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Cubic Pu from Electronic Structure Theory*

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ABSTRACT

The phonon frequencies and elastic constants of plutonium are calculated using a model for the electronic structure that treats the valence electrons as a pseudopotential and the f-electrons in tight-binding theory. An effective interaction between ions is presented with electron screening treated in the Thomas-Fermi approximation and the f-electrons contributing bonding and repulsive terms to the potential. The phonon frequencies and elastic constants are calculated using the face-centered cubic lattice structure for both the α - and δ -phases of Pu. The electronic structure predicts the qualitative behavior of the elastic constants and the transverse branches of the phonon dispersion curves in agreement with experimental values of the elastic constants for δ -phase Pu.

I. Introduction

The purpose of the present study is to provide a prediction of the phonon frequencies of Pu based upon electronic structure theory. To accomplish this task using the most accurate electronic structure currently available is an extremely challenging computational task. Here we discuss a greatly simplified description of the electronic structure that allows relatively easy calculations of the phonon frequencies over the entire Brillouin zone and thermodynamic functions that require Brillouin zone averages.

The lattice structure of δ -Pu is the fcc structure with one atom per unit cell. For α -Pu, the structure is monoclinic with 16 atoms per unit cell. We have performed all the calculations using the fcc structure because of the great simplification achieved over using the α -Pu structure. This should not tend to introduce a large error in the results particularly for quantities that are functions of weighted averages over the vibrational modes such as the characteristic temperatures. The primary dependence of such quantities will be on the density and the parameters describing the effective interactions of the ions and it is these quantities that we wish to examine in the present work.

In Sec. II we present the electronic structure model used in the study and the effective ion-ion interaction potentials used in calculating the phonon frequencies. Sec. III discusses the determination of the potential parameters. Sec. IV gives the results of the calculations of the phonon dispersion curves and the elastic constants, and Sec. V is a brief discussion of the results.

II. The Electronic Structure Model

The model that we have chosen for the description of metallic systems is based on pseudopotential theory¹ as a rigorous formulation of the bandstructure problem but permits the use of perturbation theory. Direct calculations of the vibrational spectrum are possible that are in good agreement with experiment. Using the Fermi-Thomas approximation for the electron screening, Harrison and Wills² were able to write the total energy in terms of analytic functions with a central pair-wise effective ion-ion interaction given by

$$\phi_{F.T}(r) = Z^2 e^2 \cosh^2(\kappa r_c) \frac{e^{-\kappa r}}{r} \quad (1)$$

where Z is the valence, κ is the Fermi-Thomas screening parameter, r_c is the pseudopotential core

radius, and r is the ion separation. This interaction is a nearly free-electron contribution in the context of pseudopotential perturbation theory and is appropriate for the three valence electrons of Pu.

For the actinide metals we must include a specific contribution due to the f -electrons and we follow the approach of Harrison.^{3,4} The approach for the actinides follows Harrison and Froyen⁵ for treating transition metals where the electronic states are separated into nonoverlapping d -states and free-electron states. The two sets of states are then coupled resulting in an indirect interaction between d -states on neighboring atomic sites via the plane waves of the free-electron states. The details may be found in Refs. 3 and 4 where the f - f matrix elements, spin-orbit coupling, the f -band width, the shift in the f -band center, the contribution of the f -band to the energy, volume dependent properties, representation as a two-body interaction, and electron localization are discussed.

The equations for the f -shell electrons are presented here with separate contributions resulting from the formation of bands and the nonorthogonality of orbitals on adjacent atoms. The former results in an effective ion-ion interaction that is

Figure 1. The total central pair potential ϕ_{Total} and the Fermi-Thomas potential $\phi_{\text{F-T}}$ for an empty core pseudopotential parameter $r_c = 1.52 a_0$.

Figure 2. The central pair-wise potential for the f -electrons $\phi_{\text{f-Total}}$, the attractive contribution $\phi_{\text{f-band}}$ and the repulsive contribution $\phi_{\text{f-R}}$. $\phi_{\text{f-Total}} = \phi_{\text{f-band}} + \phi_{\text{f-R}}$.

attractive and lowers the energy and the latter results in a repulsive interaction. The repulsive interactions is

$$\phi_{\text{f-R}}(r) = 2 Z_f \frac{\hbar^2}{m} (3.11 r_f)^{10} \frac{1}{r^{12}} \quad (2)$$

where Z_f is the number of f -electrons and r_f is the bandwidth parameter determined by a separate *ab initio* calculation.⁶ The band term is

$$\phi_{\text{f-band}}(r) = -Z_f \left(1 - \frac{Z_f}{14}\right) \frac{1}{\sqrt{n}} \frac{\hbar^2}{m} (5.06 r_f)^5 \frac{1}{r^7} \quad (3)$$

where n is the number of nearest-neighbor atoms ($n = 12$ for fcc). The total effective ion-ion interaction resulting from the f -electrons is

$$\phi_{\text{f-Total}}(r) = \phi_{\text{f-R}}(r) + \phi_{\text{f-band}}(r) \quad (4)$$

The contributions to the potential may be seen in Figs. 1 and 2. In Fig. 1, the total effective ion-ion potential

$$\phi_{\text{Total}} = \phi_{\text{F-T}}(r) + \phi_{\text{f-Total}} \quad (5)$$

is shown along with the contribution of $\phi_{\text{F-T}}$ and with the difference between the two curves equal to

$\phi_{f\text{-Total}}$. In Fig. 2, the separate contributions to $\phi_{f\text{-Total}}$ are shown. Although the f-electron contributions appear to be small contributions to the total energy of the system, it should be remembered that the phonon frequencies are explicit functions of the curvature of the potential ($\partial^2\phi/\partial r^2$) and are strongly affected by the f-electrons.

The description of the f-band width and center is discussed in Ref. 6 where the density dependence is given for the rare earth and actinide series. The results are in excellent agreement with more detailed calculations of the bands. The additional assumption that is used in the determination of the real space potential is the use of the constant density of states for the f-band. This has been shown to give good results for transition metals and transition metal compounds.⁷ We expect the same set of approximations to remain valid in the present study where a band description is appropriate but fail when electron localization and correlation effects become large.

The phonon frequencies are calculated using quasiharmonic lattice dynamic theory as contained in the book of Wallace.⁸ The phonon frequencies are found by diagonalizing the dynamical matrix with one atom per unit cell and given by Eq. (15.1) of Ref. 8. The calculational procedures for the phonons and the averages over the Brillouin zone necessary to determine the characteristic vibrational temperatures are also given and will not be repeated here. Lattice sums were well converged with only third neighbor interactions because of high inverse powers of the ion separations in ϕ_f and Brillouin zone averages were accurate to about 1% by using 19 **k** values in the smallest symmetry volume (1/48) of the first Brillouin zone.

For the X-point ($\mathbf{k} = 2\pi/a[0,0,1]$) in the Brillouin zone we can obtain analytic formulas for the phonon frequencies:

$$M\omega_{Xl}^2 = 32 \phi'(1) + 64 \phi'(3) + 8a^2[2\phi''(1) + 4\phi''(3)] , \quad (6)$$

$$M\omega_{Xt}^2 = 32 \phi'(1) + 64 \phi'(3) + 8a^2[\phi''(1) + 10\phi''(3)] , \quad (7)$$

where the first equation is for the longitudinal mode indicated by the subscript l and the second is for the transverse mode indicated by the subscript t. The fcc cube edge is given by a and the quantities ϕ' and ϕ'' are derivatives of the total 2-body potential given by Eq. (5):

$$\phi' = \frac{\partial\phi}{\partial(r^2)} , \text{ and } \phi'' = \frac{\partial^2\phi}{\partial(r^2)^2} . \quad (8)$$

The arguments of $\phi'(1)$, $\phi'(2)$, $\phi'(3)$ denote the first-, second-, and third-neighbor interactions; the same notation applies to ϕ'' . Similar equations are available for the other symmetry points but they will not be repeated here. These equations were used to determine the density and Z_f dependence of ω_{Xl} and ω_{Xt} instead of diagonalizing the dynamical matrix. The contributions from second-neighbor interactions in Eqs. (6) and (7) cancel out one another due to the symmetry of the fcc lattice

III. Determination of Parameters

The electronic structure model has three adjustable parameters that require additional input for their determination. These parameters are the pseudopotential core radius r_c , the f-band width parameter r_f , and the number of electrons in the f-band Z_f . The values of r_f have also been determined in other calculations for all of the f-electron elements and their good agreement with other calculations of the band width gives us confidence in their accuracy.⁶ The final parameter Z_f we take to be adjustable and match the experimentally determined value of the characteristic Debye temperature. The characteristic temperature θ_1 is determined from the phonon frequencies $\nu(\mathbf{k})$ by taking an average of the Brillouin zone as indicated by

$$k\theta_1 = \left\langle \frac{4}{3} h\nu \right\rangle_{BZ} . \quad (9)$$

The values chosen to be fitted have been determined by Wallace using elastic constant and other thermodynamic data.⁹

The largest sensitivities come from changes in r_c and r_f , but since these have independent

Figure 3. The value of θ_1 versus the number of electrons in the f-band Z_f for the α - (upper solid line) and δ -phases (lower solid line).

determinations we choose to leave them fixed at the previously determined values. The most poorly characterized parameter is Z_f and we find that a reasonable adjustment of its values allows a match to θ_1 separately for each phase.

Figure 3 shows a plot of θ_1 as a function of the number of electrons that are found in the f-band with the dotted lines showing the values from experiment. As the number of f-electrons decrease the average phonon frequency increases indicating that the potential is becoming more repulsive. However, there is considerable cancellation between the different contributions to the potential in calculating the phonon frequencies and a simple argument to show this trend has not been found. If Pu's α - and δ -phases had the same fundamental electronic structure one might expect that a single set of parameters could be found. If the transfer of electrons to and from the f-band was done in a self-consistent manner, as has been done for ionic compounds,¹⁰ the differences in Z_f might be expected. It would seem that Z_f should be larger for the α -phase because of increased electron localization in the δ -phase but that is not what we find in the present study. We are also doing the α -phase calculation in the fcc lattice instead of the more compli-

cated monoclinic α -Pu lattice with 32 atoms in the unit cell. Assuming similar bonding in both phases, θ_1 should be well approximated by the fcc calculations with density being the dominant dependent variable.

Figure 4. The value of θ_1 versus density for α - and δ -phases.

The characteristic temperature θ_1 has been calculated as a function of density and is shown in Fig. 4. The two solid square points are the estimates based on experimental data. A straight line has been drawn connecting the experimental data with a slope that is about twice that of either the α - or δ -phase curves. Although this straight line gives a slope that is typical of other metals, there is a significant disagreement with the more complete description of the present work.

Figure 5. The phonon dispersion curves for the δ -phase Pu.

IV. Phonons and Elastic Constants

The phonon dispersion curves as calculated are shown in Figs. 5, 6 and 7. Fig. 7 shows a more detailed comparison for the Γ -X and Γ -K-X branches. All the phonon curves show the features expected of a fcc lattice with most of the difference in the δ - and α -v's caused by the density difference. The parameters used in the phonon and elastic constant calculations are as determined in Sec. III above and no further adjustment was made. The fit to the characteristic temperature θ_1 will ensure that the energy scale for the phonons will be about right. The largest effect that is seen in the phonons is due to the density difference between the two phases, but also, different values of Z_f have some additional effects.

Worthy of note is the relatively flat transverse acoustic branch in the [011] direction and the [001] direction. This is related to the high ratio of the elastic constants as is discussed below. The addition of the f-electron potential has softened to total potential over the regular pseudopotential formulation. See Figs. 1 and 2. To some extent, the adjustment of Z_f to match the experimental values of the characteristic frequency has represented whatever effects of electron localization that may be present in the experiment. It would be possible to include an explicit dependence upon localization but then, one would need to refit all parameters after determining and subtracting out

Figure 6. The phonon dispersion curves in the fcc-structure symmetry directions for the α -phase.

Figure 7. A comparison of the phonon dispersion curves in the fcc-structure symmetry directions Γ to X for the [001] and [011] directions with the open symbols for the δ -phase and the solid symbols for the α -phase.

the localization effects in the experimental data. Unfortunately, the amount and accuracy of the presently available data does not warrant such a procedure. The present analysis points out the need for a full experimental determination of the phonon dispersion curves in δ -Pu.

The elastic constants may be calculated using the potentials that we have determined for both phases and the results are given in Table I. These results may be compared with the single crystal δ -Pu experimental data of Leadbetter and Moment.¹¹ In qualitative agreement with experiment is the result that the shear constants are small for the δ -phase and the ratio of the shear constants given by

$$A = \frac{B_{44}}{1/2(B_{11}-B_{12})} \quad (10)$$

is large. The magnitudes of B_{44} and $(B_{11}-B_{12})/2$ are in good agreement with Leadbetter and Moment. The largest discrepancy is for the bulk modulus which is off by about a factor of 3. One of the remarkable experimental results is the unusually high value for the ratio of the shear constants equal to 7 when typical metal values are about 2. Also, the ratio of B_{11} to B_{44} is 1.08 with the more typical value being about 2. We could improve agreement with the elastic constants by adjusting the parameters of our electronic structure model but this would affect our results for θ_1 . We might also develop a more detailed

Table I. Results of the Elastic Constant Calculations for α - and δ -Phase Pu. The ratio of the two shear coefficients is given by $A = \frac{B_{44}}{1/2(B_{11}-B_{12})}$

Phase	Z_f	B_{11} (Mbars)	B_{12} (Mbars)	B_{44} (Mbars)	B (Mbars)	$(B_{11}-B_{12})/2$ (Mbars)	$A^\dagger$
δ	5	1.04	0.91	0.32	0.95	0.065	4.9
δ	4.8	1.05	0.92	0.33	0.96	0.065	5.1
Exp. δ^{11}		0.3628	0.2623	0.3359	0.2991	0.0477	7.03
α	5	1.67	1.48	0.50	1.54	0.095	5.3
α	4.6	1.73	1.53	0.52	1.60	0.100	5.2

model for the localization of the f-electrons and their effect on the elastic constants, but additional experimental data would be needed. The overall agreement is quite satisfactory since all of the parameters were unchanged from the values used to fit θ_1 . The characteristic temperatures are functions of the entire phonon spectrum whereas the elastic constants are dependent upon the long wavelength limit of the phonon branches at the Γ -point.

V. Discussion

For the approximate electronic structure model, we do not find a consistent set of parameters that is capable of describing the α - and δ -phases of Pu. For the third row metals of the periodic chart (Na, Mg, Al) and the transition metals it is possible to find such a consistent set of parameters to describe different solid phases and the fluid phase.^{12, 13} We expect that the failure to match θ_1 for both phases with a single set of parameters to be mostly due to a change in the electronic structure from itinerant to localized f-electrons. The calculation of the elastic constants shows results that are consistent with this interpretation. The experimental measurement of the elastic constants on single crystalline δ -phase Pu from Ref. 11 are in good agreement with the results of our calculations of the shear elastic constants.

The elastic constants are given by linear combinations of the slopes of the phonon dispersion curves shown in Figs. 5 and 6. A consistent set of parameters that give both the elastic constants and the

maximum values of the phonon frequencies is difficult (or impossible) to achieve in our restricted model. This difficulty is not peculiar to the actinides but occurs in calculations for the lighter elements as well.

Further improvement in the bulk modulus might be possible without changing the agreement already obtained for the shear constants. This has not been in the present work and would require data for the bulk modulus of single crystalline α -Pu.

In Fig. 8, the straight lines labeled with the different linear combinations of B_{ij} 's are the slopes of the longitudinal and transverse phonon branches. The shear constants B_{44} and $(B_{11}-B_{12})/2$ are isolated in the [001] and [011] branches, respectively, but also affect other branches in different linear combinations. The phonon dispersion curves are for aluminum with slopes that are more typical of the elastic constants for metals, i.e., the ratio A defined in Table I. varies from 3.2 for Cu to about 1.0 for W. By comparison to the Al [011] transverse branches, we see a much larger separation of these same branches in Fig. 7 for Pu. For Al, the ratio $A=0.8$.

Based upon our prediction of the elastic constants, we believe that the separation of the [011] branches is a real effect, but further experimental validation is needed. If the prediction turns out to be accurate, then there are direct implications for the values of the vibrational entropy.

The present calculations predict a value for the density dependence of θ_1 , as given by $\partial \ln \theta / \partial \ln \rho$, to be about half of what one would estimate from taking the finite difference value given by $\Delta \ln \theta_1 / \Delta \ln \rho$. This result is another indication of a change in the nature of the electronic structure between the two phases. Fitting the curves shown in Fig. 9 for the frequency as a function of density we obtain

$$\delta: \nu = 0.070242 + 0.20816 \rho - 0.0020448 \rho^2 \quad (11)$$

$$\alpha: \nu = -0.062486 + 0.23165 \rho - 0.0012419 \rho^2 \quad (12)$$

The Grüneisen parameters as determined from the preceding equations are $\partial \ln \nu / \partial \ln \rho = 0.794$ for δ -phase and 0.881 for α -phase at their equilibrium densities. We obtain similar values for the Grüneisen parameters by taking the logarithmic derivatives of θ_1 as a function of density as can be seen in Fig. 4.

Figure 10 is a plot of the mode Grüneisen parameter γ as a function of density for the longitudinal mode for the zone boundary phonon

with $k = X_1$. For both of the phases, γ is below one, decreases further with a minimum at 22-23 gm/cm³, and then increases. The curves for the two phases are qualitatively similar as might be expected from their potentials, but the δ -phase has a more pronounced minimum. The common assumption in high pressure equation-of-state treatments is the $\rho\gamma = \text{constant}$, or, $\gamma \propto 1/\rho$. This assumption is contradicted in the present study as is evident from Fig. 10.

The present work points to the need for both more single crystal experimental data in different phases of Pu and more accurate calculations. Additional experimental measurements of second- and third-order elastic constants as a function of density would also be extremely valuable. In combination with phonon data, the unusual density dependence shown in Fig. 10 could be quantified. Analysis of shock wave data suggests similar behavior.

Figure 8. Calculated phonon frequencies for Al $V_a = 111.97 a_0^3$ and the appropriate linear combinations of elastic constants B_{ij} for the phonon branches.

One expects that the actual phonon as measured in inelastic neutron scattering experiments will show additional structure not present in the current calculations. In particular, the question of electron correlation (localization) could significantly change the phonon dispersion. Electron-phonon coupling would also be evident in the phonon spectrum near the zone boundaries. More accurate all-electron calculations with full relativistic interactions are in progress and are needed to help interpret experimental results.

Figure 9. The X-point phonon frequency as calculated from Eqs. (6) and (7) for the α - and δ -phases. The solid points are the frequencies at ambient densities.

Figure 10. The mode Grüneisen gamma for the X-point phonon for the α - and δ -phases as a function of the density.

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