

experimental resolution)⁵, a number between 0 and M^{2s-2} can be stored in a single crystal of molecular magnets with spin s . We note that the experimental overhead required by the Grover search algorithm involves only the control of $\log_M N$ frequencies, which, once available, can decode any number between 1 and N by means of a single magnetic pulse. Our proposal for implementing Grover's algorithm works not only for molecular magnets but for any electron or nuclear spin system with non-equidistant energy levels. Although such spin systems cannot be scaled to arbitrarily large spin s —the larger a spin becomes, the faster it decoheres and the more classical its behaviour will be—we can use such spin systems of given s to great advantage in building dense and highly efficient memory devices. □

Received 24 November 2000; accepted 14 February 2001.

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Acknowledgements

We thank G. Salis and J. Schliemann for useful comments. This work has been supported in part by the Swiss NSF and by the European Union Molnanomag network.

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Correlated electrons in δ -plutonium within a dynamical mean-field picture

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Given the practical importance of metallic plutonium, there is considerable interest^{1–3} in understanding its fundamental properties. Plutonium undergoes a 25 per cent increase in volume⁴ when transformed from its α -phase (which is stable below 400 K) to the δ -phase (stable at around 600 K), an effect that is crucial for issues of long-term storage and disposal. It has long been suspected that this unique property is a consequence of the special location of plutonium in the periodic table, on the border between the light and heavy actinides—here, electron wave-particle duality (or itinerant versus localized behaviour) is important⁵. This situation

has resisted previous theoretical treatment. Here we report an electronic structure method, based on dynamical mean-field theory, that enables interpolation between the band-like and atomic-like behaviour of the electron. Our approach enables us to study the phase diagram of plutonium, by providing access to the energetics and one-electron spectra of strongly correlated systems. We explain the origin of the volume expansion between the α - and δ -phases, predict the existence of a strong quasiparticle peak near the Fermi level and give a new viewpoint on the physics of plutonium, in which the α - and δ -phases are on opposite sides of the interaction-driven localization–delocalization transition.

Here we argue that the substantial volume expansion that occurs when metallic plutonium changes from the α - to the δ -phase is the manifestation of the competition between localization (caused by the electron–electron interactions) and delocalization (caused by the kinetic energy) tendencies. The modern theoretical tool to compute ground-state properties such as the volume of the solid is density–functional theory (DFT) in its local density or generalized gradient approximations (LDA or GGA; for a review see ref. 6). However, it fails here with unprecedented errors: the theoretical volume of the δ -phase is in error by 30%, and magnetic long-range order not observed experimentally is predicted^{7–9}. This illustrates the inability of traditional electronic structure methods to predict properties of strongly correlated systems.

The many-body theory of strongly interacting electrons on a lattice is an alternative approach with a long history. Hubbard¹⁰ was one of the first to point out the importance, in the solid state, of Coulomb correlations which occur inside atoms. Subsequently, attempts to build theories which interpolate between the atom and the solid were made. The many-body crystal wavefunction has to reduce to many-body atomic wavefunctions as lattice spacing is increased. Unfortunately, this limiting behaviour is missed in the density-functional method.

Over the past ten years, a modern many-body technique which is able to interpolate between band-like and atomic-like behaviour of electrons, the dynamical mean-field theory (DMFT), has been developed (for a review see ref. 11). It has resulted in a thorough understanding of the Mott transition in hamiltonians with strong repulsive interactions. It is of interest to consider if such a theory could be implemented for realistic multiband solids with a variety of details brought about by the crystallographic environment and the constituents involved—and if it would have the predictive power to explain such problems as the structural phase diagrams of plutonium, its alloys and compounds. The development of this electronic-structure method as an alternative to DFT would be an important advance in the physics of d - and f -electron systems in general, and in the problem of nuclear materials in particular. It is therefore a pressing problem in the area of strongly correlated electron physics^{11–13}.

Here we discuss an implementation of DMFT which allows us to incorporate the basic electronic structure of real materials into the DMFT equations. This permits the calculation of the total energy of a given compound. We show that this method leads us to the explanation of the basic features of the phase diagram of plutonium.

How does this method include atomic physics? We illustrate this point by looking at the atomic shell of an f -electron system—such as plutonium—embedded in the solid-state environment. First, we determine the spectrum of excitations for the shell, that is, a set of many-body levels describing processes of removing and adding electrons. In the simplified case, when every f electron has roughly the same kinetic energy ϵ_f and Coulomb repulsion energy U , the total energy of the shell with n electrons is given by $E_n = \epsilon_f n + Un(n - 1)/2$ and the excitation spectrum is given by $\epsilon_n = E_{n+1} - E_n = \epsilon_f + Un$. The constant U can be computed from first principles. Second, we take into account that in the solid, these many-body atomic states hybridize with each other and with the

itinerant s , p and d electrons. Within the DMFT method, this process is described by a frequency-dependent hybridization function, $\Delta(\omega)$, which is a measure of the ability of the f electron to delocalize. This quantity is unknown at the outset, and needs to be determined self-consistently. The entire problem is thus reduced to solving the ‘Anderson impurity model’¹⁴ (AIM) for the given f shell. This gives us the impurity Green’s function $G_f(\omega)$ and self-energy $\Sigma(\omega)$ for f electrons.

We now consider how the itinerant band aspects of the f electrons are captured by this method. The bands are described by the eigenvalues of the matrix one-electron hamiltonian $H(k)$. In our implementation, $H(k)$ is obtained by constructing the LDA Kohn–Sham hamiltonian. From this, we subtract the average of the Coulomb energy of the f electrons as the latter is treated explicitly later, using a tight-binding, linear muffin-tin orbital (LMTO) basis¹⁵. A significant development in the present method is its ability to handle realistic situations in which several bands are involved.

The important step brought by the dynamical mean-field description is to require that the impurity Green’s function $G_f(\omega)$ coincides with the full crystal Green’s function G_c evaluated at the impurity site (site-diagonal G_c). In practice, we begin with a guess for the hybridization function, compute the impurity Green’s function and then, using $H(k)$, the site-diagonal G_c . This is set equal to a new impurity $G_f(\omega)$, from which a new $\Delta(\omega)$ is determined. This iterative procedure is repeated until self-consistency in $\Delta(\omega)$ is achieved.

After the crystal Green’s function is obtained, an updated charge density is computed. The latter modifies the one-electron hamiltonian $H(k)$, which in turn modifies the self-consistent solution described above. This brings us to a second self-consistent loop, the loop over charge density similar to the one in DFT. Incorporating such an external loop into the algorithm allows us to compute from first principles a central quantity of the material: its ground-state total energy. As a consequence, a phase diagram of the solid of interest can be studied by this method. By varying lattice spacing, we can look for the total-energy minimum, and predict different crystallographic configurations.

We gain several advantages by using the many-body, instead of the density-functional, description of solids. First, our approach is designed to reproduce both ground-state properties and excitation spectra. A main shortcoming of DFT is thus overcome. Second, the method gives direct access to finite temperatures via the use of temperature Green’s functions. Then in principle, phase transition temperatures, both magnetic and crystallographic, should be accessible. Last, the method works naturally in the local-moment regime—when on a short timescale, magnetic moments exist on atoms, but on long timescales, there is no net moment on the average.

We now describe some details of the method that solves the AIM for given hybridization $\Delta(\omega)$ and resulting self-energy $\Sigma(\omega)$. The latter is in general a 14×14 matrix for f electrons. For the relativistic f level in cubic symmetry, it is reduced to 5×5 with 4 non-zero off-diagonal elements. Because the general AIM solution is a formidable numerical problem, we make several simplifications. First, off-diagonal elements are in general small and will be neglected. We are therefore left with the $5f^{5/2}$ state split into two levels which are 2-fold (Γ_7), and 4-fold (Γ_8) degenerate, and with the $5f^{7/2}$ state split into three levels which are 2-fold (Γ_6), 2-fold (Γ_7) and 4-fold (Γ_8) degenerate. Second, because in plutonium the intermultiplet spin–orbit splitting is much larger than the intramultiplet crystal-field splitting ($>5:1$), we reduce the problem of solving AIM for the levels separately by treating the $5f^{5/2}$ Γ_7 and Γ_8 levels as one 6-fold degenerate level, and the $5f^{7/2}$ Γ_6 , Γ_7 and Γ_8 levels as another 8-fold degenerate level.

To solve the AIM in the general multi-orbital case, we use an interpolation scheme for its self-energy which is very accurate at both small and large frequencies, inspired by the success of the

iterative perturbation theory¹¹. At low frequencies, the exact value of the self-energy and its slope is extracted from the Friedel sum rule and from a slave-boson treatment¹⁶. At high frequencies, the self-energy is computed using self-consistent determination of moments¹⁷. The results of a smooth interpolation between these limits were in good agreement with quantum Monte Carlo data in the regimes where this comparison was possible (small degeneracy and high temperature).

The total energy of the system is evaluated by correcting the LDA total energy—which contains all the electrons including the core electrons—for the fact that it does not treat the f electrons correctly (in the same spirit as the LDA+U method; for a review, see ref. 18). We subtract from the LDA the average interaction energy of the f electrons (double counting term) and the average kinetic energy of the f electrons, and then add improved estimates of these quantities using the solution of the self-consistent AIM. The interaction term is evaluated using the Galitski–Migdal formula¹¹, and the improved f -electron kinetic energy within the DMFT method is extracted from the hybridization of the AIM¹¹. This gives a robust total energy scheme for practical applications.

To study the phase diagram of plutonium, we implement this self-consistent dynamical mean-field method. We include relativistic spin–orbit coupling effects, which are generally important for actinide compounds. The δ -phase of plutonium has a face-centred cubic (f.c.c.) structure with one atom per cell. We determine the ground-state energy as a function of the atomic volume V for the given lattice. Our theory needs a value of the effective Coulomb interaction U between f electrons in Pu. Various estimates exist in the literature. They indicate that the average interaction among f electrons is around 4 eV (ref. 19).

To illustrate the importance of correlations in our theory, we present results for values of U equal to 0 and 4 eV. First, the total energy as a function of volume is computed for $U = 0$ (GGA curve), which indicates a minimum at $V/V_\delta = 0.7$, (V_δ is the experimental volume of the δ -phase) close to the volume of the α -phase, Fig. 1. Certainly, we expect that correlations should be less important for the compressed lattice in general, but there is no sign of the δ -phase in the $U = 0$ calculation. The total energy curve is very different for $U > 0$. The details depend sensitively on the actual value of U . The curve at $U = 4$ eV shows the possibility of a double minimum; it is

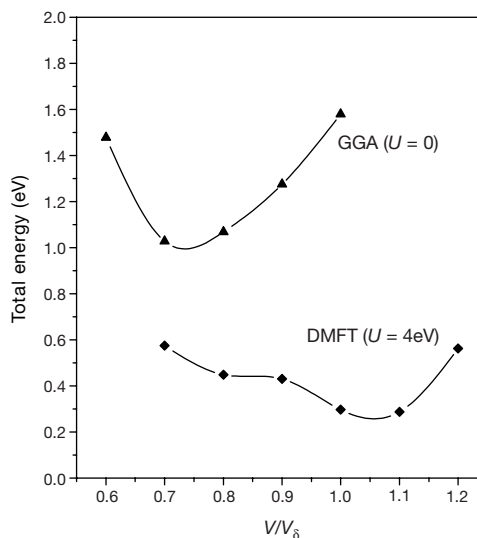


Figure 1 Calculated total energy for plutonium as a function of volume using dynamical mean-field theory (DMFT). The result of a density-functional GGA (generalized gradient approximation) calculation is also shown for comparison. Calculations were performed for the temperature 600 K, at which the δ -phase is stable. U denotes average Coulomb energy among f -electrons.

actually realized for a slightly smaller value of U . We can directly assign the small-volume feature to what would become the α -phase if we allowed for monoclinic distortions and a volume-dependent U , and assign the other feature to the δ -phase. As the energies are so similar, we may expect that as temperature decreases, the lattice will undergo a phase transition from the δ -phase to the α -phase with the remarkable decrease of volume by 25%. Our first-principles calculation contains the gist of the main features of the experimental phase diagram of plutonium.

The double-well behaviour in the total energy curve is unprecedented in LDA- or GGA-based calculations, but is a natural consequence of the proximity to a Mott transition. Indeed, recent studies¹¹ of model hamiltonian systems have shown that when the f -orbital occupancy is an integer and the electron–electron interaction is strong, two DMFT solutions, which differ in their spectral distributions, can coexist. It is natural that allowing the density to relax in these conditions can give rise to double minima, as seen in Fig. 1. This theoretical result deserves more detailed investigation, in the light of recent suggestions that the δ -phase might be metastable¹.

As a second result, we report our calculated spectral density of states for the δ -phase. We predict the appearance of a strong quasiparticle peak near the Fermi level. Recently, the δ -phase spectrum has been determined experimentally²⁰; our calculations are in accord with these measurements (Fig. 2). We note that LDA is not able to resolve a quasiparticle peak, and the electronic structure near the Fermi level falls into a deep minimum contrary to experiment. Even the LDA+ U theory^{21,22} fails to show the Kondo-like peak near the Fermi level. The DMFT description brings this feature into the spectrum, and the peak is quite narrow owing to both small hopping integrals and strong Coulomb interactions.

A simple physical explanation drawn from these calculations suggests that in the δ -phase the f -electron is slightly on the localized side of the interaction-driven localization–delocalization transition, with a sharp and narrow Kondo-like peak and well-defined upper and lower Hubbard bands. It therefore has the largest volume across all phases as has been found by previous GGA+ U

calculations^{21,22} that take into account Hubbard bands only. The low-temperature α -phase is more metallic; that is, it has larger spectral weight in the quasiparticle peak and smaller weight in the Hubbard bands. It will therefore have a much smaller volume that is eventually reproduced by LDA/GGA calculations which neglect both Coulomb renormalizations of quasiparticles and atomic multiplet structure. The delicate balance of the energies of the two minima may be the key to understanding the anomalous properties of Pu, such as the great sensitivity to small amounts of impurities (which would raise the energy of the less-symmetric monoclinic structure, thus stabilizing the δ -phase to lower temperatures) and the negative thermal expansion. We note, however, that the α -phase is not a weakly correlated phase: it is just slightly on the delocalized side of the localization–delocalization transition. This is a new view of plutonium; traditionally, the α -phase is regarded as well understood within LDA. However, the correlation viewpoint is consistent with a series of anomalous transport properties in the α -phase that are reminiscent of heavy-electron systems. For example, the resistivity of α -Pu around room temperature is anomalously large, temperature independent, and above the Mott limit²³ (the maximum resistivity allowed to the conventional metal). The same is true for the thermoelectric power²⁴. □

Received 21 December 2000; accepted 21 February 2001.

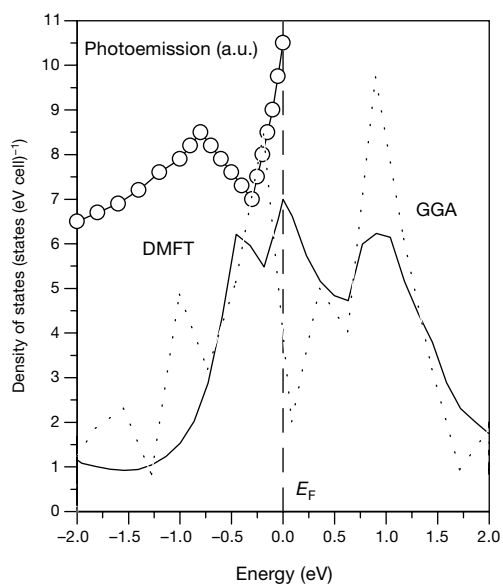


Figure 2 Comparison between calculated density of states for δ -plutonium using dynamical mean-field theory (DMFT; solid line) and recent photoemission experiments²⁰ (circles). The result of a density-functional GGA calculation is also shown for comparison (dotted line). Calculations are performed for the temperature 600 K at which the δ -phase is stable. E_F denotes the position of the Fermi level.

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Acknowledgements

We thank A. Lichtenstein for discussions. This work was supported by the DOE division of Basic Energy Sciences and by Los Alamos National Laboratory.

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