structure calculations. At Los Alamos, we are currently making tiny single crystals of plutonium and related materials with techniques that had been used decades ago at Rocky Flats and Argonne National Laboratory. As reported in this volume, we are measuring these tiny samples with ultrasound, neutrons, and x-rays.

Although we may eventually understand the electronic structure of plutonium single crystals, the landscape of close-lying but different states cannot be removed to give homogeneity when we make a large plutonium casting. And because plutonium is radioactive, its atoms will always be converted into impurities, and this process damages the lattice. Nevertheless, if we know how single crystals behave, it is much simpler to model a collection of them in a large casting than to reverse-engineer a large piece to see its components. This is why we are looking forward to more progress in these areas.

We must study plutonium and its neighbors, alloys, and compounds because we deal with them all in weapons. We may never know what ideal plutonium is. However, the gift from nature is that this most-complicated element teaches us about all the elements and shows us that there still is new science to discover. ■

Further Reading

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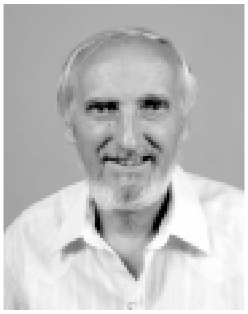

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James L. Smith received his B.S. in Physics from Wayne State University and his Ph.D. in Physics from Brown University. He is currently a Los Alamos Laboratory Fellow in the Materials Science and Technology Division. Jim is also an adjunct professor at several universities, editor of *Philosophical Magazine B*, and member on the board of the Brown University Alumni Association. His research interests include superconductivity, magnetism, actinides, high magnetic fields, electronic properties of metals, experimental physics, and new materials. During his career, Jim published more than 350 papers. For his work, he received the E. O. Lawrence Award from the Department of Energy in 1986 and the American Physical Society International Prize for New Materials in 1990.