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Electronic and phonon properties of six crystalline phases of Pu metal

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In the light actinides Th to Np, and in the low-temperature α phase of Pu, the $5f$ electrons are itinerant, while in the five higher-temperature phases of Pu, and in the heavy actinides from Am on, the $5f$ electrons are localized to varying degrees. To understand the physics of $5f$ localization is a current problem in electronic-structure theory. The kind of experimental data that can help in solving this problem is not available. In this paper, thermodynamic data for Pu metal are analyzed to extract the quantities important for electronic-structure theory. For each of the six crystal phases, the following quantities are evaluated: (a) the static lattice potential, which is the ground-state energy of electronic-structure calculations, (b) central moments of the phonon distribution, which can be compared to any theoretical calculation of phonon frequencies, and (c) a measure of combined anharmonic and electronic excitation contributions to entropy, which contains information on the electronic density of states. Though at present we are not able to separate anharmonic and electronic excitation effects, the last named quantity will help to do so in the future. [S0163-1829(98)00448-2]

I. INTRODUCTION

Electronic structure, and the corresponding total potential energy, is a foundation theory of crystalline materials. In the development and improvement of this theory, over the years, the availability of accurate experimental data has been essential. For simplicity of argument here, we will limit our discussion to the elements. For most elements, electronic-structure calculations are currently capable of verifying experimental results for the lowest-lying crystal structure as function of density, i.e., for the stable structure at $T=0$, including cases where structural phase transitions occur upon compression.[1] Such calculations are so well tested that they are often regarded as predictive. Further, by calculating potential energies of configurations where the nuclei are displaced from crystal-lattice sites, one determines the quasiharmonic phonon frequencies.[2] Here the development of reliable electronic-structure theories has been strongly assisted by inelastic neutron-scattering measurements of phonon-dispersion curves. We mention in passing the development of pseudopotential perturbation theory for the electronic structure of nearly-free-electron metals, where all electronic and structural properties are expressed in a unified theoretical framework.[3–5]

The current testing ground for electronic structure theory of the elements is the actinide metals, the last period of the Periodic Table. Recent calculations are able to reproduce the stable crystal structure and density at $T=0$ for the light actinides Th, Pa, U, Np, and Pu.[6] From Th to Pu, the $5f$ electrons are metallic, and as the number of these bonding electrons increases, the cohesion increases and the volume decreases (except for a slight increase of volume from Np to Pu). But the nature of the bonding changes dramatically with Am, and the $T=0$ volumes of Am, Cm, Bk, and Cf are an enormous 37–50 % larger than that of Pu.[7] In addition, as a function of temperature at zero pressure, Pu exhibits six stable crystal phases, and all the elevated temperature phases (β, γ, δ, δ', and ε) have volumes much larger than the low-temperature α-phase volume. Following the early suggestion of Zachariasen,[8] it is presumed that the large-volume actinide structures result from a localization, and corresponding nonbonding character, of the $5f$ electrons. An electronic-structure calculation in which the $5f$ electrons are placed *a priori* in localized states gives ground-state energies and volumes in approximate agreement with the experimental implications for δ-Pu and Am.[9] The problem facing us now is to refine this model by including *in the Hamiltonian* the physical effects responsible for localizing the $5f$ electrons.

To understand the competition between localization and delocalization of $5f$ electrons, Pu is the crucial element, since the character of the $5f$ electrons apparently varies from nearly pure metallic in α-Pu, to varying degrees of localization in the elevated temperature phases. Temperature-induced phase transitions correspond to higher entropy in the higher-temperature phase, and the dominant source of entropy in crystals is phonons. Consequently, we expect a qualitative shift toward lower phonon frequencies, from each Pu phase to its next-higher-temperature phase. The experimental data providing the most severe constraints for electronic-structure theory will be the ground-state energies of each phase, relative to the α phase, and the phonon spectrum of each phase. At the present time, none of these data are available. In particular, not a single phonon frequency has been measured for any Pu phase.

In the present paper, we shall evaluate the most important quantities to be verified by electronic-structure calculations, for the six crystal phases of Pu metal. To do this, we will exploit the wide range of application of lattice dynamics plus statistical mechanics theories. In the lattice dynamics Hamiltonian, the potential energy is just the ground-state energy as a function of the nuclear positions.[10] This Hamiltonian, together with phonon statistics, provides the theory for the free-energy of crystals.[10] Over the years, we have extended and refined the theory of thermodynamic functions of crystals.[5,11] The complete free energy is the sum of four terms: the static lattice potential, the quasiharmonic phonon contribution, and small terms representing anharmonicity and thermal excitation of electrons from their ground state. The last term includes nonadiabatic effects, in the form of electron-phonon interactions. Contrary to the widely used Debye model, the lattice dynamics theory expresses the free energy in terms of the correct moments of the correct phonon distribution. Here we will turn around our usual theoretical procedure, and will start with the measured thermodynamic properties, and extract the more primitive quantities related to the Hamiltonian.

In Sec. II, the theoretical equations for crystal thermodynamic functions are written and briefly discussed. The thermodynamic data for Pu are analyzed in Sec. III, and the results are summarized and discussed in Sec. IV

II. THEORY OF THERMODYNAMIC FUNCTIONS

Formulation of the crystal free energy was briefly outlined in Sec. I. For a crystalline system of N ions plus their associated electrons, occupying a volume V, we will write the Helmholtz free energy F in the form

$$F=\Phi_0+F_H+F_{AE}. \tag{1}$$

Here $\Phi_0(V)$ is the static lattice potential, i.e., the energy of the crystal with ions located at the lattice sites and electrons in their ground state, and $F_H(V,T)$ is the quasiharmonic phonon-free-energy. F_{AE} is the sum of two small terms,

$$F_{AE}=F_A+F_E, \tag{2}$$

where $F_A(V,T)$ is the anharmonic free energy, due to phonon-phonon interactions, and $F_E(V,T)$ represents thermal excitation of electrons from their ground state, and includes nonadiabatic effects in the form of electron-phonon interactions.

In general, the temperature dependence of F is dominated by F_H (except, for example, for a metal at low temperatures, where the T^2 form of F_E dominates the T^4 form of F_H). The behavior of F_H is expressed in terms of a few phonon characteristic temperatures θ_n, defined by

$$\ln(k\theta_0)=\langle\ln(\hbar\omega)\rangle_{\mathrm{BZ}}, \tag{3}$$

$$k\theta_1=\tfrac{4}{3}\langle\hbar\omega\rangle_{\mathrm{BZ}}, \tag{4}$$

$$k\theta_2=[\tfrac{5}{3}\langle(\hbar\omega)^2\rangle_{\mathrm{BZ}}]^{1/2}, \tag{5}$$

where $\langle\cdots\rangle_{\mathrm{BZ}}$ indicates a Brillouin zone average of a function of the phonon frequencies ω. At $T=0$, F_H is just the phonon zero-point energy F_{H0},

$$F_{H0}=\tfrac{1}{2}\Sigma\hbar\omega=\tfrac{9}{8}Nk\theta_1. \tag{6}$$

The leading low-temperature dependence of F_H is T^4/θ_D^3, where θ_D is the Debye temperature. We shall not be interested in this low-temperature regime in the present paper. The high-temperature expansion of F_H is

$$F_H=-3NkT[\ln(T/\theta_0)-\tfrac{1}{40}(\theta_2/T)^2+\cdots], \tag{7}$$

where the final term continues the power series in T^{-2}. Keeping only the two terms written in Eq. (7), this expansion is sufficiently accurate for the present analysis at $T\gtrsim\theta_2$, and θ_2 for the Pu crystal phases is $\leqslant 162$ K. Therefore, Eq. (7) will be the primary equation in the present analysis. Also, θ_0 is the key phonon quantity in our analysis, while θ_1 and θ_2 play secondary roles, and approximations for them will suffice. We therefore evaluate θ_1 and θ_2 from the approximation[12]

$$\theta_1\approx\theta_2\approx e^{1/3}\theta_0. \tag{8}$$

The primary thermodynamic data we shall analyze for Pu are the entropy S and the internal energy U. The following expressions are derived from the free energy:

$$S=S_H+S_{AE}, \tag{9}$$

$$U=\Phi_0+U_H+U_{AE}. \tag{10}$$

At $T=0$ the entropy is zero, and the internal energy is U_0,

$$U_0=\Phi_0+\tfrac{9}{8}Nk\theta_1+U_{A0}, \tag{11}$$

where U_{A0} is the anharmonic zero-point vibrational energy, and we have used the property $U_E=0$ at $T=0$. The high-temperature expansions are

$$S_H=3Nk[\ln(T/\theta_0)+1+\tfrac{1}{40}(\theta_2/T)^2+\cdots], \tag{12}$$

$$U_H=3NkT[1+\tfrac{1}{20}(\theta_2/T)^2+\cdots]. \tag{13}$$

The specific heat at constant volume is $C_V=C_H+C_{AE}$. Although this function is not independent of S, or of U, it will be useful in our analysis because of its simple nature at high temperatures:

$$C_V=3Nk[1-\tfrac{1}{20}(\theta_2/T)^2+\cdots]+C_{AE}. \tag{14}$$

Now, of course, all the complications are in the anharmonic and electronic-excitation terms. But much has been learned from previous studies of the elements, and this will provide guidance for the present work. Consider first the anharmonicity. From highly accurate analyses for 27 elements, anharmonic contributions to entropy and energy are found to be important in only two situations:[11–13] (a) for the refractory metals Cr, Mo, and W, where we presume the significant anharmonicity is due to some directional (covalent) character of the bonding, and (b) for Ti and Zr, where in the vicinity of the hcp-bcc phase transition, the approach of mechanical instability leads to phonon softening at temperatures above and below the transition temperature. While covalent bonding is presumably not present in any phase of Pu, there are five temperature-driven solid-solid phase transitions in Pu, lying in the narrow temperature range 397.6–755.7 K, so that phonon softening is probably the normal state of affairs in crystalline Pu. Hence, in Pu we expect a strictly anharmonic phonon softening with complicated temperature dependence, superimposed on a set of quasiharmonic phonon distributions, one distribution for each phase. But the affect on thermodynamic functions should still be relatively small, as it is for Ti and Zr,[13] and indeed for all elements so far studied,[11] so we expect S_A and U_A to be relatively small, with complicated temperature dependence for each phase of Pu.

Let us now consider the electronic excitation free energy F_E. We assume that all phases of Pu have nonmagnetic ground states, so the zero-field magnetic contribution to F_E is zero. At low temperatures, the electron-phonon interaction enhances F_E, while at temperatures $T \gtrsim \theta_2$ this enhancement disappears, except possibly for a constant in the entropy. While this point of the theory needs to be completed,[14] we will assume that F_E goes to the bare electronic free energy as T increases above θ_2.[15] This bare F_E is given by an integral over the electronic density of states, and the corresponding S_E has been calculated as a function of T and V for several transition metals.[13] For Pu, the electronic density of states is still larger than it is for the transition metals. On the other hand, Pu melts at 913 K, or approximately 6 m Ry, and we presume this energy is small on the scale of a major structure in the electronic density of states. We can therefore use the leading low-temperature expression for the bare electronic free energy,

$$F_E = -\Gamma T^2, \tag{15}$$

where $\Gamma(V)$ depends on $n(\varepsilon_F)$, the density of electronic states per atom at the Fermi energy,

$$\Gamma = \tfrac{1}{6}\pi^2 N k^2 n(\varepsilon_F). \tag{16}$$

The corresponding entropy S_E and internal energy U_E are

$$S_E = 2\Gamma T, \tag{17}$$

$$U_E = \Gamma T^2. \tag{18}$$

In analyzing the thermodynamic data for Pu, it will not be possible to separate the anharmonic and electronic contributions. We will, therefore, keep these contributions combined in the free-energy term F_{AE} [Eq. (1)], and will use the empirical form, which turns out to be consistent with the available data,

$$F_{AE} = -DT^2, \tag{19}$$

where $D = D(V)$. For each of the six crystal phases of Pu, the quantity D can then be interpreted in view of the preceding discussion of anharmonicity and electronic excitations.

III. ANALYSIS OF EXPERIMENTAL DATA

Our study is made possible by the availability of heat capacity measurements for ^{242}Pu from 4 to 300 K by Gordon *et al.*,[16] and for an isotope mixture close to 239 from 330 to 700 K by Oetting and Adams.[17] The latter authors extended their data set to 1000 K by selecting values from published sources.[18] The data tables of Ref. 17 include measured phase-transition temperatures, and enthalpies of transition.

The theoretical quantities Φ_0, θ_0, and D are all functions of volume for each phase. But our primary thermodynamic data, $S(V,T)$ and $U(V,T)$ at zero pressure, correspond to varying volume V for each phase, due to thermal expansion. For an accurate determination of the theoretical quantities, we need to remove the thermal expansion contribution to the primary thermodynamic data. To do this, we choose a reference volume V_0 for each phase, and make a small correction of the primary data to obtain $S(V_0,T)$ and $U(V_0,T)$ at the fixed volume V_0 for each phase. We choose V_0 for the α phase to be the volume at $T=0$, and for each remaining phase to be the volume at the lower temperature of the phase-stability range. With this choice V_0 is not universal, but varies from phase to phase, and the thermal expansion corrections are kept small for each phase.

Volume corrections are derived from the Taylor series, and standard thermodynamic manipulations.[5] At a fixed temperature, the zero-pressure volume is V, and we define

$$\eta = \frac{V - V_0}{V}. \tag{20}$$

Then $S(V_0)$ and $U(V_0)$ can be evaluated from the following expressions, correct to second order in η,

$$S(V_0) = S(V) - \beta V B_T \eta - \tfrac{1}{2} a V B_T \eta^2, \tag{21}$$

$$U(V_0) = U(V) - T\beta V B_T \eta + \tfrac{1}{2} V B_T (1 - aT)\eta^2, \tag{22}$$

where β is the thermal-expansion coefficient, B_T is the isothermal bulk modulus, and where

$$a = \frac{\partial \ln B_T}{\partial T}\bigg|_P + \beta \frac{\partial B_T}{\partial P}\bigg|_T. \tag{23}$$

The coefficients of η and η^2 in Eqs. (21) and (22) are evaluated at V, i.e., at zero pressure.

To evaluate the volume corrections for each of the six Pu phases, a considerable collection of thermodynamic data is required. The available set of thermodynamic data for Pu is among the least reliable of all the elements. The reasons for this include that Pu is scarce, is difficult to handle, and is constantly undergoing damage and heating from self-irradiation. In the following paragraph we describe our data evaluation and selection.

The density of each solid phase is taken from Table 3.1 of Ref. 19. Thermal expansion data for each solid phase are taken from Ref. 20. Note that the negative expansion at low temperatures, shown in Fig. 3.1 of Ref. 19, is apparently incorrect. For the adiabatic bulk modulus B_S, we use the results of Calder, Draney, and Wilcox[21] for the α phase, and for the δ phase we use the results of Calder, Draney, and Wilcox[21] for δ-stabilized Pu-1 wt % Ga. Even though the experimental technique of Calder, Draney, and Wilcox is unconventional, their room-temperature value $B_S = 50.6$ GPa implies $B_T = 45.4$ GPa, in reasonable agreement with the diamond-cell measurement $B_T = 42.2$ GPa of Roof.[22] Also for the δ-stabilized alloy, the room-temperature value of Calder, Draney, and Wilcox, $B_S = 32.4$ GPa, is close to the ultrasonic value $B_S = 29.9$ GPa of Ledbetter and Moment.[23] In comparison with the results of Calder, Draney, and Wilcox, the values of B_T for the α phase listed in Table 4.2 of the Ref. 19 are quite inaccurate below room temperature, but are within 10% above room temperature. We therefore take B_T for β and γ phases from Table 4.2 of Ref. 19. No compressibility data were found for δ' and ε phases.-

TABLE I. Experimental data needed to make volume corrections for entropy and internal energy, and the volume-corrected results $S(V_0)$ and $U(V_0)$. Parentheses indicate estimated values.

T (K)	V (cm^3/mol)	β (10^{-4}/K)	B_S (GPa)	$\frac{C_p}{Nk}$	γ	$\frac{S(V_0)}{Nk}$	$\frac{U(V_0)}{Nk}$ (K)
α phase							
0	11.712	0	(61.5)	0		0	0
220	11.92	1.27	(54.1)	3.434	(2.87)	5.301	525.8
240	11.95	1.31	(53.2)	3.515	(2.85)	5.579	589.1
260	11.98	1.35	(52.4)	3.596	(2.83)	5.834	652.8
280	12.01	1.38	(51.5)	3.678	(2.79)	6.079	717.9
300	12.05	1.41	50.6	3.797	2.72	6.309	783.0
320	12.08	1.44	49.7	3.905	2.66	6.528	850.3
340	12.12	1.47	48.9	4.013	2.61	6.740	919.2
360	12.15	1.49	48.0	4.121	2.54	6.945	989.6
380	12.19	1.51	47.1	4.229	2.47	7.144	1061.8
397.6	12.22	1.53	46.3	4.323	2.41	7.314	1126.0
β phase							
397.6	13.40	1.12	35.6[a]	3.922	1.64	8.835	1679.2
420	13.44	1.12	33.3[a]	3.957	1.52	9.034	1760.3
440	13.47	1.12	31.4[a]	3.989	1.43	9.208	1834.7
460	13.50	1.12	29.4[a]	4.020	1.33	9.377	1910.0
487.9	13.54	1.12	26.5[a]	4.064	1.19	9.605	2016.9
γ phase							
487.9	13.91	1.04	24.9[a]	3.996	1.08	9.769	2097.2
520	13.96	1.04	23.9[a]	4.085	1.02	10.013	2219.5
540	13.99	1.04	23.3[a]	4.140	0.99	10.160	2297.3
560	14.02	1.04	22.8[a]	4.195	0.95	10.304	2375.9
593.1	14.07	1.04	21.8[a]	4.287	0.90	10.536	2508.3
δ phase							
593.1	15.01	−0.26	25.0	4.196	−0.28	10.722	2618.6
620	15.00	−0.26	24.5	4.231	−0.27	10.908	2731.5
660	14.99	−0.26	23.7	4.283	−0.26	11.174	2901.3
700	14.97	−0.26	23.0	4.335	−0.25	11.425	3072.6
736.0	14.96	−0.26	22.6	4.382	−0.24	11.644	3228.9
δ' phase							
736.0	14.94	−0.48	(23)	4.277	−0.46	11.66	3242
755.7	14.92	−0.48	(23)	4.277	−0.46	11.77	3324
ε phase							
755.7	14.47	1.10	(23)	4.056	1.09	12.07	3547
780	14.51	1.10	(23)	4.056	1.09	12.18	3637
820	14.57	1.10	(23)	4.056	1.09	12.37	3785
860	14.64	1.10	(23)	4.056	1.10	12.54	3930
900	14.70	1.10	(23)	4.056	1.10	12.71	4076
913.0	14.72	1.10	(23)	4.056	1.10	12.76	4123

[a] B_S was calculated from the experimental B_T.

However, the graph of B_S vs density for the other four crystal phases, and the liquid also, presents a reasonably smooth curve, and by interpolation yields the value $B_S = 23$ GPa for δ' and ε phases. Specific heat data for all phases are from Refs. 16 and 17.

In the above comparisons of data, the conversion between B_S and B_T is done by the relation $B_S = (1 + T\beta\gamma)B_T$, where γ is the Grüneisen parameter $\gamma = V\beta B_S/C_P$. Likewise the conversion between C_P and C_V is given by $C_P = (1 + T\beta\gamma)C_V$. To make the volume corrections in Eqs. (21) and (22), only the term linear in η is significant for all phases except α. This is because each phase endures for only a narrow temperature range, across which the total thermal expansion is small, so that η is always very small. For the α phase, η is not so small, and the term in η^2 becomes barely significant at the highest temperatures, say above 300 K. To evaluate the function a, Eq. (23), we take $(\partial B_T/\partial P)_T$ as constant at the value 10.5 given by Roof,[22] and we find $(\partial \ln B_T/\partial T)_P$ is constant at the value $-0.0012\ \mathrm{K}^{-1}$ from 200 to 400 K. The data needed for volume corrections and for

TABLE II. Results of the thermodynamic analysis for Pu metal.

Phase	Structure	V_0 (cm^3/mol)	θ_0 (K)	θ_2 (K)	$\frac{\Phi_0}{Nk}$ (K)	$\frac{2D}{Nk}$ (10^{-3}/K)
α	simple monoclinic	11.712	116	162	−196	1.5
β	bc orthorhombic	13.40	71.3	99.5	347	1.7
γ	fc monoclinic	13.91	67.4	94.1	428	1.7
δ	fcc	15.01	66.1	92.2	500	1.92
δ'	bct	14.94	60.8	84.9	599	1.6
ε	bcc	14.47	45.2	63.1	1045	0.82

$B_S - B_T$ conversions, and the final values of entropy and internal energy corrected to the reference volumes, are listed in Table I.

We now describe our procedure for fitting theoretical expressions to the experimental data for each Pu phase. The expression we use for the constant-volume specific heat at high temperatures is

$$C_V = 3Nk[1 - \tfrac{1}{20}(\theta_2/T)^2] + 2DT, \tag{24}$$

where the last term is our empirical approximation for combined anharmonic and electronic excitation contributions, from Eq. (19). The first term can be evaluated accurately for $T \gtrsim \theta_2$, with only an approximate value of θ_2, so the experimental C_V gives a direct measure of the unknown quantity $D(V)$. In practice, however, because of a compounding of errors, this relation is not so helpful as it would appear. First, there is error in the measured C_P (note in Table I that only a constant C_P is tabulated for δ' and ε phases), and then there is error in the correction to C_V. The result for C_V is still at the varying zero-pressure volume V, and we are not able to evaluate the correction to the fixed volume V_0 with even qualitative reliability. In contrast, both $S(V,T)$ and $U(V,T)$ are accurate functions, being evaluated as integrals of the measured $C_P(V,T)$ data, and we can make accurate volume corrections for $S(V,T)$ and $U(V,T)$. The complete expressions we use for entropy and internal energy at high temperatures are, from Sec. II,

$$S(V_0,T) = 3Nk[\ln(T/\theta_0) + 1 + \tfrac{1}{40}(\theta_2/T)^2] + 2DT, \tag{25}$$

$$U(V_0,T) = \Phi_0 + 3NkT[1 + \tfrac{1}{20}(\theta_2/T)^2] + DT^2, \tag{26}$$

where the unknown parameters θ_0, Φ_0, and D are evaluated at V_0, and where we use the approximation (8) for θ_2. We start by using Eq. (24) to find an estimate for D, then we solve Eq. (25) for θ_0 and Eq. (26) for Φ_0, and finally we make small changes in D until θ_0 and Φ_0 have no sensible temperature dependence. The final value of D is always within 7% of the initial estimate. The fitting is done for $S(V_0,T)$ at $T \gtrsim 220$ K, and for $U(V_0,T)$ at $T \gtrsim 260$ K, for α-Pu, and at all temperatures for the remaining five phases.

IV. RESULTS AND DISCUSSION

A. General thermodynamic properties

For each of the six crystalline phases of Pu, the crystal structure, the reference volume V_0, and the fitted parameters θ_0, Φ_0, and D are listed in Table II. These parameters, together with Eqs. (25) and (26), reproduce the experimental data to an accuracy well within experimental error, having mean-fitted error around 1 part in 5000 for entropy at $T \gtrsim 220$ K, and of around 1 part in 1000 for internal energy at $T \gtrsim 260$ K. Hence, we have achieved, at the very least, an accurate analytic representation of the thermodynamic functions of Pu at the temperatures cited.

The most obvious physical property emerging from our analysis is that the anharmonic and electronic-excitation contributions to thermodynamic functions are small compared to the quasiharmonic contributions. Hence, in first approximation, each crystalline phase of Pu is an ordinary quasiharmonic crystal. To make this notion quantitative, it suffices to look at the entropy, and to define the relative combined anharmonic and electronic excitation contribution S_{AE}/S. For the six phases of Pu, and at $T \gtrsim 220$ K, this quantity is 6–12 %. This is larger than the range $\lesssim 2\%$ for nearly-free-electron elements,[12] and is in the same range as the transition metals.[13] Hence, for Pu, as for all other elements we have studied, and in agreement with the discussion of Sec. II, the thermal free-energy is dominated by F_H.

B. Static lattice potentials

The values of Φ_0 in Table II increase monotonically, from each phase to the next-higher-temperature phase. While this behavior is not *required* by theory, it is generally to be expected, since otherwise the free-energy curves for two phases have multiple crossings. The six Φ_0 are very close together, and pose an enormous challenge to electronic-structure theory. The Φ_0 should be accurate to around 10%. Estimated error limits for all the fitted parameters are listed in Table III.

The zero of energy is the α-phase energy at zero temperature and pressure. From Eq. (11) for U_0, we have $\Phi_0 + \frac{9}{8}Nk\theta_1 + U_{A0} = 0$ for α-Pu at the volume V_0, and we expect U_{A0} to be quite small. In units of temperature, $\Phi_0/Nk = -196$ K from Table II, and with $\theta_1 = e^{1/3}\theta_0$, we find $\frac{9}{8}\theta_1 = 182$ K. These results imply $U_{A0}/Nk = 14$ K, with total error estimates around ±30 K. The nearly complete cancel-

TABLE III. Estimated percentage error limits in the fitted parameters for Pu metal.

Phase	Φ_0	θ_0	D
α	11	3	10
β	10	4	10
γ	8	4	8
δ	10	4	8
δ'	9	4	18
ε	10	6	29

lation between Φ_0 and $\frac{9}{8}Nk\theta_1$ constitutes an independent confirmation of our data analysis for α-Pu.

C. Phonon characteristic temperatures

Any of the central moments of the phonon distribution, i.e., the 0, 1, and 2 moments, provides a measure of the overall magnitude of the phonon frequencies, hence a measure of the strength of the interionic forces. These moments are related by Eqs. (3)–(5) to the characteristic temperatures θ_0, θ_1, and θ_2. The second moment is the simplest to calculate theoretically, since it is a trace over all dynamical matrices, and hence can be reduced to a sum over interionic forces.[5] The θ_0 values are expected to be quite accurate (see Table III), and in the absence of direct measurements of phonon dispersion curves can provide checks for electronic-structure calculations of phonon frequencies.

The θ_0 in Table II decrease monotonically, from each phase to the next-higher-temperature phase. This confirms the qualitative shift to lower-phonon frequencies, with each entropy-driven phase transition, as anticipated in Sec. I.

In order to compare among elements the strength of interionic forces, one must compare the dynamical matrix eigenvalues $M\omega^2$, or equivalently, one must compare $\sqrt{M}\theta_0$, where M is the atomic weight. This latter quantity is listed in Table IV for the six Pu crystal phases, and also for several other heavy metals, whose θ_0 are determined from inelastic neutron-scattering experiments.[12] Apparently, the several crystal phases of Pu possess interionic forces with magnitudes resembling those of several different metals. For example, $\sqrt{M}\theta_0$ for α-Pu is close to Au, and is significantly less than gold's neighbor Pt, and significantly more than the actinide metal Th. $\sqrt{M}\theta_0$ for β, γ, δ, and δ' phases of Pu decreases uniformly through a narrow range, and at the lower end of the range, $\sqrt{M}\theta_0$ is essentially the same as for Hg and Pb. The Pu phase with weakest interionic forces is ε-Pu, for which $\sqrt{M}\theta_0$ is roughly the same as for Ba. The value of $\sqrt{M}\theta_0$ for Cs is estimated from experimental values for the lighter alkali metals, and shows that the forces in these metals are much weaker than for any phase of Pu. Aside from Pu, each metal listed in Table IV exhibits a single-crystal structure, from $T=0$ to melting, and each has no significant anharmonicity in its thermodynamic functions, and no significant phonon softening. Hence, in the strength of interionic forces, each Pu crystal phase is comparable to a well-behaved representative of the periodic table.

TABLE IV. Quantity $\sqrt{M}\theta_0$, in units of amu$^{1/2}$ K, for the six crystal phases of Pu, and for several other heavy metals.

Metal	$\sqrt{M}\theta_0$	Metal	$\sqrt{M}\theta_0$
α-Pu	1793	Pt	2284
β-Pu	1102	Au	1747
γ-Pu	1042	Th	1517
δ-Pu	1022	Pb	923
δ'-Pu	940	Hg	916
ε-Pu	699	Ba	779
		Cs	(380)

D. Anharmonicity and electronic excitations

The bare electronic entropy is $2\Gamma T$, where Γ is given by Eq. (16) in terms of the density of states at the Fermi energy. At the low temperatures $T \ll \theta_2$, this is renormalized to $2\Gamma(1+\lambda)T$, where λ is the electron-phonon enhancement. Specific heat measurements for ^{239}Pu below 8 K give $2\Gamma/Nk=2.77(10^{-3}/\mathrm{K})$.[16] Our determination of the combined anharmonic and electronic entropy $2DT$ gives $2D/Nk=1.5(10^{-3}/\mathrm{K})$ for α-Pu at $T>\theta_2$. If this is all electronic, then $D=\Gamma$, and the electron-phonon enhancement is $\lambda=0.85$. This value is in line with estimates of λ for other metals.[24–28]

The electronic density of states has been calculated for α-Pu at the room-temperature volume of 12.04 cm^3/mol, with the result $n(\varepsilon_F)=3.5$ states/atom eV.[29] The corresponding bare electronic entropy coefficient is $2\Gamma/Nk=0.99(10^{-3}/\mathrm{K})$, and this has two implications. First, our combined anharmonic and electronic entropy coefficient $2D/Nk$ would have the contribution $0.99(10^{-3}/\mathrm{K})$ from electronic excitations, and the remaining $0.51(10^{-3}/\mathrm{K})$ from anharmonicity. This is a large anharmonicity, but is still within the range of anharmonicities exhibited by the transition metals.[13] Second, the electron-phonon enhancement would now have the unusually large value $\lambda=1.80$.

Obviously, the present state of affairs is inconclusive. The quantity D, listed in Table II, will help in eventually sorting out anharmonicity and electronic excitations in Pu metal.

E. Notes on estimated errors

The primary experimental data are C_P, plus the transition temperatures and transition enthalpies. C_V, S, and U are derived from these primary data. For each crystal phase, the temperature range of the fit of theory to experiment is small, so it is mainly the magnitude of C_V, S, and U that determines, respectively, the quantity D, θ_0, and Φ_0. We have, therefore, tried to estimate magnitude errors, but not slope errors, in $C_V(V,T)$, $S(V_0,T)$, and $U(V_0,T)$. The interdependence of errors in D, θ_0, and Φ_0 is, therefore, contained in the interdependence of errors in C_V, S, and U. We have assumed that the errors in the experimental C_P, the experimental transition enthalpies, and the computed C_P-C_V correction or volume corrections, are statistically independent. The results are listed in Table III.

[1] For example, M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982); P. Söderlind, O. Eriksson, B. Johansson, and J. M. Wills, *ibid.* **52**, 13 169 (1995).

[2] For example, R. Heid, K.-P. Bohnen, and K. M. Ho, Phys. Rev. B **57**, 7407 (1998); G. K. Straub, J. B. Aidun, J. M. Wills, C. R. Sanchez-Castro, and D. C. Wallace, *ibid.* **50**, 5055 (1994).

[3] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[4] L. J. Sham, Proc. R. Soc. London, Ser. A **283**, 33 (1965).

[5] D. C. Wallace, *Thermodynamics of Crystals* (Dover, Mineola, NY, 1998).

[6] P. Söderlind, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **55**, 1997 (1997).

[7] D. A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).

[8] W. H. Zachariasen, in *The Metal Plutonium*, edited by A. S. Coffinberry and W. N. Miner (University of Chicago Press, Chicago, 1961), p. 99.

[9] O. Eriksson, J. D. Becker, J. M. Wills, and A. V. Balatsky, Europhys. Lett. (to be published).

[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[11] D. C. Wallace, Phys. Rev. E **56**, 1981 (1997).

[12] D. C. Wallace, Proc. R. Soc. London, Ser. A **433**, 631 (1991).

[13] O. Eriksson, J. M. Wills, and D. C. Wallace, Phys. Rev. B **46**, 5221 (1992).

[14] D. C. Wallace, *Thermodynamics of Crystals* (Ref. 5), p. vi.

[15] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981).

[16] J. E. Gordon, R. O. A. Hall, J. A. Lee, and M. J. Mortimer, Proc. R. Soc. London, Ser. A **351**, 179 (1976).

[17] F. L. Oetting and R. O. Adams, J. Chem. Thermodyn. **15**, 537 (1983).

[18] F. L. Oetting, M. H. Rand, and R. J. Ackermann, *The Actinide Elements* (IAEA, Vienna, 1976).

[19] *Plutonium Handbook*, edited by O. J. Wick (Gordon and Breach, New York, 1967).

[20] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, *Thermal Expansion*, Thermophysical Properties Research Center Data Series (Plenum, New York, 1975), Vol. 12.

[21] C. A. Calder, E. C. Draney, and W. W. Wilcox, J. Nucl. Mater. **97**, 126 (1981).

[22] R. B. Roof, in *Advances in X-Ray Analysis*, edited by D. K. Smith, C. Barrett, D. E. Leyden, and P. K. Predecki (Plenum, New York, 1981), Vol. 24, p. 221.

[23] H. M. Ledbetter and R. L. Moment, Acta Metall. **24**, 891 (1976).

[24] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[25] G. S. Knapp, R. W. Jones, and B. A. Loomis, in *Low Temperature Physics-LT13*, edited by K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel (Plenum, New York, 1974), Vol. 3, p. 611.

[26] S. D. Bader and G. S. Knapp, Phys. Rev. B **11**, 3348 (1975).

[27] G. Grimvall, *The Electron-Phonon Interaction in Metals* (Ref. 15), Table 11.1.

[28] P. B. Allen, Phys. Rev. B **36**, 2920 (1987).

[29] John Wills (private communication).