

Nanostructured Actinide Materials: Lead-Plutonium Superlattices

Sven P. Rudin, T-1

The patterning of materials with nanometer-scale structures can strongly affect physical properties and in some systems even induce them. The effects change as the structural parameters vary, making it possible to fine-tune desired (or undesired) attributes. Such a fine-tuning could yield improved scientific understanding and greater technological control of actinide material characteristics. These characteristics frequently relate to the nature of the 5f electronic states as they vary from itinerant to localized. Designing nanostructures to tailor the 5f electron localization would allow fine-tuning of the associated properties.

Density Functional Theory (DFT) calculations on lead-plutonium (Pb-Pu) superlattices indicate that these form nanostructures with two competing phases strongly related to the alpha and face-centered cubic (fcc) phases of bulk plutonium. Unlike the bulk phases the superlattice phases transform into each other by an easily described distortion, the pairing of Pu planes (see Fig. 1). This pairing occurs with a volume collapse and a delocalization of the 5f electrons along the lines of the Mott transition associated with the bulk phases. Furthermore, the bond lengths between Pu atoms in paired and unpaired planes take on values very close to the short and long bonds of alpha-Pu, respectively.

Figure 1 shows unit cells of Pb-Pu superlattice geometries with itinerant 5f electrons. The layers of Pb atoms remain highly symmetric with equal distances between planes. The layers of Pu atoms

distort with neighboring planes pairing up especially for structures with even numbers of monolayers.

Figure 2 shows that the two superlattice phases appear equally favorable in energy for even numbers of monolayers, where for itinerant 5f electrons the Pu planes all pair up successfully. Calculations allowing localization of the 5f electrons let the system lower its energy without the distortions present in the itinerant case, resulting in a much less dramatic dependence of the energy on layer thickness. With increasing layer thickness the energy of the systems with localized 5f electrons tend towards the value obtained from averaging bulk fcc Pb and bulk fcc Pu (with localized 5f electrons). Similarly the volume shows little dependence on layer thickness.

The toxicity of both elements, the radioactivity of Pu, and shielding properties of Pb make Pb-Pu superlattices unlikely candidates for technological applications, but this system illustrates the rich potential in imparting actinide materials with nanostructures. The strong similarities between the two phases that appear in Pb-Pu superlattices and the alpha and fcc bulk phases of plutonium point to underlying principles that determine Pu's behavior as a solid. In particular the emergence of bond lengths between Pu atoms in paired planes that mirror the two ranges of the bond lengths found in alpha Pu is remarkable and evidence of one such fundamental principle.

For more information contact Sven Rudin at srudin@lanl.gov.

Funding Acknowledgements
 NNSA's Advanced Simulation and Computing (ASC), Enhanced Surveillance Program.

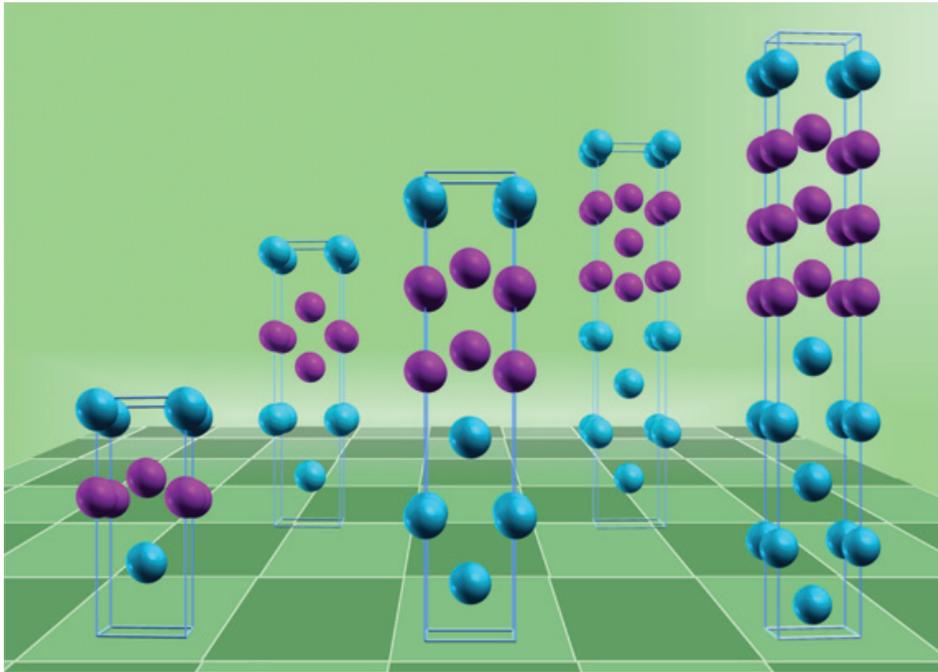


Fig. 1. Unit cells of Pb-Pu superlattice geometries with itinerant 5f electrons. Pb atoms are colored teal, while the Pu atoms are colored magenta. The foreground shows structures with even numbers of monolayers. For odd numbers of monolayers, not all planes can pair up and these frustrated systems cannot lower their energy enough to be favored.

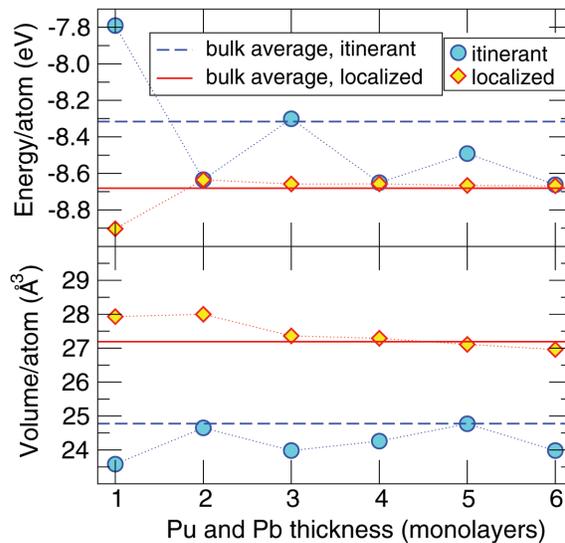


Fig. 2. Energies and volumes for Pb-Pu superlattices as a function of layer thickness and dependent on whether the 5f electrons are treated as localized or itinerant. The average energies and volumes stem from separate pure fcc Pu and pure fcc Pb calculations.