Annual Report DE-FG07-97ER45671
(ID 59925) Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems

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**Research Objective:**

The problem being addressed is to establish standards for temperature conditions under which plutonium, uranium, or neptunium from nuclear wastes permeates steel, with which it is in contact, by diffusion processes. The primary focus is on plutonium because of the greater difficulties created by the peculiarities of face-centered-cubic-stabilized (delta) plutonium (the form used in the technology generating the waste).

Temperature is the key controllable diffusion processes, i.e., temperature controls the rate of diffusion. The scientific goal of this project is to predict diffusion constants on an ab initio basis, i.e. diffusion distances in specified time at specified temperature for plutonium from plutonium-based waste materials into various steels or technologically-pertinent metallic alloys. This predictive ability will help to provide information relevant to setting temperature standards for maintaining structures, ducts, equipment, or waste-containing vessels until such time as decontamination and decommissioning and/or permanent storage can be carried out. In addition, this knowledge will aid in assessing the depth of penetration that must be dealt with in any surface treatment for decontamination.

The scientific steps of the methodology are (1) to recognize the stabilizing mechanism and the electronic structure pertinent to that stabilization for face-centered-cubic (fcc) delta-stabilized plutonium, (2) to extract the information needed to perform dynamic simulations from ab initio electronic structure calculations, (3) to perform and report the dynamic simulations predicting the diffusion behavior.

**Research Progress and Implications:**

This report summarizes progress after 2 1/2 years of a 3-year project. We have completed step (1) recognizing the stabilizing mechanism and the electronic structure pertinent to that stabilization for face-centered-cubic (fcc) delta-stabilized plutonium; and the substantial computations and modeling for (2) and (3) are in progress. The related experimental work is underway at Los Alamos National Laboratory, and the linkage been our work and that at LANL has been established in detail.

To model diffusion of the stabilizing element atoms, e.g., gallium, within delta (fcc) plutonium wastes and then into the steel of containers requires obtaining information about the electronic structure of fcc Pu in physically accurate yet tractable form. We are working on several aspects of developing that methodology and generating that necessary information. This work falls within a conceptual framework based on our understanding of the unusual structural behavior found in elemental plutonium. It has been evident for some time that this behavior is related to the localization mechanism for the 5*f* electrons in going from alpha to delta (fcc) plutonium. We explain this behavior on the basis of a multistep 5*f* localization process involving spatially nonuniform localization. That is, we suggest that a disordered array of two types of plutonium on crystallographically equivalent fcc sites breaks the translational symmetry and provides an entropy generating mechanism that drives these transitions. The two types of plutonium sites are: first the fluctuating para sites, at which the number of localized *f* electrons fluctuates between $f^4$ and $f^5$ because of hybridization with non-*f* band electrons, and second the localized ortho sites, at which the number of localized *f* electrons remain stable at $f^5$. It is the entropy of mixing between these two types of sites that drives the thermal stepwise (via beta and gamma) transition from the monoclinic alpha ground state to the face-centered-cubic delta phase.

(1) We are implementing our theory that provides fundamental understanding of the phase stabilization of fcc Pu on the basis of a stepwise localization of the 5*f* electrons into a solid-solution-like phase, as described above. We have designed and are carrying out large-scale calculations that will reproduce the fully self-induced or stabilizer-nucleated Anderson (disorder) localization that leads to this phase. These calculations involve two-electron dynamics as opposed to the one-electron dynamics of LDA (local density approximation)-based methods.

(2) Until such time as the very large-scale calculations required in (1) are fully implemented, we are pursuing an immediately practical alternative for generating the data needed to model diffusion. We have developed variations of both the LDA+U and LDA-SIC (self-interaction-corrected) methods appropriate to *f*-state localization and applied these to fcc plutonium. These calculations give an atomic volume of fcc Pu about 6% smaller than the experimental value. Having the total energy from such a calculation together with that from a conventional LDA calculation for the monoclinic alpha ground state also enables us to predict the stabilization temperature of the delta (fcc) phase.

(3) We have recognized the importance of correctly treating the localization of the 6p as well as the 5*f* electronic states in fcc Pu, and thereby recognized the importance of specific relativistic effects for the 6p electrons. We are developing methodology to treat these effects.

**Planned Activities:**

As stated above, we have developed a detailed technical plan for proceeding with steps (2, extracting the information needed to perform dynamic simulations from ab initio electronic structure calculations) and (3, performing and reporting the dynamic simulations predicting the diffusion behavior). We currently are proceeding systematically through the detailed parts of this plan.

**Information Access:**

**Publications:**
"The Role of Anderson Localization in Causing the fcc Stabilization and the Depressed Melting Temperature of Plutonium" B.R. Cooper, to appear in Los Alamos Science, 2000.

"A Theoretical Study of Relativistic Effects in the Electronic Structure of Pu", accepted to appear in Physical Review B (2000). (G.W. Fernando, E.H. Sevilla, and B.R. Cooper).

"Correlation Effects on Stability in Pu Metal and Its Alloys", pp 531-537 in Electron Correlations and Materials Properties (A. Gonis and N. Kioussis, Eds., Plenum Publishing, 1999) (B.R. Cooper with P.E.A. Turchi, A. Gonis, N. Kioussis, and D.L. Price).

"From Heavy Fermions to Random-Localized-Site Behavior Via Anderson Localization", Philosophical Magazine B 79, 683 (1999). (B.R. Cooper with O. Vogt, Q.G. Sheng, and Y.L. Lin).

“Calculated Lattice Relaxation in Pu-Ga Alloys”, Journal of Alloys and Compounds 271-273, 367 (1998). (B.R. Cooper with J.D. Becker, J.M. Wills, and L.

“Calculated Lattice Relaxation in Pu-Ga”, Phys. Rev. B 58B, 5143 (1998). (B.R. Cooper with J.D. Becker, J.M. Wills, and L. Cox).

**Invited Talks at International Conferences:**

"From Heavy Fermions to Random-Localized-Site *f*-Electronic and Magnetic Behavior Via Anderson Localization", European Conference on Physics of Magnetism 99", Poznan, Poland, June 21-25, 1999.

"The Role of Exchange in Correlated-Electron Dynamics", Czech-US Workshop on Prospects of a Realistic Description of Strong Electron Correlations in Solids, Prague, October 1-6, 1999.

“Treating Electronic and Magnetic Properties of Actinide-Based Materials Beyond One-Electron Dynamics”, School of Actinide Physics and Chemistry, Uppsala, Sweden, May, 1998.

"Synthesis of Many-Body Theory and Electronic Structure", International Workshop on Electron Correlations and Materials Properties, Heraklion, Crete, Greece, June 28-July 3, 1998.

**Contributed Presentation at Conferences:**

“Structural Relaxation in Pu-Ga via Full-Potential LMTO Calculations”, Actinides 97 International Conference, Baden-Baden, Germany, September, 1997. (B.R. Cooper with J.D. Becker, J.M. Wills, and L. Cox).

“Diffusion of Plutonium into Transition Metallic Alloys and of Transition Metal Species into Plutonium”, Eighth Conference on Computational Research on Materials, Lakeview, WV, May, 1998. (B.R. Cooper with S. Beiden).

"Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems", Environmental Management Workshop, Chicago, July, 1998. (B.R. Cooper with S. Beiden).

"Portable Detection and Analysis of Plutonium Content", Workshop on Environmental Management Science: Integration with End User Needs, Savannah River Site, November, 1998. (B.R. Cooper with D. Leder

"Modeling of Diffusion of Plutonium", Workshop on Environmental Management Science: Integration with End User Needs, Savannah River Site, November, 1998. (B.R. Cooper with S. Beiden).

"Modeling of Interdiffusion of Plutonium and Other Metals", Materials Research Society Meeting, Boston, November, 1998. (B.R. Cooper with S. Beiden).

"Anomalous Electronic Behavior and Relationship to Thermostructural Behavior of Light Actinides", American Physical Society Meeting, Atlanta, March, 1999.

"Electronic Structure of Alpha and Delta Plutonium", American Physical Society Meeting, Atlanta, March, 1999. (B.R. Cooper with N. Kioussis, P.E.A. Turchi, A. Gonis and D.L. Price).

"Equilibrium Lattice Volume of fcc Pu", American Physical Society Meeting, Atlanta, March, 1999. (B.R. Cooper with E.H. Sevilla and G.W. Fernando).

"Random 5*f* Localization and the fcc Transition and Depression of Melting Temperature in Plutonium, 29$^{th}$ Journees des Actinides Conference, Luso, Portugal, April 1999.

# Electronic Structure of Delta (fcc) Pu: Extracting and Using Information for Diffusion Modeling

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Diffusion of the stabilizing element atoms, e.g., gallium, within delta (fcc) plutonium wastes and then into the steel of containers is an important effect on the corrosion resistance of these containers. To model such diffusion requires obtaining information about the electronic structure of fcc Pu in physically accurate yet tractable form.

## STEPS TO DEVELOP METHODOLOGY AND GENERATE NECESSARY INFORMATION

I. This work is bg done within a conceptual framework based on our understanding of the unusual structural behavior found in elemental plutonium. The conceptual framework has been developed; detailed modeling and experimental validation is in process.

II. Implementatio(modeling) of conceptual understanding of the stabilization of delta (fcc) plutonium (multiyear effort needed).

III. We are pursuing an immediate practical alternative to II.--- LDA and LDA-SIC calculations: (1) to extract the energy (temperature) equivalent of the entropy that stabilizes delta Pu in the model of I & II, and (2) to provide a data base for extracting information needed for diffusion modeling.

IV. Recognition of role of localization (and associated relativistic effects) of 6*p* as well as 5*f* electrons in fcc Pu

## CONCEPTUAL FRAMEWORK

It has been evident for some time that the unusual structural behavior found in elemental plutonium is related to the localization mechanism for the 5*f* electrons in going from alpha to delta (fcc) plutonium. We explain this behavior on the basis of a multistep 5*f* localization process involving spatially nonuniform localization. That is, we suggest that a disordered array of two types of plutonium on crystallographically equivalent fcc sites breaks the translational symmetry and provides an entropy generating mechanism that drives these transitions. The two types of plutonium sites are: first the fluctuating para sites, at which the number of localized *f* electrons fluctuates between $f^4$ and $f^5$ because of hybridization with non-*f* band electrons, and second the localized ortho sites, at which the number of localized *f* electrons remain stable at $f^5$. It is the entropy of mixing between these two types of sites that drives the thermal stepwise (via beta and gamma) transition from the monoclinic alpha ground state to the face-centered-cubic delta phase.

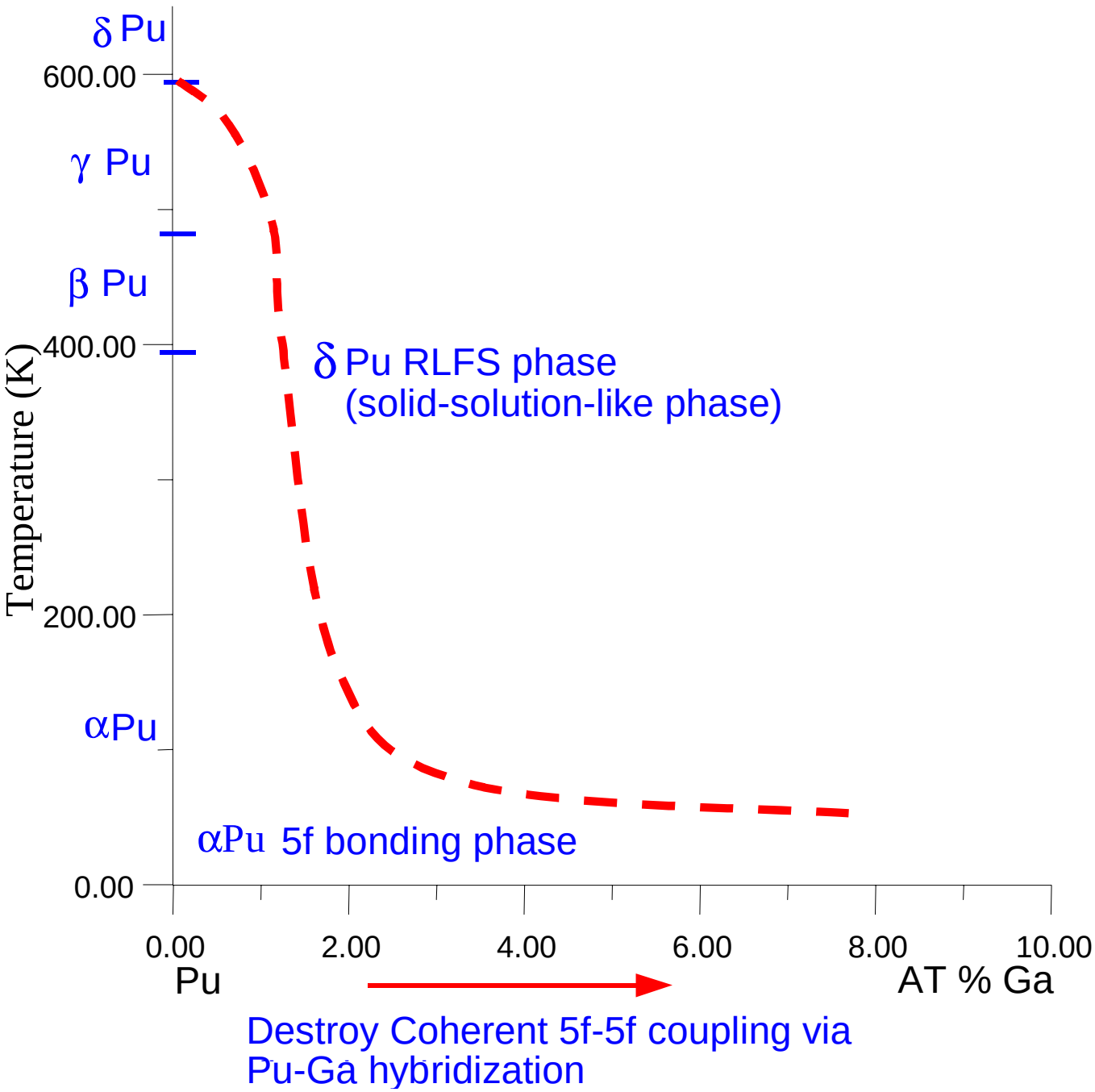
## STABILIZATION OF fcc PLUTONIUM: ENTROPY GENERATION AND SELF-INDUCED ANDERSON (DISORDER) LOCALIZATION

We picture the transition of pure plutonium to the low density delta phase at 592K as being due to a self-induced Anderson (disorder-induced) localization of the 5*f* electrons driven by the configurational entropy of a random distribution (solid solution) of (ortho) stable $f^5$ and (para) fluctuating $f^5/f^4$ Pu sites.

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

$$T_{Aloc} \sim 158E_{f\ bond}/\ln 2 \sim 228E_{f\ bond} \qquad (1)$$

At this temperature, the loss of bonding energy per atom would be balanced by the increase in entropy per atom (which is equal to ln2 for the transition to the RFLS phase because each atom now has two possible states, ortho or para). Equation (1) predicts that this transition at 592K corresponds to a loss of 5*f* bonding energy per atom of 2.6mRy, which falls at the expected value. (This is about 1percent of the total cohesive energy per atom of 255mRy for plutonium.)


δ Pu
600.00
γ Pu
β Pu
400.00
δ Pu RLFS phase
(solid-solution-like phase)
Temperature (K)
200.00
αPu
αPu 5f bonding phase
0.00
0.00
2.00
4.00
6.00
8.00
10.00
Pu
AT % Ga
Destroy Coherent 5f-5f coupling via
Pu-Ga hybridization

## Using Susceptibility to Monitor Changes in Stabilization of fcc Plutonium

The experimental signature of the solid-solution-like phase is a high-temperature magnetic susceptibility ($\chi$) that combines Curie-Weiss and enhanced Pauli contributions.

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

$$\chi_{CW} = \frac{C}{T - \theta_p} \tag{2b}$$

$$\chi_{\text{Pauli}} = \chi_0 \, [1 - (\pi^2/12)(k_B T/E_F)^2] \tag{2c}$$

A possible way to quantify the distribution between para and ortho plutonium as a function of gallium content in gallium-stabilized delta plutonium is based on the prediction that an increase of hybridization (with consequent increase in number of para sites) would lead to a decrease in the low temperature ordered moment for certain related ferromagnetic uranium compounds. That decrease would correspond to an increase in the Pauli paramagnetic component of the paramagnetic susceptibility above $T_c$ . This correspondence (that the increase in Pauli susceptibility quantitatively corresponds to the decrease in ordered moment) is presently being experimentally validated for a number of magnetically ordered uranium compounds. If quantitatively validated, it will be justified to use measurement of the susceptibility of gallium-stabilized fcc plutonium with varying gallium content, to quantify the distribution between para (fluctuating $5f^4/f^5$) configuration and ortho (stable $5f^5$) plutonium. One would expect that the Curie-Weiss component of susceptibility (the number of ortho sites) would increase with gallium content because the hybridization weakens with increasing gallium content. This would then validate the use of susceptibility measurements to quantify changes induced by effects of aging.

We are implementing our theory that provides fundamental understanding of the phase stabilization of fcc Pu on the basis of a stepwise localization of the 5 electrons into a solid-solution like phase, as described above. We have designed and plan to carry out large-scale calculations that will reproduce the fully self-induced or stabilizer-nucleated Anderson (disorder) localization that leads to this phase. These calculations involve two-electron dynamics as opposed to the one-electron dynamics of LDA (local density approximation)-based methods.

Until such time as the very large-scale calculations required in (1) are fully implemented, we are pursuing an immediately practical alternative for generating the data needed to model diffusion. We have developed variations of both the LDA+U and LDA-SIC (self-interaction-corrected) methods appropriate to *f*-state localization and applied these to fcc plutonium. These calculations give an atomic volume of fcc Pu about 6% smaller than the experimental value. Having the total energy from such a calculation together with that from a conventional LDA calculation for the monoclinic alpha ground state enables us to predict the stabilization temperature of the delta (fcc) phase.

## Role of 6*p* Localization

The commonly employed second variational treatment of the spin-orbit splitting in Pu is found to have a large (≅25%) error in dealing with the 6*p* semicore states but not with the 5*f* states of the Pu atom. In fcc Pu, this error implies a corresponding nontrivial effect on various calculated equilibrium properties including the lattice volume. This points to the importance of correctly treating the localization of the 6*p* as well as the 5*f* electronic states in fcc Pu and thereby recognizing the importance of specific relativistic effects for the 6*p* electrons that appear to have been ignored up to now. We are developing methodology to treat these effects.

# PRESENT APPROACH

- Prior to studying a binary alloy picture of the dynamically fluctuating state envisioned for delta plutonium, a simpler static approach is being followed. This permits a first examination of the validity of the model.

- A full potential LDA-LMTO computation (of E vs V) is used to represent the delocalized (alpha) state.

- A SIC-LDA-LMTO computation is used to represent the localized (delta) state.

  - The f electrons are placed in the core, with the assumption that the localized f-states are confined to one site.

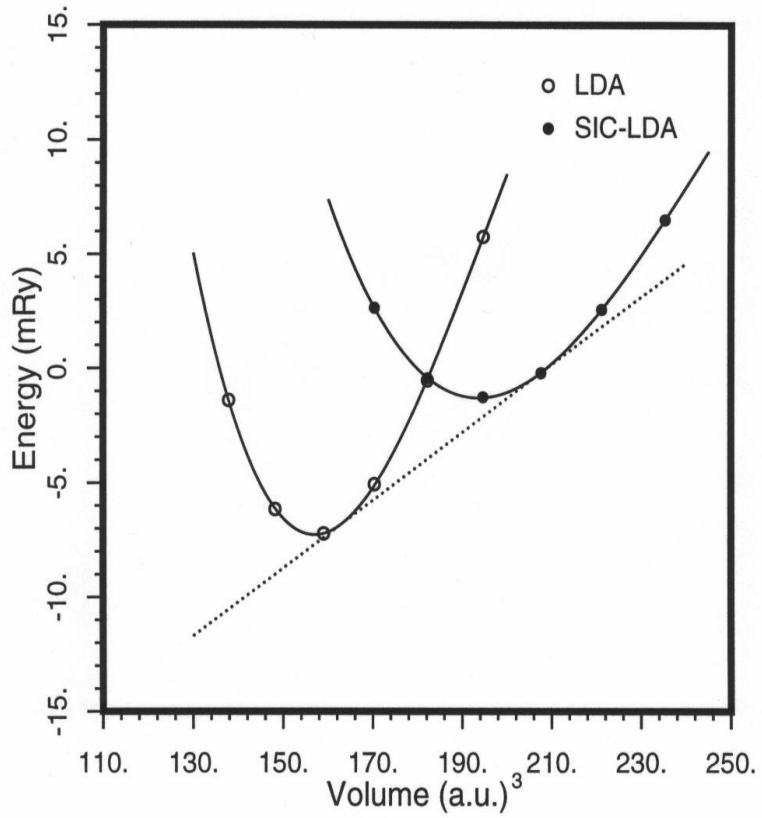
  - The self-interaction correction (SIC) is computed for each localized site, using the spherically averaged density of the core-f state.

  - In order to study situations where only some of the 5f electrons are localized, the projection operator $\mathbf{E_o\ |f_i><f_i|}$ is incorporated into the valence Hamiltonian ($E_o$ = 200Ry). This makes the state energetically unfavorable for occupation.

  - The SIC-LDA total energy in this scheme is an upper bound to the energy of the localized system. Orthogonality of localized states of neighbouring sites is assisted by a potential barrier introduced in the interstitial region.

  - The contribution of the non-spherical components of the potential are included perturbatively.

- Applying this method to fcc cerium (one f electron) results in a good estimate of the volume collapse from alpha to gamma phases (18.6% as opposed to 17% experimentally). **(D. L. Price, Phys. Rev. B 60, 10588 (1999))**

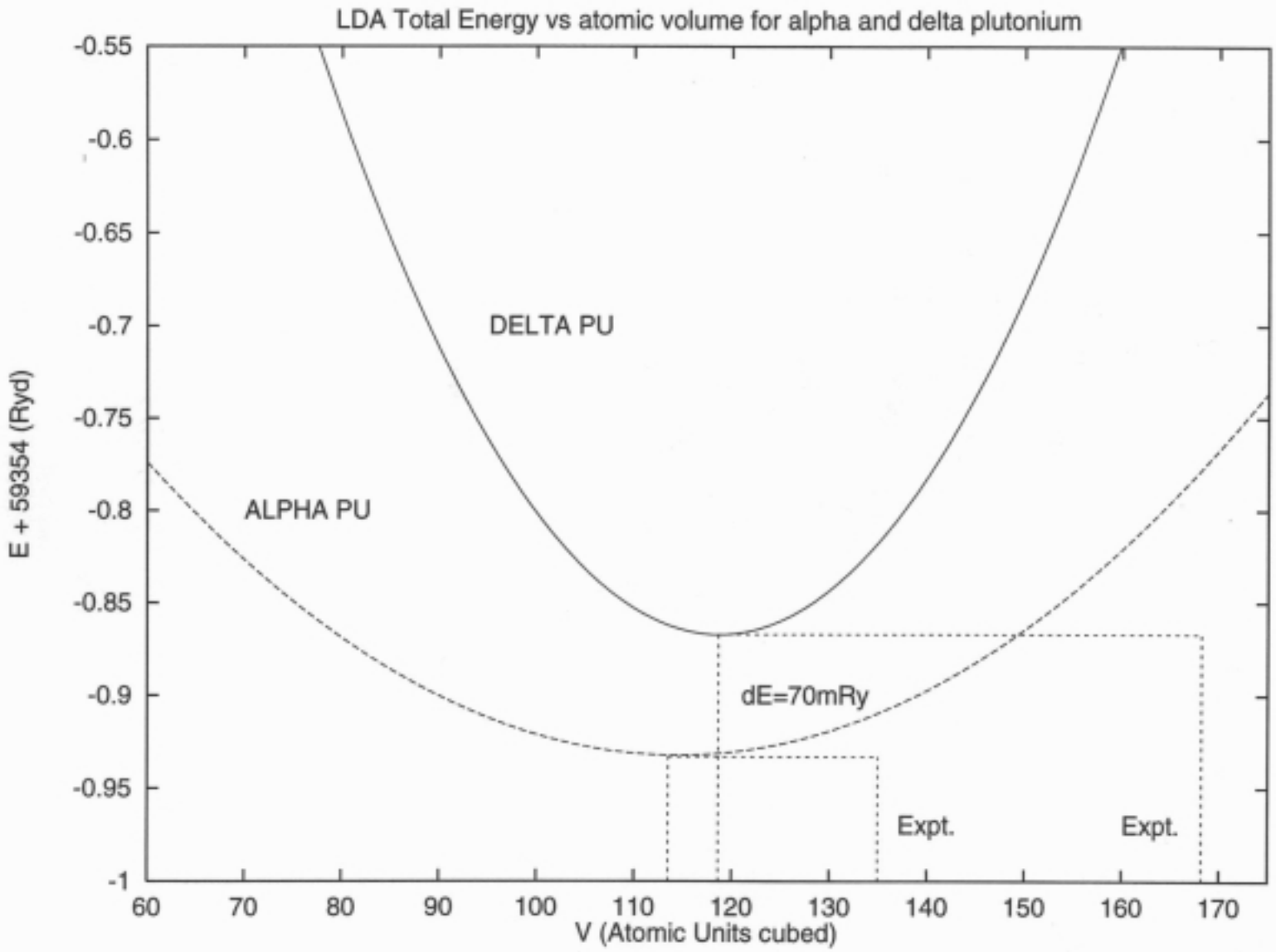



Total energy as a function of volume for fcc cerium. The LDA curve represents alpha cerium, while the SIC-LDA curve indicates the higher volume gamma phase with one localized f electron.
D.L. Price, Phys. Rev. B 60, 10588 (1999)

**LDA results for delta and alpha plutonium**

- The LDA atomic volume obtained from our calculations for fcc delta plutonium is indicative of strong overbonding, being 30% smaller than the experimental value of **168.2(A.U.)$^3$.** An LDA contraction of this magnitude is unique to delta Pu and is comparable to that obtained by other studies.

- The LDA atomic volume for monoclinic alpha plutonium is about 16% smaller than the experimental value (this can also be compared with the 8% error of the GGA study of P. Soderlind et al, PRB 55, 1997 (1997). The total energy is lower than that for delta plutonium by about 70mRyd, indicating as expected, that the low temperature alpha phase is the ground state.


LDA Total Energy vs atomic volume for alpha and delta plutonium
E + 59354 (Ryd)
-0.55
-0.6
-0.65
-0.7
-0.75
-0.8
-0.85
-0.9
-0.95
-1
60
70
80
90
100
110
120
130
140
150
160
170
V (Atomic Units cubed)
DELTA PU
ALPHA PU
dE=70mRy
Expt.
Expt.

## The SIC-LDA computations for delta plutonium

- An equilibrium atomic volume significantly closer to the experimental value is obtained (13% smaller than experiment).

- In the case of cerium, there was little sensitivity to the barrier potential, indicating that cerium f states were well localized near the nucleus. For plutonium a greater sensitivity to the barrier height was found.

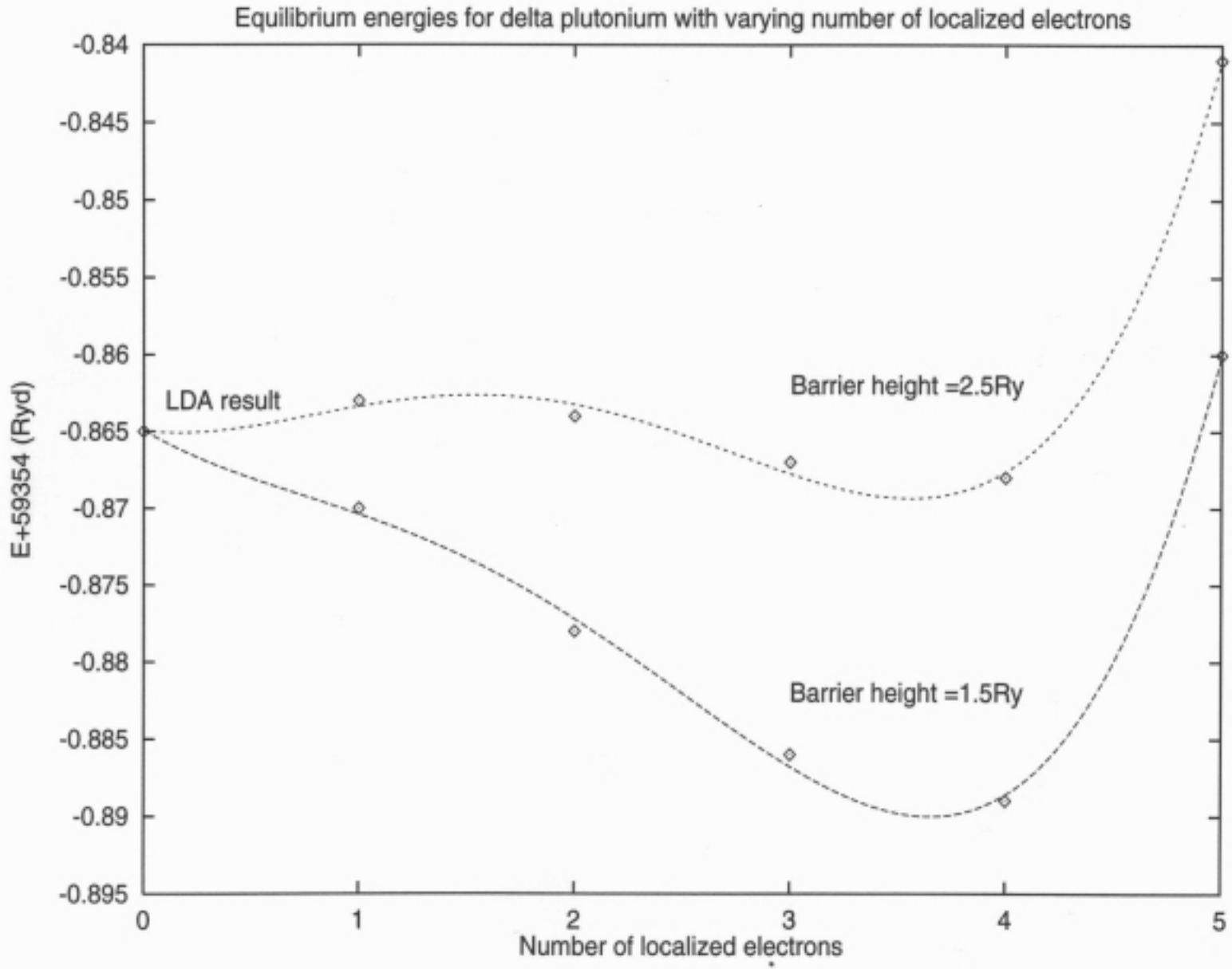
- For a barrier height large enough to well confine the 5f states, the SIC-LDA energy for delta plutonium was lower than the LDA energy, suggesting that localization is favoured in delta plutonium.

- The energy difference compared to the alpha phase is substantially larger than that predicted by the crude entropy calculation This is expected to improve on:

    - Inclusion of the perturbative corrections to the 5f wavefunctions (from the non-spherical components of the potential) in the SIC correction is expected to lower the total energy. Preliminary results confirm this.

    - Incorporation of f state orthogonalization into the computation would reduce the energy further (and would eliminate the necessity for the barrier).

    - The overall energy minimum occurs for four localized electrons, Independent of the barrier height; however the energy for the state with three localized electrons is close to that for four (this explains, in principle, the negative expansion coefficient for plutonium).


Equilibrium energies for delta plutonium with varying number of localized electrons
E+59354 (Ryd)
-0.84
-0.845
-0.85
-0.855
-0.86
-0.865
-0.87
-0.875
-0.88
-0.885
-0.89
-0.895
0
1
2
3
4
5
Number of localized electrons
LDA result
Barrier height =2.5Ry
Barrier height =1.5Ry

## Present results and future efforts

- Studies of LDA and SIC-LDA total energies as a function of atomic volume for alpha and delta plutonium show that:
    - The alpha phase has lower total energy than delta phase and is therefore the ground state.
    - The SIC-LDA energy (while there is a significant dependence on barrier height) indicates that localization is favoured in the delta phase which supports the premise of a (partially) delocalized delta phase.
    - The equilibrium atomic volume of delta plutonium is improved by the LDA-SIC computation.
    - The study indicates that four localized electrons are favoured in the delta phase over three by a small energy difference (which explains, in principle, the negative expansion coefficient of delta plutonium).
- Inclusion of the perturbative corrections to the 5f wave functions, from the non-spherical components of the potential, in the SIC correction is expected to lower the total energy.
- A closer study of the barrier dependence is indicated; a check by performing a supercell calculation with the incorporation of explicit orthogonalization of the 5f localized states into the self-consistent iterative procedure is possible.
- A study of the random disordered phase in delta plutonium using a 'random alloy' picture with the inclusion of two-electron correlations is in active development.