

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 (δ) 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) δ -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) δ -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 between our work and that at LANL has been established in detail.

To model diffusion of the stabilizing element atoms, e.g., gallium, within δ (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 $5f$ electrons in going from α to δ (fcc) plutonium. We explain this behavior on the basis of a multistep $5f$ 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 $5f$ 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 $5f$ 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. Cox).

"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 $5f$ Localization and the fcc Transition and Depression of Melting Temperature in Plutonium, 29th Journées des Actinides Conference, Luso, Portugal, April 1999.