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Lattice dynamics and thermodynamics of light actinides

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Abstract

In this paper, we present an *ab initio* study of the lattice dynamics of two light actinides, namely thorium and uranium. We worked within the framework of the quasi-harmonic approximation and by using density-functional theory, pseudo-potential method and linear response theory. We compare the phonon spectrums we obtained with inelastic neutron-scattering experiments.

Keywords: Actinides; Phonons

1. Introduction

Details about the phonon-dispersion relationships of actinides are very limited. For 30 years, experimental data were only available for Th and U. But recently, several works, using inelastic X-ray scattering, mostly on U [1,2] and Pu [3] have been published. Theoretical works are needed to tackle the f-electrons systems elastic properties. Unfortunately, these calculations are far from straightforward. The most important problem comes from the difficulty to treat correctly the f-electrons. To our knowledge, there is only one spectrum for a f-element beyond the semi-empirical methods, which was obtained by Dai et al. [4] using dynamical mean field theory (DMFT) on fcc plutonium.

In the harmonic approximation, the crystal free energy is built by adding to the 0 K isotherm a dynamical contribution which is approximated by the free energy of a system of harmonic oscillators. A step beyond the harmonic approximation can be made by allowing phonon frequencies to depend on crystal volume, the so-called quasi-harmonic approximation. Here, we apply the quasi-harmonic approximation to the study of the thermal properties of Th metal, such as thermal expansion, bulk modulus or Debye temperature. We show also the phonon spectrum of U.

2. Computational details

Our calculations are performed within the generalized gradient approximation (GGA) to density-functional theory, as implemented in the ABINIT package [5,6]. Technical details on the computation of responses to atomic displacements can be found in Ref. [7] while Ref. [8] presents the subsequent computation of dynamical matrices and interatomic force constants.

The pseudo-potentials used in this work and their generation have been presented in Ref. [9]. They are norm conserving Trouillier and Martins [10] using GGA according to the recipe of Perdew et al. [11]. It has been shown that GGA represents a significant improvement on local density approximation (LDA) for f-elements. The kinetic energy cut-off of the plane wave bases is 160, 180 and 220 Ry for Th, U and Pu respectively. With these cut-offs, energy differences are converge within 1 mRy/at, and phonon frequencies within 0.01 T Hz. A Gaussian smearing of 0.02 Ry has been applied for Brillouin Zone integrations, which results in a metallic correction less than 0.1 mRy/at. In the electronic structure calculations, the exchange-correlation functional was consistent with the one used for the pseudo-potential generation.

3. Results and discussion

3.1. Thorium

We start with thorium which is the first 5f element with one electron f in the valence shell. The vibrational frequencies of Th were determined at several volumes within linear response framework. Dynamical matrices are computed at 19 wave (**q**) vectors in the irreducible wedge of BZ, i.e., on a $8 \times 8 \times 8$ **q** grid, and are used for interpolation to obtain the bulk phonon dispersions. We present in Fig. 1, the phonons spectrum we ob-

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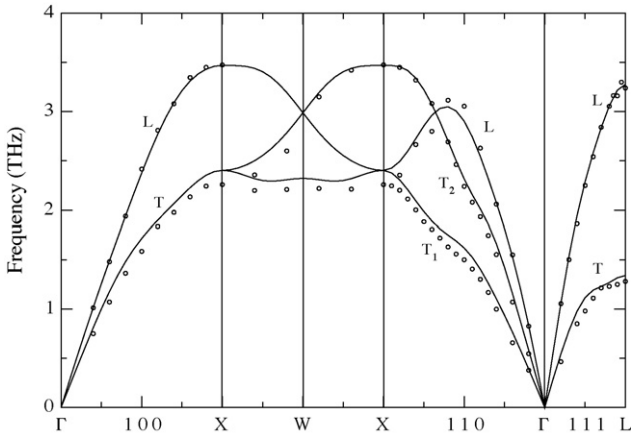

Fig. 1. Calculated phonon dispersion curves for fcc Th at the lattice parameter corresponding to static equilibrium. Experimental neutron-scattering data [12] are denoted by circles.

tained along several symmetry directions at zero pressure conditions. The neutron-scattering data obtained by Reese et al. [12] at room temperature are shown for comparison. The calculations reproduce really well the kinks observed in the T_1 and T_2 branches in the [1 1 0] direction. We have also calculated the phonons spectrum of Th in the bct structure. The results are presented in Fig. 2, and compared to the phonon dispersions of fcc. The T_1 branch strongly softens during the phase transition in fcc and becomes imaginary (plotted with negative values) near the Γ point, in contrary, the frequencies of this branch increase with pressure in bct. This observation indicates that the fcc structure at this pressure is dynamically unstable.

Using the quasi-harmonic approximation, we have calculated the linear thermal expansion coefficient, α_L. The value we obtained at room temperature, $10 \times 10^{-6}\,K^{-1}$ [13] is very closed to the experimental value of $11 \times 10^{-6}\,K^{-1}$ [14].

3.2. Uranium

The discovery of several charge density waves transition at low temperature in U is closely related to neutron-scattering experiments [15,16]. They showed that α-U has very unusual dispersion curves in the [1 0 0] direction. In particular, the longitudinal optic-like mode, Σ_4 shows a pronounced dip around [0.5, 0, 0]. The frequency of this mode decreases considerably with temperature [15,16]. At 70 K, it even contains an elastic component. Smith et al. concluded that the unit cell is doubled along the [1 0 0] direction and that a periodic lattice distorsion has taken place.

In Fig. 3, we compare our results at 0 K to the neutron-scattering data obtained at room temperature. Let us mentioned that we found no influence of the spin–orbit coupling term on the phonon frequencies. We have followed the notation of Crummett et al. [15] to label the branches. As for thorium, the results are close to the experiments. The dip in the Σ_4 mode is well reproduced. We found a more pronounced dip in the Σ_1 branch than the one observed experimentally. This suggest that this branch is also strongly temperature-dependent. The motions associated with the lower Σ_1 mode are primarily longitudinal acoustic-like

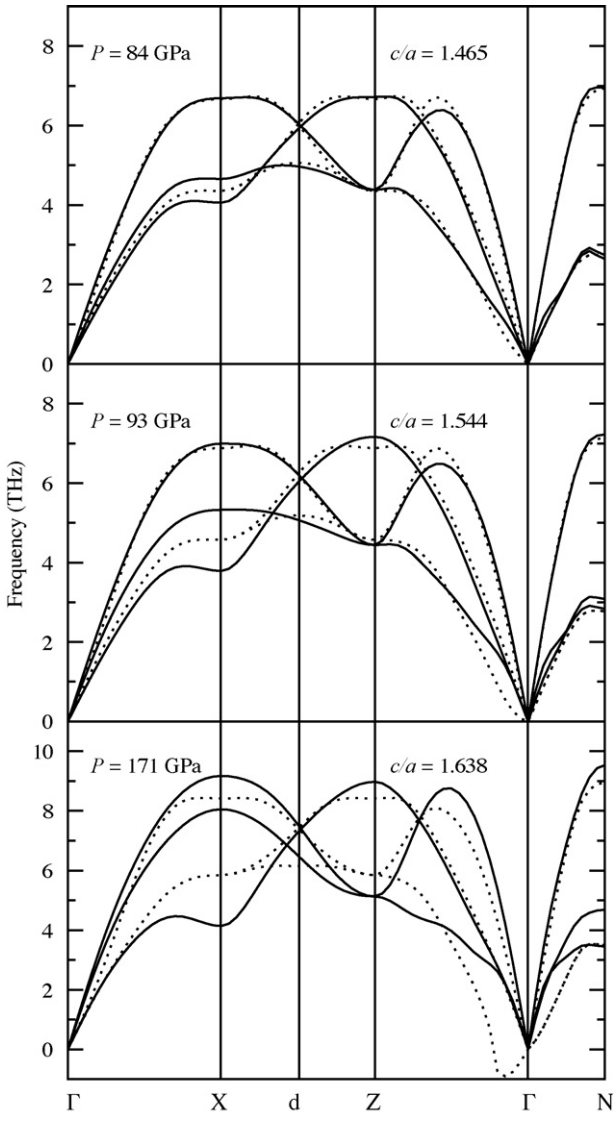

Fig. 2. Calculated phonon dispersion curves for bct (solid lines) and fcc (dashed lines) Th for pressures and c/a ratios in the transition region. The symmetry directions are those of fcc, the corresponding ones for bct are Γ-X-W-X-Γ-L.

[15]. Therefore, Σ_4 and Σ_1 corresponds to out-of-phase and in-phase atomic displacements in the x-direction, respectively. The phase associated with the atomic motions involved in the CDW in the x-direction is $(99 \pm 3)^\circ$ [17]. The motion is essentially optic (90°) but the acoustic part cannot be neglected and is reproduced in the softening observed in the Σ_1 branch. The discrepancies we found between the theoretical and experimental spectrums are for branches related to an atomic motion in the x-direction, as Δ_4 and Λ_2. This is the direction where the largest atomic displacement occurs in the CDW, almost six times larger than the motions in y- and z-directions [18].

3.3. Conclusion

Phonon spectrum of the light actinides are now accessible with density-functional perturbation theory. We can now explore the phases diagrams of this class of materials in the framework of the quasi-harmonic approximation and obtain thermodynamic

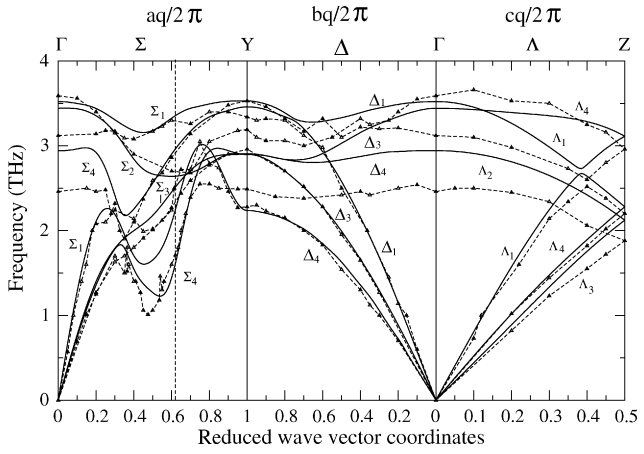

Fig. 3. Calculated phonon dispersion curves for α-U at the lattice parameter corresponding to static equilibrium. The triangles are experimental neutron-scattering data [15].

quantities. This is very important since experiments are really difficult to realize in this class of materials.

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