High-pressure lattice dynamics and thermodynamic properties of Th:
An *ab initio* study of phonon dispersion curves

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Phonon dispersion curves and thermodynamics of actinides are hardly accessible for both theory and experiments. In this paper we present an *ab initio* study of the thermodynamics properties of thorium within the framework of the quasiharmonic approximation and by using density-functional theory and the pseudopotential method. First we compare the phonon spectrum we obtained at zero pressure with inelastic neutron scattering experiments. Thereafter we use the phonon dispersions to obtain the *PVT* equations of state and derive thermodynamic quantities from the free energy. Then we compare our results for the thermal volume expansion, bulk modulus, heat capacity, or Debye temperature with experimental values when existing. The results show a promising agreement with experiment and propose several predictive behaviors.

I. INTRODUCTION

Despite general interest in *f*-electron elements, details about their phonon-dispersion relationships are very limited. Experimentally, this fact is due to the great difficulty of realizing such experiments. The usual technique for the study of phonons, based on neutrons scattering, needs crystals large enough and isotopes with a small neutron absorption cross section. Lanthanides and actinides hardly fulfill these two conditions, not to mention the radioactivity of some of them. But recently, a new hope has emerged with several works, using inelastic x-ray scattering, mostly on U Refs. [1] and [2] and Pu.[3,4] Nevertheless all these experimental issues show that theoretical works are needed to tackle the *f* electrons systems elastic properties. Unfortunately these calculations are far from being straightforward. Theoretically, the most important problem comes from the difficulty to treat correctly the *f* electrons and the relativistic effects needed in such heavy materials. Some attempts have been made, using effective or model potentials,[5–7] but all these works bring limited improvement in the understanding of elastic properties of *f* materials. To our knowledge there is only one spectrum for a *f* element beyond the semiempirical methods, which was obtained by Dai *et al.*[8] using dynamical mean field theory (DMFT) on fcc plutonium. This first step brought new ideas and new insight into lattice dynamical properties of Pu and more generally into *f* electrons behavior. But the difficulty to treat the strongly correlated *f* electrons, of fcc Pu, and the approximations made to handle this problem limited the conclusions of these results. In fact, compared to experiments, the theoretical spectrum shows large discrepancies, mostly in the [111] direction, where the difference between theory and experiments is about 20% for the frequencies of L mode.

Th is fcc in its equilibrium structure. Under pressure it undergoes a transition toward a body centered tetragonal structure (bct) around 60 GPa[9] and this structure is found stable until at least 300 GPa. Th is usually compared to Ce metal because they both begin a series of *f* elements and crystallize in the fcc (*α*) near ambient conditions. Furthermore, under pressure Ce adopts a bct structure with similar internal parameters and, as in Th, this structure has a very wide range of stability. For both metals there is an increase of the *f* occupation as a function of pressure[10] so it is not surprising to find bct, the equilibrium structure of the following element in the periodic table, namely Pa.

Density functional perturbation theory (DFPT) is a well-established tool for calculating the vibrational properties from first principles in the framework of the harmonic approximation. The crystal free energy is easily built in this approximation by adding to the phonon contributions the 0 K isotherm, accessible to standard density functional theory (DFT) calculations. A step beyond the harmonic approximation can be made by allowing phonon frequencies to depend on crystal volume, the so-called quasiharmonic approximation. This approach has been shown to give an accurate description of the thermodynamic quantities of many bulk materials below the melting point. Taking into account the anharmonic effects through the volume dependence gives access to thermal expansion, phase transition, and crystal stability. In the past 10 years few *ab initio* calculations of the thermodynamics of metallic systems have been published. Results have been obtained on simple metals,[11] silver[12] or tungsten,[13] or intermetallics. Never on *f*-electron elements.

In this paper we apply the quasiharmonic approximation to the study of the thermal properties of Th metal, such as thermal expansion, bulk modulus, or Debye temperature. To proceed we first calculated the phonon dispersion curves as a function of volume by using DFPT for both fcc and bct structures. Our results demonstrate the validity of this parameter-free method.

The paper is organized as follows. In Sec. II we give some equations for the thermodynamic properties in the framework of the quasiharmonic approximation, next in Sec. III we give the details of the calculations. Sec. IV is devoted to our results, their comparison with the available experimental values, and the discussion. Finally, in Sec. IV we give our conclusions to this work.

II. THEORY

In the quasiharmonic approximation the Helmholtz free energy is given by

$$F(V,T) = E(V) + F_{vib}(V,T), \qquad (1)$$

where E is the static contribution to the internal energy, i.e., the cold curve energy at the volume V, while

$$F_{vib}(V,T) = k_B T \sum_{q,j} \ln \left\{ 2 \sinh\left(\frac{\hbar \omega_j(\mathbf{q})}{2 k_b T} \right) \right\} \qquad (2)$$

represents the vibrational contribution to the free energy. $\omega_j(\mathbf{q})$ is the frequency of the jth phonon mode at wave vector $\mathbf{q}$ and depends on the unit-cell volume and the masses of the constituent atoms. We assume that all temperatures of interest in this work are well below the electronic energy scale and so we have neglected the contribution of electronic excitations. The equation of state is given by the definition of pressure

$$P = -\left(\frac{\partial F}{\partial V} \right)_T. \qquad (3)$$

By derivating Eq. (1) and using Eq. (2) we obtain the expression for the pressure

$$P(V,T) = -\frac{\partial E}{\partial V} - \sum_{q,j} \frac{\hbar}{2} \frac{\partial \omega_j(\mathbf{q})}{\partial V} \coth\left(\frac{\hbar \omega_j(\mathbf{q})}{2 k_B T} \right). \qquad (4)$$

Introducing the mode Grüneisen parameter $\gamma_j(\mathbf{q})$

$$\gamma_j(\mathbf{q}) = -\frac{V}{\omega_j(\mathbf{q})} \frac{\partial \omega_j(\mathbf{q})}{\partial V} \qquad (5)$$

and $\langle \varepsilon[\omega_j(\mathbf{q})] \rangle_T$ the mean vibrational energy corresponding to the $(\mathbf{q}, j)$ phonon

$$\langle \varepsilon[\omega_j(\mathbf{q})] \rangle_T = \frac{\hbar \omega_j(\mathbf{q})}{2} \coth\left(\frac{\hbar \omega_j(\mathbf{q})}{2 k_B T} \right) \qquad (6)$$

we obtain the well-known[14] expression for the equation of state

$$P(V,T) = -\frac{\partial E}{\partial V} + \frac{1}{V} \sum_{q,j} \gamma_j(\mathbf{q}) \langle \varepsilon[\omega_j(\mathbf{q})] \rangle_T. \qquad (7)$$

We can see from Eq. (5) that the Grüneisen parameter expresses the volume dependence of the phonon frequencies, without this term there would be no thermal contribution to the free energy and so no thermal expansion of the crystal (harmonic approximation). The volume thermal expansion coefficient is defined as

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{B} \left(\frac{\partial P}{\partial T} \right)_V, \qquad (8)$$

where we have introduced the isothermal bulk modulus $B \equiv -V(\partial P / \partial V)|_T$. The anharmonicity enables us to differentiate the heat capacity at constant volume C_V from the heat capacity at constant pressure C_P. The relation between C_P and C_V is

$$C_P - C_V = \alpha_V^2(T) B V T \qquad (9)$$

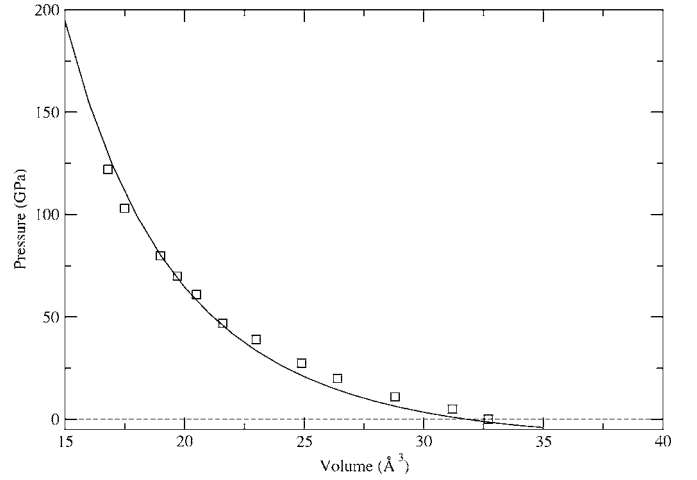and $C_V = \sum_{q,j} \partial \varepsilon[\omega_j(\mathbf{q})] / \partial T|_V$ is given by

FIG. 1. Equation of state for Th. Experimental results are marked with open squares, theory is given by the solid line.

$$C_V = k_B \sum_{q,j} \left(\frac{\hbar \omega_j(\mathbf{q})}{2 k_b T} \right)^2 \frac{1}{\sinh^2[\hbar \omega_j(\mathbf{q}) / 2 k_b T]}. \qquad (10)$$

We can deduce from Eq. (9) the vibrational entropy in the quasiharmonic approximation:[14]

$$\Delta S = S_p - S_V = \int_{T_1}^{T_2} \frac{C_p - C_V}{T} dT = \alpha_V^2(T) B V \Delta T. \qquad (11)$$

III. COMPUTATIONAL DETAILS

Our calculations are performed within the generalized gradient approximation (GGA) to density-functional theory, as implemented in the ABINIT package.[15,16] Technical details on the computation of responses to atomic displacements can be found in Ref. 17 while Ref. 18 presents the subsequent computation of dynamical matrices and interatomic force constants.

The pseudopotential used in this work and its generation have been presented in Ref. 19. It is a norm conserving Trouillier-Martins[20] using the GGA according to the recipe of Perdew, Burke, and Erzhof (PBE96).[21] It has been shown that GGA represents a significant improvement on local density approximation (LDA) for f elements. The kinetic energy cutoff of the plane wave bases is 160 Ry. With this cutoff, energy differences converge within 1 mRy/at, and phonon frequencies within 0.01 THz. 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 calculation, the exchange-correlation functional was consistent with the one used for the pseudopotential generation.

IV. RESULTS AND DISCUSSION

A. Static lattice

Figure 1 shows the equation of state $P-V$ for Th at 0 K. Our conclusions are similar to those found in Ref. 19 so we will just summarize the main results in this work. We obtain
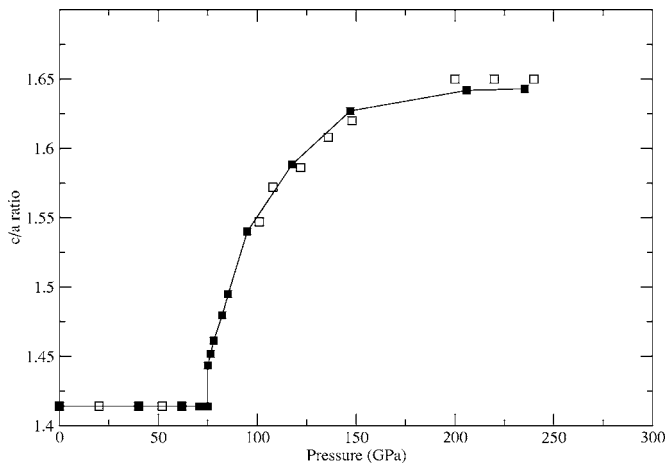
FIG. 2. Variation of c/a ratio in the bct structure for theory (closed squares) and experiment (open squares). The value $c/a = \sqrt{2}$ corresponds to fcc structure.
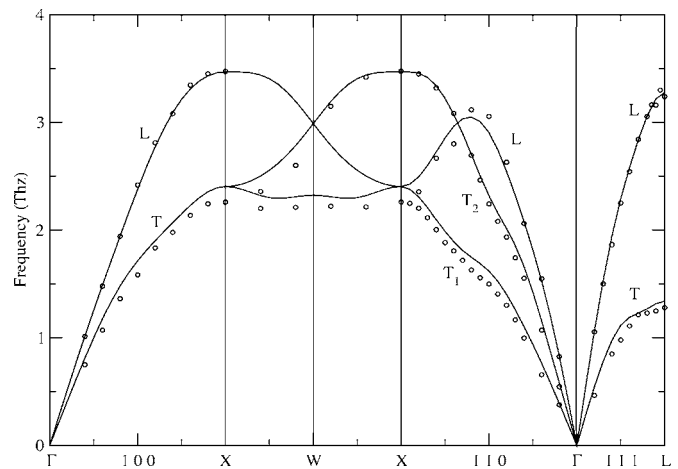

FIG. 3. Calculated phonon dispersion curves for fcc Th at the lattice parameter corresponding to static equilibrium. Experimental neutron-scattering data (Ref. 25) are denoted by circles.

an equilibrium volume of 31.7 $Å^3$ compared to the experimental value of 32.8 $Å^3$,[22] and a bulk modulus of 56 GPa, compared to the experimental value of 58 GPa.[23] The transition pressure between fcc and bct is found to be around 75 GPa, a value comparable to the experimental value of 63 GPa.[9] We performed careful calculations to analyze the nature of the transition between fcc and bct. Around the transition pressure the enthalpy difference between fcc and bct is very small, close to the uncertainty of the calculations, so it is difficult to be categorical. The values we obtained for c/a in the function of pressure are presented in Fig. 2 and compared with the experimental ones. The agreement is very good and the transition region between $c/a = \sqrt{2}$ and $c/a = 1.65$ is really well-reproduced. We found a first order transition, with a discontinuity in the values of c/a. This ratio jumps from the value $\sqrt{2}$ (corresponding to fcc) to 1.44 at a pressure of 75 GPa, before this pressure, $\sqrt{2}$ is the optimized value. The discontinuity in the volume we observed is really small, less than 0.1%, as found experimentally.[9] Our conclusions are consistent with Anderson's theorem, who have shown in the framework of Landau's theory of phase transitions that a cubic to tetragonal transition can only be of first order.[24] Concerning the spin-orbit (SO) coupling, we have checked its influence on the GGA results. The volume is just improved, $V = 32.30$ $Å^3$, but the bulk modulus is worse $B = 51.3$ GPa. We considered the effect of the SO coupling as negligible for the ground state properties of Th, a conclusion already reached in other works.[19]

B. Lattice dynamics

The vibrational frequencies of Th were determined at several volumes within the 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. In Fig. 3 we display the phonon dispersion curves as calculated along several symmetry directions at zero pressure conditions (equilibrium volume). Our results are in very good

agreement with neutron-scattering data at ambient condition.[25] All the kinks, specially in the transversal modes in the [110] direction, are nicely reproduced. Let us mention that to observe these features it is crucial to have a thorough q-point sampling. It is worthwhile to emphasize that these features were not observed in the previous theoretical works,[5,6] so an adequate description of the ions motion in DFPT is really necessary. As already mentioned by Reese *et al.*, the interatomic force constants drop off really rapidly for Th, the first-neighbor force constants are over 10 times as large as any other force constants. These large first-neighbor interactions are mainly due to the spatial extent of the f-electron wave function around each atom, an observation already used by Harrison[26] to calculate the phonon spectrum of Pu by taking into account only the nearest-neighbor interactions. The result of this effect is a very simple spectrum for Th with any pronounced structure, contrary to what is found in lead which is the closest fcc element to Th, but with s and p electrons in the valence states. On the other hand, materials with a strong d character, as noble metals or Ni,[27] show a spectrum similar to Th and interatomic force constants with nearly the same behavior. These strong and directional first neighbor interactions are typical of light actinides where the bonding is dominated by the f bands.[28]

Reese *et al.*[25] found two distinct anomalies in the T_1 and T_2 branches along the [011] direction, situated at $(2\pi/a) \times (0, 0.7, 0.7)$ and $(2\pi/a)(0, 0.5, 0.5)$, respectively, see Fig. 3. However, they could not conclude on the presence of a similar anomaly in the L branch for this direction. Our theoretical spectrum helps to solve these experimental questions. Since we reproduce quite accurately the shape and the positions of the dips of the T_1 and T_2 branches and we found no anomalous behavior in the L branch, we can affirm that the difference in shape between the longitudinal and transverse branches along [110] was not an experimental artifact.

To compare the phonon spectrum of fcc Th with the other actinides we can make some comments on the recent results obtained on plutonium.[3,8] What is interesting is that the kink for T_1 has been found in δ fcc Pu-2 at. % Ga,[3] although differently located along the symmetry direction. Wong

TABLE I. Elastic constants in GPa for Th. The experimental data have been obtained at 77 K.

	This work	FPLMTO (Ref. 29)	Expt. (Ref. 30)
C_{11}	86.0	55.3	77.7
C_{12}	39.5	35.3	48.2
C_{44}	58.4	45.9	51.1
C'	23.3	10.0	14.8

et al.[3] attributed this kink to Kohn anomalies and electronic effects. A conclusion refuted by Harrison and his model.[7] We cannot conclude on the origin of this anomaly for Th as it is still the subject of strong debate and more detailed analysis of the electron-phonon interactions in the actinides are necessary. The kink in T_2 is not present in the experimental and the theoretical spectrums of Pu, but there is not enough points in the spectrums to be conclusive. Concerning the softening of the transverse phonons around the L point found in Pu but also in two other fcc materials, Ce and La, we found nothing similar in Th. This feature has been attributed to a transition between fcc and hcp-type structures and there is no such transition in the phase diagram of Th.

DFPT calculations including the SO coupling were performed, any notable differences were found in the phonon spectrum. Its influence is negligible on the phonon frequencies (~ 0.01 THz), as it was for the ground state properties.

We can obtain the elastic constants of Th from the phonon spectrum. Our results are presented in Table I and compared to the results obtained with the *full potential linear muffin-tin orbitals* (FPLMTO) method[29] and the experimental data.[30] Our results show an average error of about 15% compared to experiment, similar to the previous results obtained for Th and in other metals. The elastic constant C' is too large in our calculations. This is consistent with the overestimation of the transition pressure between fcc and bct since C' is directly related to the energy difference between the two structures.

We have calculated the phonon spectrum of Th for different pressures to follow this effect, the results we obtained are shown in Fig. 4 for 4, 20, and 60 GPa. The kink in T_1 and T_2 is still present at high pressure, smoother because the slope of the branch is steeper.

Dispersion curves for mode Grüneisen parameters at zero pressure are shown in Fig. 5. The dispersions are discontinuous at the BZ center, a consequence of the anisotropy and polarization dependence of the sound velocities. The Grüneisen parameters are found to be positive throughout the BZ for all branches, suggesting that there is no anomalous negative thermal expansion.

To go further we have also calculated the phonons spectrum of Th in the bct structure, for several pressures in the transition region and different c/a ratios. The results are presented in Fig. 6, where we have indicated the symmetry directions of bct, the corresponding directions for fcc are $\Gamma - X - W - X - \Gamma - L$. We have also shown the phonon dispersions of fcc for comparison. Except for the appearance of more branches due to the lower symmetry of bct, the main difference is situated in the [110] direction. The T_1 branch
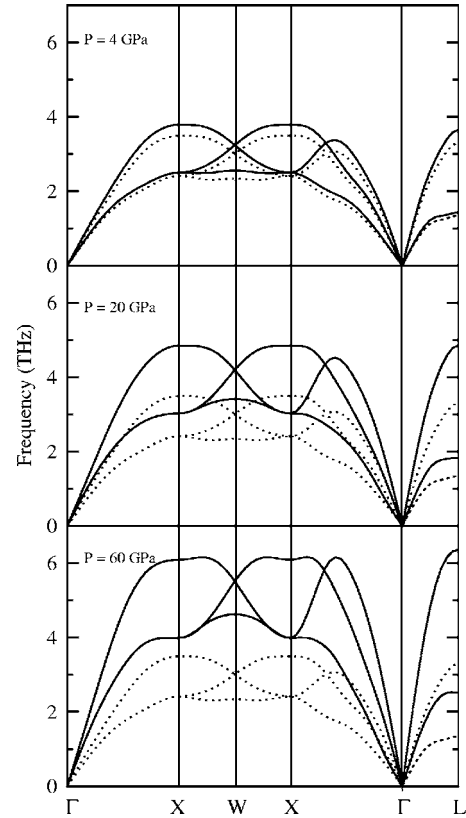

FIG. 4. Calculated phonon dispersion curves at 4, 20, and 60 GPa. The spectrum at 0 GPa is given by the dashed lines for comparison.

strongly softens during the phase transition in fcc and becomes imaginary near the Γ point, on the contrary, the frequencies of this branch increase with pressure in bct. The T_1 mode is directly related to the elastic constant C' which measures the rigidity of the cubic cell against a tetragonal deformation. If fcc is unstable against a tetragonal distortion C' is negative and the T_1 branch is imaginary near the Γ point. We found fcc dynamically unstable, but at a pressure higher than the transition pressure, see Fig. 6. A result consistent with a first order transition between fcc and bct since there is a
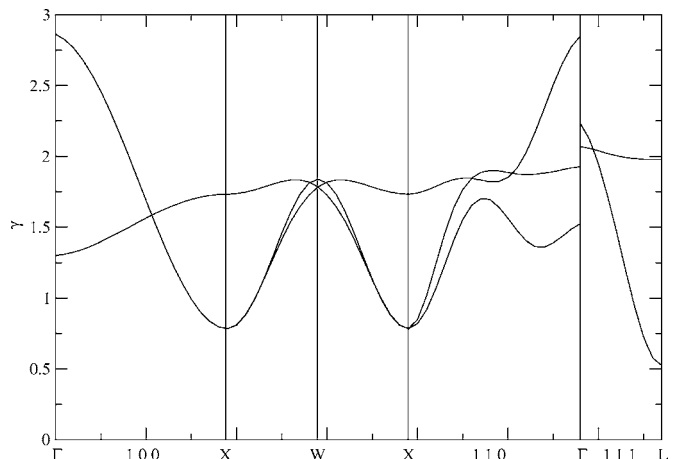

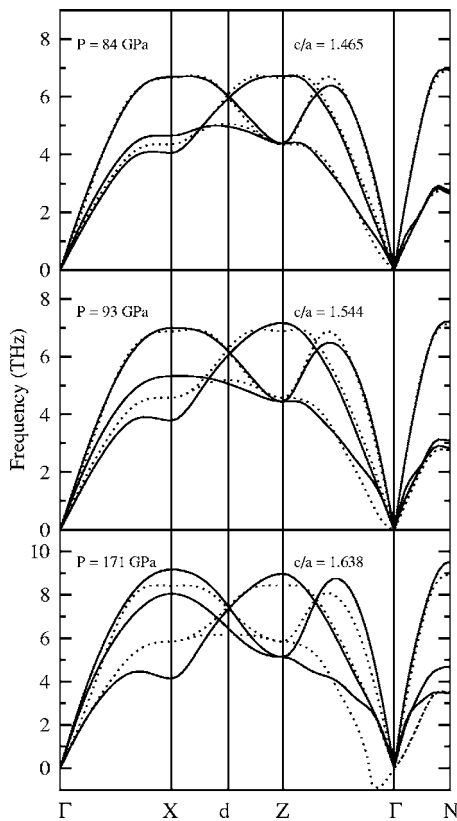FIG. 5. Mode Grüneisen parameters at zero pressure.

FIG. 6. 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 $\Gamma-X-W-X-\Gamma-L$.

range of pressure where fcc and bct are both dynamically stable.

C. Thermodynamic properties

Knowing the variations of the phonons frequencies with the volume we can now obtain the *equation of state* via Eq. (7). Figure 7 shows the pressure as a function of the volume for several temperatures. The intersection between the curve and the $P=0$ line gives the equilibrium volume V_0 for each temperature. We can see that the room temperature value of the equilibrium volume (32.0 Å^3) is in better agreement with the experimental one than the $T=0$ curve. In the inset we show also V_0 as a function of T. The volume increases linearly in the range of temperatures considered here. The linear thermal expansion coefficient can be obtained using Eq. (8), the results are shown in Fig. 8. α_L increases exponentially with T at low temperatures to reach a nearly constant value around 150 K. The value we obtained at room temperature is very close to the experimental value of 11.2×10^{-6} K^{-1},[31] and close to the value of 12.3×10^{-6} K^{-1} obtained by Söderlind et al. using a quasiharmonic Debye-Grüneisen model.[32] We see also that the effect of the pressure is to reduce the thermal expansion as observed in other materials.[33,34] The variation of the bulk modulus with pressure is shown in Fig. 9. B increases almost linearly with P.
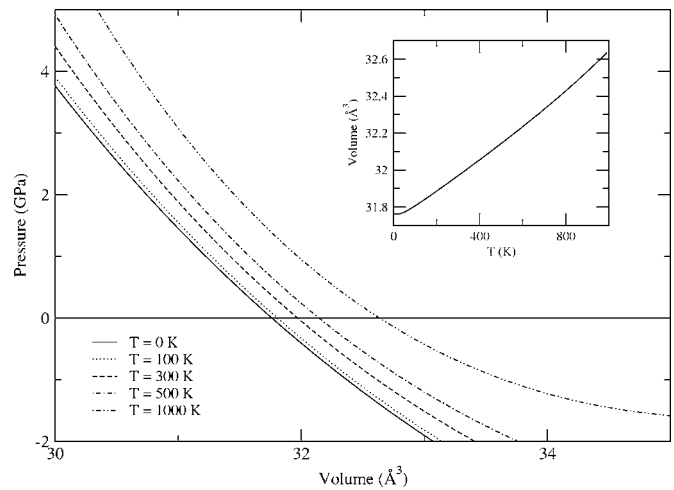

FIG. 7. Calculated equation of state of Th for different temperatures. The inset shows the equilibrium volume vs T.

Our results for the Debye temperature are displayed in Fig. 10 with the values obtained by Reese et al.[25] Once again the agreement is remarkable. After 90 K, the Debye temperature reaches a constant value of 144 K, close to the experimental value of 143 K.

If the q-point sampling was essential to describe the anomalies in the phonon spectrum, it is no more the case for the thermodynamic properties. This can be explained by the fact that those are integrated properties and the small features in the phonon branches do not influence the phonon density of state.

D. Validity of the quasiharmonic approximation

Recent measurements of the phonon density of states on uranium by Manley et al.[1] have shown an unusually large thermal softening of phonon frequencies over the range of stability of the α-phase (50–913 K). Comparing the entropy change predicted with Debye-Waller factors, around $1.5k_B$/atom, and the entropy expected from the volume expansion, around $0.16k_B$/atom, they suggested that the phonon
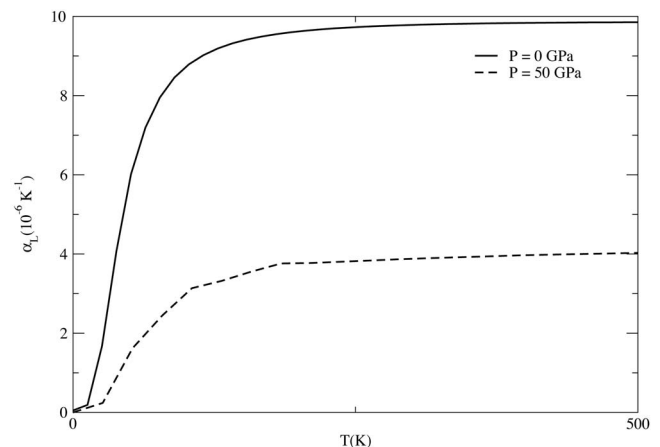

FIG. 8. Variation of the linear thermal expansion coefficient α_L with temperature and for several pressures.
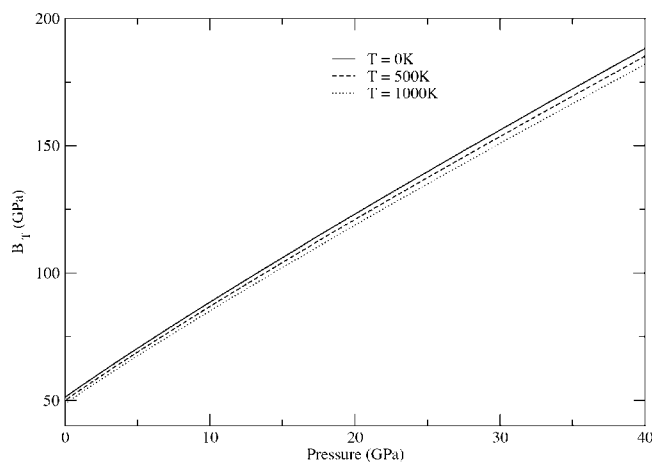
FIG. 9. Variation of the bulk modulus of Th with pressure and for several temperatures.

FIG. 10. Debye temperature for Th vs temperature. The open circles are results from Ref. [26].

softening comes from the weakening of force constants in a harmonic solid, as opposed to the softening in a anharmonic potential. This modification of the force constants with temperature would be due to a change in electronic structure. This would involve the nonvalidity of the quasiharmonic approximation for uranium. In fact the quasiharmonic approximation takes into account the anharmonicity by allowing phonon frequencies to depend on crystal volume, but ignores completely the change in electronic structure with temperature and its effect on the lattice dynamics. This approximation is valid for a large class of materials but if it is adequate for U, we can expect to encounter the same problem in the other light actinides. Using our results we can test these conclusions for Th, the first actinide, and so less subject to this phenomena. For Th, Lawson *et al.*[35] express the Debye temperature as $\theta_D \cong (163 - 0.014T)$ K, where T is temperature. This gives a vibrational entropy of $\Delta S = 3k_B \ln(\theta_{0\,K}/\theta_{1600\,K}) = 0.44k_B$/atom, for the temperature range of the fcc phase. From the volume expansion we can obtain the vibrational entropy from Eq. (11). Using our values we found $0.22k_B$/atom, about half of the value predicted with Debye-Waller factors. This is large but far from what is found in U where the effect of the volume expansion on the elastic softening can be completely neglected. This is not the case in Th, where the volume expansion will give the most important contribution to the vibrational entropy at low temperature. So we can expect that the quasiharmonic approximation is reliable until a temperature around 4 or $5\theta_D$. An
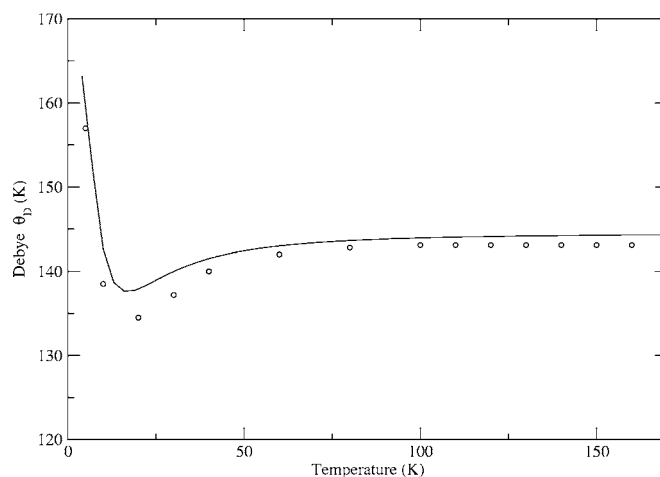
estimated value confirmed by the deviation of the mean-square atomic displacement to the universal Debye behavior, the deviation is important only at high temperatures.[35]

V. CONCLUSION

We have shown that we are now in position to obtain precise phonon spectra for the light actinides using the linear response theory. This is very important since experiments are really difficult to perform in this class of materials. Moreover, we have been able to study the thermodynamic properties of Th such as thermal expansion coefficient, Grüneisen parameters, bulk modulus, and Debye temperature using the quasiharmonic approximation. The lack of experimental values makes almost all these results predictive and shed light on the temperature and pressure dependence of those quantities. We have now the possibility to explore the first order phase transition between fcc and bct structures as a function of the temperature, and to explore the phase diagram of Th. It will be really valuable to apply this approach to the new experimental data obtained on the other actinides,[1,3] as U and Pu where the electronic correlations are much more important. This work is in progress.

ACKNOWLEDGMENT

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