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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

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Phase Change in Uranium: Discrepancy Between Experiment and Theory

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Abstract

Using a diamond-anvil cell (DAC) phase transformation and room temperature Equation of State (EOS) for some actinides and lanthanides were studied to multimegabar (megabar = 100 GPa) pressures. Experimental data are compared with the theoretically predicted crystal structural changes and the pressure-volume relationships.

There is a general agreement between theory and experiment for the structural changes in the lighter actinides, however in detail there are some discrepancies still. A generalized trend for the phase transformations in the lanthanides can be seen, which again has broad agreement with theory.

We conclude that an accurate and robust theoretical base for predicting the phase transformations in the f-electron metals can be developed by incorporating the DAC data.

Introduction: Using a diamond-anvil cell (DAC) phase transformations and room temperature equation of state for uranium have been studied to multimegabar (megabar=100 GPa) pressures because it is an important weapons' related material and also to gain a better understanding for the high pressure behavior of 5f elements.^{1,2,3} Söderlind⁴ has recently performed total-energy calculations as a function of volume on uranium. However, both studies have arrived at differing conclusions with regard to structural phase changes in uranium. The purpose of this report is to examine the different conclusions arrived at in these two studies, and discuss what could be done to resolve the issue.

Experimental details

We used Mao-Bell type diamond-anvil cells.⁵ Diamond-anvils with 300 μm culet with 50 μm central flat and 7.5° bevel angle are used. The depleted uranium sample used for these experiments is from an electro-refined rod. X-ray diffraction data were obtained by the energy dispersive method at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory. The resulting accuracy in the calculated volumes from the crystallographic data ranges between 1–2 percent and the sample pressure measured *in situ* with platinum internal marker are accurate to ± 1 –1.5 GPa. A description of the DAC experimental procedures are detailed elsewhere.⁶

Results

Experimental:

Akella et al¹ in their first study of uranium have reported the appearance of two new reflections from an exploratory run made at 71 GPa compared to the ambient spectrum. They surmised further that this could be an indication for a structural phase change in uranium. However, in another study by Akella et al², to 100 GPa, no growth in the intensity of these lines was observed and also no conversion of the low pressure phase totally to a new high pressure phase was seen even at 100 GPa. This implied that the appearance of the "two new reflections" could be due to some other reason than a possible structural change.

A most recent study of uranium to multi-megabar pressure (Akella et al³) has reconfirmed the above observations to conclude further that indeed there is no high pressure structural change in uranium. Appearance of the "new reflections" is attributed to an anisotropic compression of the crystal axis a , b and c . In this context the following observations are relevant.

1. As pressure is increased, compression in the c axial direction is less than in a and b .
2. Beyond 70 GPa pressure the relative compressibilities of a and b axis flip and b becomes more compressible than a .
3. Initially the (021) and (022) reflections of the ambient orthorhombic uranium phase overlap each other. However, because the (021) line is compressing faster than the (002) line, as the pressure is increased the (002) line emerges from overlap with the (021) line. This accounts for one of the "new reflection," which actually is not due to a phase

change. The second reflection has a very low intensity and does not show any change.

4. Pressure range at which a/a_0 and b/b_0 axial ratios intersect (Fig. 1) is approximately the pressure at which theory predicts bct structure stable.

Theoretical Calculations

Eriksson and Johansson from Uppsala University, J.M. Wills and colleagues from Los Alamos National Laboratory, and Söderlind and Moriarty from Lawrence Livermore National Laboratory have extensively worked on theoretical calculations to predict the crystal structural changes and pressure volume relationships for actinides.

Wills and Eriksson,⁷ and Eriksson, et al.⁸ have done calculations for Th, Pa, and U, and Th, respectively. Söderlind, et al.⁹ extended these calculations to all the lighter actinides in order to develop a unified picture. These calculations were done by means of first-principles total-energy calculations using the linear 'muffin-tin' orbital method with a self-consistently calculated potential.¹⁰ The only input data for their calculation, as reported by them, are the atomic number, the crystal structure and the atomic volume.

In the case of thorium, Eriksson, et al.⁸ calculations could confirm the experimentally determined crystallographic phase transition from fcc $\rightarrow$ bct, albeit at a slightly high pressure 100 GPa versus experimental 72 GPa. For another lighter actinide Np, the structural sequence with increasing pressure from theory¹¹ was orthorhombic $\rightarrow$ (bct) $\rightarrow$ bcc. Calculations failed to predict a stability region for the bct neptunium phase, however experimental data showed an intermediate phase between the orthorhombic and the bcc, which has a narrow stability region and is

considered to be a body-centered tetragonal structure (experiments for a positive reconfirmation are planned).

The predicted crystal structure sequence from theory for uranium is α u (orthorhombic) $\rightarrow$ bct $\rightarrow$ bcc. The first transformation from α u to body-centered tetragonal phase is predicted to be at 80 GPa pressure. As was mentioned already, experimentally in uranium no phase change could be detected even up to multi-megabar pressures at room temperature.

The fortuitous intersection of the a/a_0 and b/b_0 axial ratios at about 100 GPa pressure is approximately the pressure at which bct structure was predicted. However, unfortunately this observation does not confirm the theoretically predicted orthorhombic to bct structural phase change in uranium.

Discussion:

Even though there is a general agreement between theory and experiment for the structural changes in the lighter actinides, there are discrepancies still in detail. They need to be resolved for a better agreement, so that theory can predict materials' properties to tens of megabar pressures.

The discrepancy between theoretical prediction and the experimental observation regarding the structural change in uranium is noteworthy. Söderlind, et al⁴ used fixed values of b/a and c/a (as observed at ambient pressure) in their total energy calculations on the orthorhombic phase. Presumably, optimized b/a and c/a values would lower the orthorhombic total energy at high pressure, possibly eliminating the intermediate bct phase. It is also interesting to note that so far uranium is the only lighter actinide which does not go through a structural phase change at room temperature and high pressures.

If the structural change is an extremely sluggish phase transformation at room temperature, possibly it could be missed experimentally. In such a case, if experiments are conducted at slightly elevated temperatures (e.g. ohmic heating), the transformation may be accelerated. A concurrent effort to do theoretical calculations utilizing the experimentally determined axial and volume compression data (Fig. 2) under pressure could resolve the structural transformation discrepancy, and may also shed light on the differences in the high pressure behavior of uranium compared to other lighter actinides.

Acknowledgments

The authors would like to thank Drs. John Moriarty, Richard Grover, John Wills, Olle Eriksson, Per Söderlind, and Börje Johansson for critical discussions. Funding for this work is provided by the B-Division at Lawrence Livermore National Laboratory under DAC actinides research project. We are grateful to Drs. Bruce Goodwin and Mike Anastasio for their constant encouragement and financial support. Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

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Figure Captions:

Fig. 1 The axial ratios for uranium plotted as a function of pressure. Note the change in the relative compressibilities of a and b axis.

Fig. 2 Volume compression data V/V_0 plotted against pressure.

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