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Calculation of the phonon spectrum in thorium

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Due to the comparatively extended *d* states in the transition metal thorium, it is argued that the pseudopotential method may be a fairly realistic approach to this element. Calculations of the phonon spectrum with an empirically derived form factor are shown to give quite good agreement with recent experiments. Also the calculated values of the elastic constants, the bulk modulus, the Debye temperature, and the binding energy are found to be most reasonable.

I. INTRODUCTION

During the last decade, accurate measurements of the phonon spectrum of many of the metals in the Periodic Table have been performed. Even for some of the rare-earth metals such experiments have been reported. For these latter elements no particular effect was found which could be directly traced back to the $4f$ electrons. This supports the picture of the $4f$ electrons as essentially core electrons as far as binding properties are concerned. In the early actinide elements, however, the $5f$ electrons are itinerant[1-3] and should accordingly be expected to have a significant influence on the phonon frequencies. For these elements, however, experimental difficulties have so far prohibited such measurements. This situation was recently changed when a single crystal of thorium was grown and the phonon frequencies were measured.[4]

The atomic configuration of thorium, the second actinide element, is $7s^2 6d^2$ outside a radon core. Therefore, one expects that the $5f$ state will remain essentially unoccupied also in the metallic state. Band calculations[2] and other estimates[5] show that the $5f$ state is located a few electron volts above the Fermi energy. This result seems to be supported by photoemission experiments.[6] Therefore, even though thorium is an actinide element, it is not especially informative as far as effects of $5f$ electrons are concerned. The unoccupied $5f$ level is believed to be of itinerant character,[2,6] and its hybridization with the conduction band may therefore be quite appreciable and even influence on states down at the Fermi level. For bulk properties, however, this should not be expected to give rise to any significant effects. This is supported by, for example, its cohesive energy (143 kcal/mol), which is almost identical with that of other tetravalent transition elements (Zr, Hf). Further, its melting point (1960 K) is in accordance with the values found in the other tetravalent elements. Also, its compressibility is quite normal.

On the theoretical side, the introduction of the pseudopotential concept[7] has made possible a quantitative study of phonons in metals. This method, however, is in its usual form only justifiable for simple metals with s- and p-type valence electrons. Due to computational simplifications, it has become quite common to use an analytical representation of the pseudopotential, containing a few parameters which are adjusted to fit some of the known data about either the metal or the corresponding free atoms. The experience from such an approach has been that phonon frequencies are very sensitive to the potential and therefore provide quite an exigent test on the reliability of the potential.[8] Such a totally empirical approach has recently been taken to the rare-earth metals and some of their neighboring elements.[9] A scaling procedure was used which made it possible to derive pseudopotential parameters for rubidium and thorium, among others. In order to test the potential and the scaling method, the phonon frequencies of rubidium were calculated, and the agreement with experiments was found to be excellent.[10] Now, when the phonon spectrum of thorium has become experimentally available, it should be appropriate to test this method for this element also. Further, a working potential for thorium in itself should be of interest. Naturally, one is very hesitant about the applicability of a pseudopotential to a transition metal like thorium, due to the presence of the d band. For bulk or integrated properties, a good account of the electronic structure may be less important. However, coming down to microscopic properties such as the vibrational modes, the detailed form of the potential is much more crucial. Even though thorium is a transition element, it turns out that some features of this element are quite favorable from the pseudopotential point of view. First of all, its density relative to the extension of the atomic $6d$ orbital is unusually high. (This effect is a general one as one proceeds downwards in a column in the Periodic Table.) This gives rise to very broad d bands[2]—of the order of 12–15 eV. Therefore, in fact, the d bands in thorium are in a way more similar to p bands than to d bands in the $3d$-$5d$ transition series. With this in mind, the pseudopotential method seems much more appropriate than one at first might expect. A more severe deficiency may be that the present pseudopotential approach completely leaves out the $5f$ states from consideration. However, since these states are unoccupied, their effect on the phonon frequencies should be of secondary importance only. Some other known properties of thorium seem to support this view. Thus, for example, the superconducting properties of thorium are better described by the simple BCS theory than they are for many other nontransition metals.[11] Further, Fisher[12] applied the free-electron Bohm-Staver coupled plasma model to calculate the longitudinal sound velocity and found a quite good agreement with the measured value. Therefore, although thorium nominally is a transition metal, some of its properties may very well turn out to be describable within a free-electron-like type of approach. On the other hand, band calculations have shown that the Fermi surface is rather remote from a spherical shape.[2] Part of this is due to the d band itself, but also, effects originating from the (sd)-f hybridization seem to have some influence. In any case, this shows that the present pseudopotential approach must have its limitations. Still, at the present state it is not unequivocally settled which physical properties are going to be most severely affected by such shortcomings in the detailed description of the electronic structure.

II. PSEUDOPOTENTIAL

In our calculations of bulk properties for the rare earths and neighboring elements in the Periodic Table the Krasko-Gurskii (KG) model potential was used.[9,13] Its Fourier transform is given by

$$v(r_c, q) = \frac{4\pi Z e^2}{\Omega q^2}\,\frac{(2a-1)(qr_c)^2 - 1}{[(qr_c)^2+1]^2}\,, \tag{1}$$

where Z is the ionic charge and Ω the atomic volume. The parameter a was chosen equal to 3.0 for all the elements considered. This was done in order to reduce the otherwise rather formidable number of possible variations. With a fixed value of a, the second parameter r_c essentially characterizes the spatial extension of the potential. Thus, r_c should be directly related to the extension of the orthogonalizing inner core.[14] The values of this parameter were therefore chosen as directly proportional to the radius of the core orbitals, the latter values taken from the atomic calculations by Waber and Cromer.[15]

To account for the equilibrium volume Ashcroft and Langreth[16] introduced a different core parameter for the $q=0$ component of the empty core pseudopotential. Also, here a second radius r_c' is introduced replacing r_c when $q=0$ in Eq. (1). This was done in order to account for the equilibrium density of *gadolinium*, which element was chosen as the starting point for the above-mentioned scaling procedure.[9] The choice which had to be made was $r_c' = r_c + 0.05$ (a.u.) This relation between r_c' and r_c was then used for all elements treated. The values for thorium of r_c and r_c', derived in our original work by fitting equilibrium volumes[9] 0.433 and 0.483 a.u., respectively, must now however be slightly changed. This is so since in that paper the Lindhard dielectric function[17] was used, but in the present calculation of the phonon spectrum a more subtle screening is introduced. This improvement resulted in $r_c = 0.425$ and $r_c' = 0.467$ a.u.

The introduction of a second core radius r_c' causes a discontinuity of the potential at $q=0$. Since in the calculation of phonon frequencies all the q components of the pseudopotential enter the equations, a smoothening procedure is then required in the vicinity of $q=0$. For this purpose, a smoothing function[18] $R(q)$, defined as

$$R(q) = \begin{cases} \tfrac{1}{2}[1+\cos(q\pi/q_0C)], & q \leq Cq_0, \\ 0 & , \quad q > Cq_0 \end{cases} \tag{2}$$

is introduced. Here C is an arbitrary constant, and q_0 denotes the value of q for which expression (1) equals zero. The smoothing is then accomplished by redefining the potential as

$$v(q) = [v(r_c', q) - v(r_c, q)]R(q) + v(r_c, q). \tag{3}$$

That is, for small values of q the potential is essentially characterized by r_c', but otherwise by r_c. The final results were found to be rather insensitive to the value of C. In this paper, C is chosen as 0.1. Finally, to improve numerical convergence, a damping factor multiplying $v(q)$, of the form

$$D(q) = e^{-\alpha(q/k_F)^2}, \tag{4}$$

where $\alpha = 0.03$, was applied.

The dielectric function used in this work is the Geldart-Vosko screening function,[19] that is

$$\epsilon(q) = 1 + Q_0(q)/[1 - f(q)Q_0(q)]\,, \tag{5}$$

where $-(q^2/4\pi e^2)Q_0(q)$ is the Lindhard expression for the electron polarizability. The function $f(q)$ has the form

$$f(q)=\tfrac{1}{2}q^2/(q^2+\xi k_F^2), \tag{6}$$

where ξ in the interpolation scheme of Nozières and Pines[20] is chosen to satisfy the compressibility sum rule, and is given by

$$\xi=2/(1+0.026r_s)\ . \tag{7}$$

Here r_s is the radius of the sphere containing one electron. For the correlation energy, the expression given by Pines and Nozières[17] was used.

III. METHOD OF CALCULATION

By evaluating the expressions for the dynamical matrix, the polarization vectors and phonon frequencies were calculated directly from the model potential. To determine the harmonic phonon frequency distribution, the formalism presented by Gilat and Raubenheimer[21,22] was applied. However, their procedure was somewhat modified here in order to obtain an accurate representation of the contribution to the spectrum from degenerate modes along the [111] direction.

For the calculation of the frequency distribution, a volume per mesh point in reciprocal space of approximately $10^{-4}(2\pi)^3/\Omega$ was used. This would give a spectrum accurate within 2 or 3%, according to the experience of Pynn and Ebbsjö.[23]

The elastic constants C_{ij} can be derived from the long-wavelength limit of the phonon spectrum. They can also be evaluated by means of homogeneous deformation. To second-order (as well as to any finite order) perturbation expansion these two approaches give different results. However, for a local pseudopotential it has been shown[24,25] that inclusion of appropriate three- and four-particle interactions in the method of long waves will bring these two methods in exact agreement. In the present paper, we have calculated the second-order elastic constants from homogeneous deformation, where the expressions for the second-order derivatives of the total crystal energy with respect to certain deformations have been given, e.g., by Wallace.[26] The derivatives originating from the band-structure energy were performed analytically. The electrostatic contributions to the elastic constants were calculated from the structure coefficients tabulated by Fuller and Naimon.[27] From a knowledge of C_{11}, C_{12}, and C_{44} the stiffness coefficient Q_{111} can be calculated from the relation

$$Q_{111}=\tfrac{1}{3}(C_{11}+2C_{12}+4C_{44}). \tag{8}$$

IV. RESULTS OF CALCULATION

For the lattice parameter the room-temperature value of 5.0856 Å (Ref. 28) was used, and for the atomic mass a value of 232.038 amu.[29] In Fig. 1, the calculated phonon dispersion curves along three principal symmetry directions, as well as along the $[0, \zeta, 1]$ direction, are compared with the measurements of Reese, Sinha, and Peterson.[4] The largest deviation is found in the $[0, \zeta, 1]$ direction. It should be noted, however, that a similar discrepancy was found in the seventh nearest-neighbor force-constant-model fit used by Reese *et al.*[4] These authors also used their fit to calculate the phonon frequency distribution. In Fig. 2, we compare our calculated frequency distribution with theirs. (Our calculated curve contains some numerical noise due to a more limited mesh.) The overall agreement between the two curves is reasonable, except that our curve contains a stronger maximum around 2.03 THz. This maximum can be traced back to our inability to account for the anomalous behavior of the T_1 branch along the $[0, \zeta, \zeta]$ direction. The general pattern of our calculation seems to be a shift towards somewhat too high frequencies.

From the frequency distribution, the Debye temperature was calculated as a function of temperature. In Fig. 3, we compare our result with the experimentally assigned Debye temperatures.[30] In this figure, we have also included the results of Reese *et al.*[4] The experimental assignments are, however, based on a value of 19×10^{-4} cal mole^{-1} K^{-2} for the linear coefficient of the electronic specific heat. More recent work has indicated a lower value, and experiments of several groups seem to have converged on a value 10.24×10^{-4} cal mole^{-1} K^{-2}.[31] If this is accounted for, it will cause a reduction in the deduced experimental Debye temperatures at higher temperatures.

Our results for the elastic constants, as calculated by means of the homogeneous deformation method, are given in Table I, and a comparison to the measurement by Armstrong *et al.*[32] is made. In view of the fact that thorium is, in principle, a transition metal, the agreement is quite satisfactory. In this table, we have also included the modulus C', defined as

$$C'=\tfrac{1}{2}(C_{11}-C_{12}). \tag{9}$$

TABLE I. Room-temperature value of elastic constants, bulk modulus, stiffness constant, and modulus C' (10^{11} dyn/cm^2) compared with present calculation.

	C_{11}	C_{12}	C_{44}	B	Q_{111}	C'
expt	7.53	4.89	4.78	5.77	12.14	1.32
calc	7.84	5.38	3.98	6.20	11.51	1.23

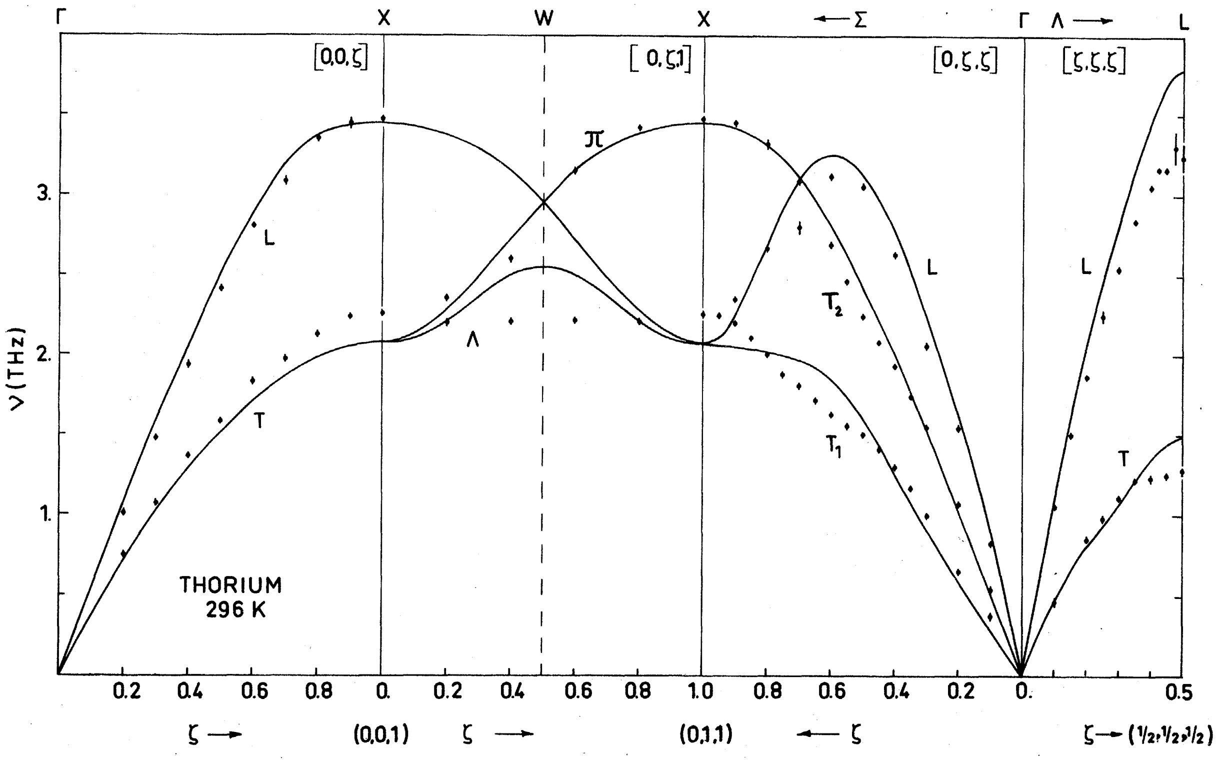

FIG. 1. Phonon dispersion of thorium. Solid curves denote the present calculation, points denote the experimental results with error bars included, of Ref. 4.

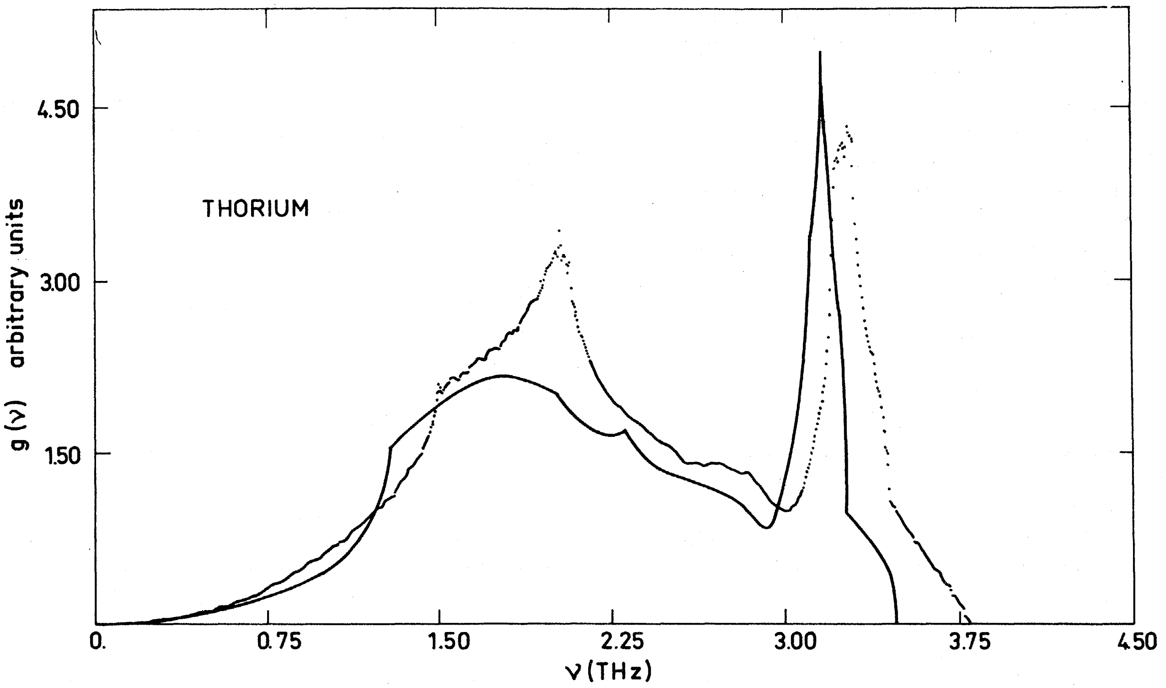

FIG. 2. Phonon frequency distribution in thorium. Solid curve is the result of the force-constant-model fit made in Ref. 4. Dotted curve denotes the result of the present calculation.

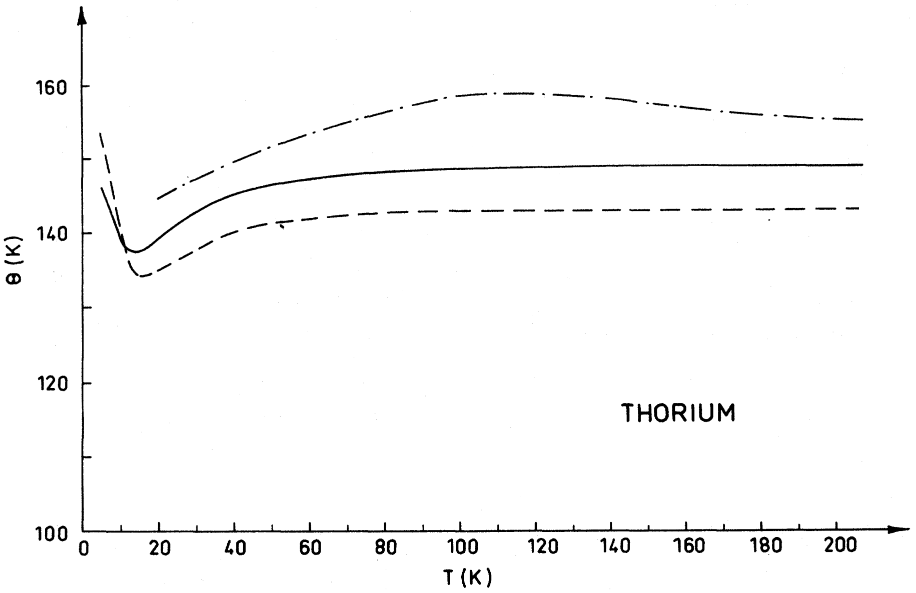

FIG. 3. Debye temperature as a function of temperature. Solid curve denotes the result of this calculation, dashed curve denotes the results of Ref. 4, and the point-dashed curve denotes the experimental assignments of Ref. 28.

This quantity is usually very difficult to account for theoretically. Therefore, the rather close agreement of our calculation with experiment is gratifying.

Within the present pseudopotential approach we could also compare the electronic energies for different crystal structures. The fcc structure was found to be definitely favored over the bcc structure. However, the hcp structure was found to be the energetically most favorable one, in contradiction to experiment. For the fcc structure, our calculation gives a value of 5.67 Ry/atom for the binding energy, to be compared with the experimental value of 5.34 Ry/atom.[33-35] At high temperatures, thorium undergoes a phase transformation to a bcc structure. A calculation of the phonon frequencies of this phase with the present pseudopotential gave imaginary frequencies in the $[\xi, \xi, 0]$ direction.

V. DISCUSSION

From the obtained agreement with experiments, we conclude that the present pseudopotential accounts quite well for the vibrational properties of thorium. However, this does not mean that thorium in all respects can be described by such an approach. In fact, already the sometimes quite marked deviations in our calculations from the experimental phonon branches point towards a more complicated behavior. Therefore, superimposed on the present effective ion-ion interaction, there should be further effects left out in our present treatment.

The T_1 and T_2 branches along the $[0, \xi, \xi]$ direction show a quite pronounced dip from a smooth behavior. As pointed out in Ref. 4, these anomalies are too broad to be ascribed to the Kohn effect.[36] A possible mechanism responsible for this anomalous behavior is that there is a large peak in the generalized susceptibility function $\chi(\vec{Q})$.[4,37] Such a peak is likely to occur when $\vec{Q}$ connects two nested regions of the Fermi surface. However, calculations based on band-structure calculations give peaks that do not fit with the positions of these phonon anomalies.[4] From the calculation of $\chi(\vec{Q})$, one also expects an anomaly in the $[0, 0, \xi]$ direction, but as can be seen from Fig. 1, no evidence of such a behavior is found in the experiments. Thus, there seem to be difficulties with an explanation of the anomalies, due to the detailed form of the Fermi surface. Therefore, as also mentioned in Ref. 4, it may be that the presence of the unoccupied $5f$ band is responsible for the dips. Virtual excitations to this state can, via dielectric screening, influence the ion-ion interaction, and the expected high density of states of the $5f$ band could further enhance this mechanism. However, in order to give a significant contribution, the $5f$ state must not be too far away from the Fermi energy. In the photoemission experiments,[38] the presence of $5f$ states in the energy region 1–5 eV above the Fermi energy was concluded. Being itinerant, the $5f$ state hybridizes significantly with the (sd) band and may therefore influence states quite far below its own energy position. Thus, it seems that the "virtual $5f$ mechanism," for the moment, cannot be ruled out as the origin of the anomalies.

Further evidence of a more complicated behavior in thorium than that describable by a simple pseudopotential is also found in some other experiments. For example, the resistivity obeys a Bloch-Grüneisen relation up to about 80 °K but then deviates somewhat from this behavior.[39] This deviation increases with temperature. Also the magnetic susceptibility shows a slight positive slope with temperature, which is thought to be caused by a temperature-dependent electronic structure.[40] Again, this may be caused by the $5f$ state. The position of this state is quite sensitive to the potential, and if it moves somewhat with temperature, it may via hybridization effects cause some changes near the Fermi surface.

In their measurements of the elastic constants, Armstrong *et al.*[32] concluded a contribution from core-core interaction. However, even though the core extension relative to the atomic volume is unusually large in thorium, we believe that it is still not sufficient to give substantial contributions under equilibrium conditions. Instead, the quoted core-core interaction may have a different origin than a simple core overlap in that it may be simulated by the "virtual $5f$ mechanism."

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