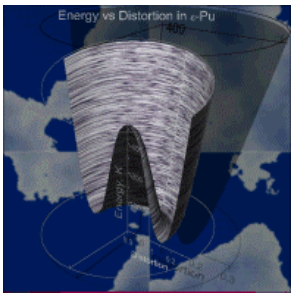
Phonons and Phases of Plutonium

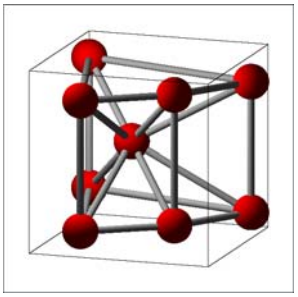


Cooperative Research Team on

Predictive Capabilities for Strongly Correlated Systems

Abstract

Plutonium, a key element of the energy industry is not well studied either experimentally or theoretically due its toxicity, radioactivity, and importance of many body electronic correlations. We develop a new approach to study its properties based on a combination of dynamical mean field and linear response theories. This allows us for the first time to look into vibrational spectra of Pu. Very recently our predictions have been confirmed experimentally.



Plutonium (Pu) is a material with very unusual solid-state properties. Despite its scientific and technological importance, many of its key properties, such as the spectrum of lattice vibrations, remain uninvestigated. It has not been possible to measure that spectrum experimentally because of Pu's extreme toxicity and radioactivity. It has not been possible to compute the spectrum theoretically, because Pu is strongly correlated, and the traditional electronic structure methods fail to describe it even qualitatively. These studies are, however, essential to be able to address the factors that govern the lattice stability of Pu, an issue that is important for Pu's storage and disposal over long time scales.

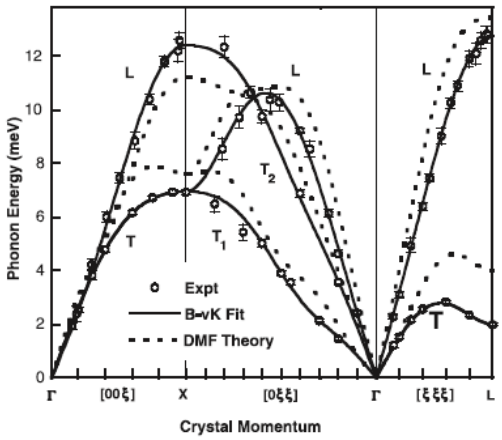


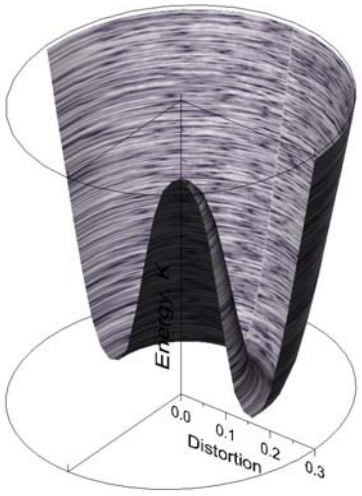
Fig. 1 Measured phonon frequencies of δ-Pu (circles connected by full lines), which have confirmed our theoretical predictions [2] (dashed lines). Data are reproduced from the experimental work [3].

In order to treat structural, spectroscopical and lattice dynamical properties of materials such as Pu we have developed an *ab initio* approach which takes into account many-body Coulomb correlations among the electrons [1]. Our method allows us to include dynamical self-energy effects in calculating total energies, spectra, and phonon dispersions [1,2]. Its foundation is provided by the dynamical mean field theory (DMFT), which treats systems with competing localization and delocalization tendencies of the electrons, where such methods as the density

functional theory in its local density approximation (LDA) or generalized gradient approximations (GGAs) have limited applicability.

Fig. 1 shows a comparison between calculated by us (dashed lines) phonon dispersion relations for the delta-phase of Pu (May 9, 2003 issue of ***Science,*** [2]) which only very recently were confirmed (circles) by the experiments conducted in Lawrence Livermore National Laboratory (August 22, 2003 issue of ***Science***, [3]).

Fig. 2 Total energy vs. distortion for one of the soft phonon modes in ε-Pu which reveals a double well behavior and highlights the importance of anharmonic effects. After [2].



We have further studied the lattice dynamical properties of the highest temperature bcc phase of Pu, which is called ε-phase. Several soft phonon modes has been predicted which point out that ε-Pu has strongly anharmonic lattice vibrations. Corresponding total energy calculation using dynamical mean field method reveals a double well behavior (See. Fig. 2) and emphasizes the importance of the phonon entropy in understanding variety of structures in the phase diagram of Pu.

References

[1] S. Savrasov, G. Kotliar, and E. Abrahams, "Electronic correlations in metallic Plutonium within dynamical mean-field picture", Nature **410**, 793 (2001).

[2] X. Dai, S. Y. Savrasov, G. Kotliar, A. Migliori, H. Ledbetter, E. Abrahams "Calculated Phonon Spectra of Plutonium at High Temperatures", Science **300**, 953-955 (2003).

[3] J. Wong, M. Krisch, D. L. Farber, F. Occelli, A. J. Schwartz, T.-C. Chiang, M. Wall, C. Boro, R. Xu, "Phonon Dispersions of fcc-Plutonium-Gallium by Inelastic X-ray Scattering", Science **301**, 1078-1080 (2003).

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