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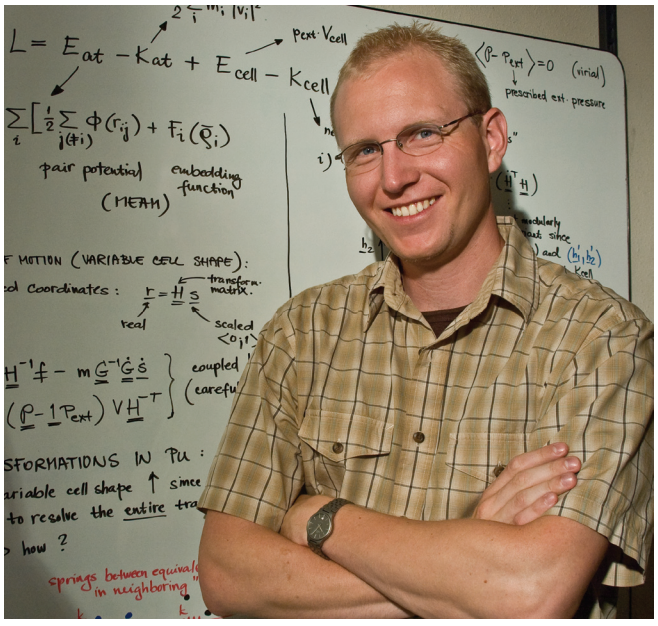
Chain-of-states atomistic calculations of the pathways and energetics of structural phase transformations in plutonium

Understanding structural phase transformations in plutonium is an important step toward obtaining thermodynamic and kinetic descriptions of this material. At ambient pressures, plutonium exists in six crystal structures that range from the highly symmetric face-centered cubic δ phase with four atoms per unit cell to one of the least symmetric structures: the monoclinic low-temperature α phase with 16 atoms per unit cell. Just above room temperature, plutonium transforms to its body-centered monoclinic β phase whose unit cell is experimentally predicted to consist of 34 atoms, an unusual number.

Some insight into the nature of the phase transformations between various allotropes of plutonium has been gained recently using the Modified Embedded Atom Method (MEAM). These calculations not only correctly predict the order of the crystal structures and their stabilities but also reproduce the large 25% volume difference between the α and δ phases. However, the time scale required for observing a phase transformation between two phases is typically beyond the reach of conventional molecular dynamics simulations.

To probe the structural phase transformations in plutonium, we use a chain-of-states calculation implemented within the so-called nudged elastic band (NEB) method. We consider a chain of states {0, 1, 2, …, M+1} of M+2 replicas (images) of the system, that is a discrete representation of the transformation



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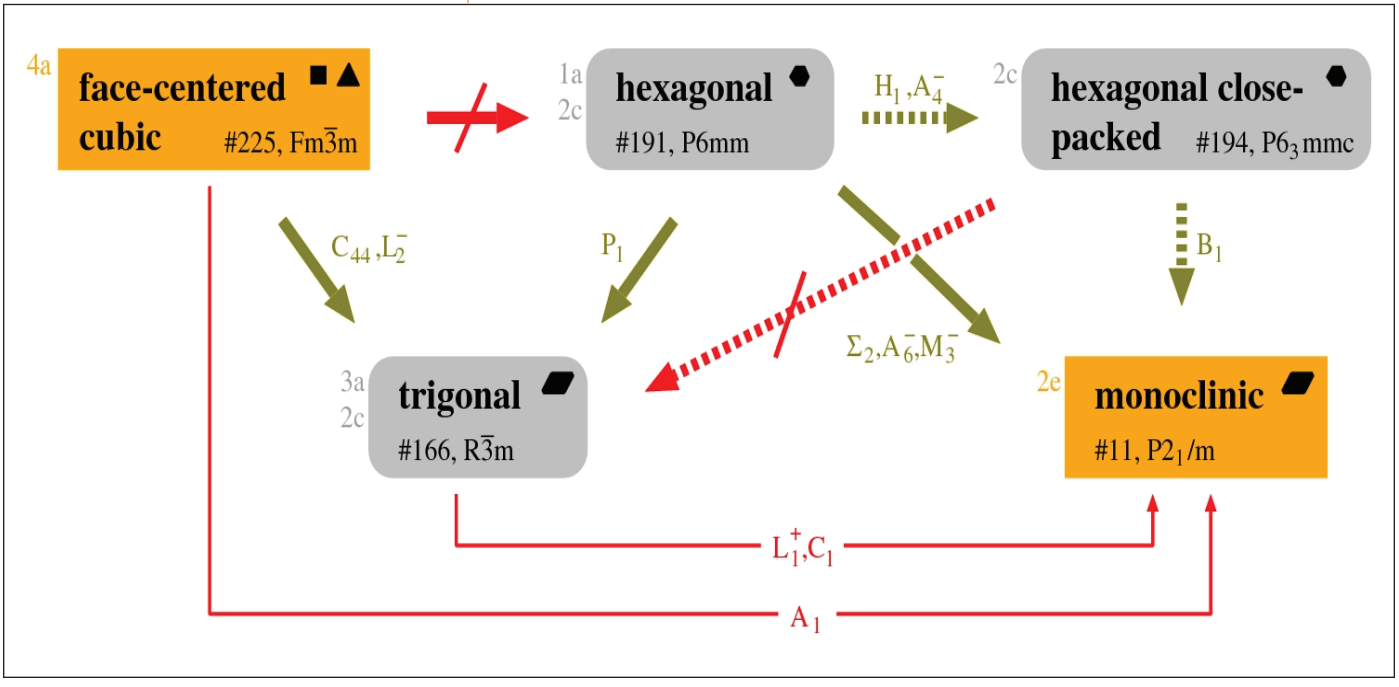
The phonon mechanism for δ ↔ (α) α′ phase transformation proposed by Turab Lookman, Avadh Saxena, and Robert Albers is shown below. The green arrows indicate displacive (martensitic) transformations between structures that are group–subgroup related. The crossed red arrows show reconstructive transformations between structures without any group–subgroup relation. An exhaustive search reveals that the displacive transformation between the face-centered cubic and monoclinic phases proceeds via intermediate trigonal and hexagonal structures. The labels attached to individual arrows indicate specific phonons that drive the corresponding transformation; the Wyckoff symbols of each structure are attached to the left of each box. (A Wyckoff symbol determines positions and multiplicity of atoms in the unit cell, e.g., "2c" means two atoms in the c positions.)

pathway. The atoms in the images 0 and M+1 are fixed and correspond to the initial and the target states of the system, while the remaining M movable images form the so-called elastic band. The atomic structure of each image is determined by the $3N$ positions of atoms, each of which is connected to its counterpart in the neighboring image by a linear spring to obtain a discrete representation of the transformation pathway. The coordinates of atoms in the M intermediate images are then determined by minimizing the total potential energy, represented by the objective function

$$\mathcal{S}(\{\mathbf{r}_{j=1,\ldots,N}^{(i=0,\ldots,M+1)}\}) = \sum_{i=1}^{M} E(\{\mathbf{r}_1^{(i)},\ldots,\mathbf{r}_N^{(i)}\}) + \sum_{i=1}^{M+1}\sum_{i=1}^{N} \frac{1}{2}k\left[\mathbf{r}_j^{(i)} - \mathbf{r}_j^{(i-1)}\right]^2$$

with respect to the positions of atoms in images. The potential energy E of every image i can be calculated readily by using empirical or semi-empirical potentials, in our case the MEAM potential for plutonium. The relaxed configuration corresponds to zero forces on all atoms due to the interatomic potential and is largely independent of the choice of the spring constant k. The obtained coordinates of atoms in images 1 to M can be used to search systematically for the symmetry, space group, and Wyckoff positions by using the Rietveld refinement. Importantly, the variation of the potential energy E along the elastic band provides a direct measure of the energy barrier that has to be surmounted to transform between the given crystal structures.



Plutonium crystal structure

These are the six ambient-temperature phases of plutonium and their crystal lattice structures:

α	alpha	simple monoclinic
β	beta	body-centered monoclinic
γ	gamma	face-centered orthorhombic
δ	delta	face-centered cubic
δ′	delta prime	body-centered tetragonal
ε	epsilon	body-centered cubic

The main goal of this project is to couple the NEB method with the semi-empirical MEAM potential for plutonium to elucidate the mechanism of structural phase transformations in elemental plutonium and its dilute alloys. The current calculations aim to determine the energy barriers for $\alpha \leftrightarrow \beta$, $\beta \leftrightarrow \gamma$, $\gamma \leftrightarrow \delta$ and $\delta \leftrightarrow \varepsilon$ phase transformations that are required for reliable formulation of the activation enthalpies and the free-energy functional of plutonium. The calculations of the energy barriers for $\alpha \leftrightarrow \beta$ with the β structure containing both 32 and 34 atoms and the subsequent comparison of the calculated photoemission spectra with experimental measurements will shed new light on the still controversial structure of the β phase.

Moreover, Los Alamos researchers Turab Lookman, Avadh Saxena, and Robert Albers of the Statistical Physics and Condensed Matter Group have recently proposed a phonon mechanism for the $\alpha(\alpha') \leftrightarrow \delta$ phase transformation in plutonium that is based purely on symmetry relations (group–subgroup) and which predicts an existence of intermediate trigonal and simple hexagonal phases. The existence of these intermediate structures, and thus the validity of this model, can be checked by examining the calculated transformation pathway between the α and δ phases. The same method will be used to investigate the influence of alloying on the transformation pathway and shape of the energy barrier between the α′ and δ phases.