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Theory of the thermal properties of δ-plutonium

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The thermal properties of δ-plutonium are studied in terms of the elementary electronic structure, and contrasted to those of aluminum. In both metals the thermal expansion can be understood as from the pressure of the gas of phonons, a negative expansion in the case of plutonium because of negative Grüneisen constants for some transverse modes. Thermal expansion in aluminum is found positive, in agreement with experiments. This phonon gas also has a bulk modulus, negative for plutonium, which dominates the observed negative temperature dependence of the bulk modulus for plutonium, with a smaller negative contribution arising from the thermal expansion (in contrast to contraction for pure plutonium) of the alloys on which it is measured. For aluminum, the phonon-gas contribution is negligible and thermal expansion causes the bulk modulus to decrease with temperature, as in experiments. The Debye-Waller temperature, another measure of rigidity, contains a small positive contribution to the temperature dependence from thermal expansion in plutonium and a negative contribution in aluminum. There is also a much larger negative contribution to the temperature dependence of the Debye-Waller temperature in both (in accordance with experiments for plutonium) arising from anharmonicity of some transverse modes. The nearest-neighbor, central-force interactions used here inevitably lead to sizable errors in some elastic constants, and replacement of Brillouin-zone averages by averages along the [100] and [111] directions is very questionable for some properties. However, the simplification is major and the results appear to reveal which contributions are important.

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I. INTRODUCTION

Plutonium is probably the most complex metallic element, followed by cerium and iron, because of the intermediate strength of the electron correlations. The possibility of understanding plutonium has been greatly enhanced by the recent determination of the vibration spectrum by Wong *et al.*[1] using inelastic x-ray scattering, and by the confirming results deduced from a phonon density of states from inelastic neutron scattering by McQueeney *et al.*[2] We interpreted these by using an earlier simple description of the electronic structure[3,4] based upon a Friedel model of the density of f states, $n_f(\varepsilon)=14/W_f$, an empty-core pseudopotential treatment of the three sd electrons per atom, and inclusion of correlations through a generalization of an exact result for a two-level, two-electron problem.[5] This description leads[3,5] to two-body, central-force interactions $V(d)=V_{fe}(d)+V_f(d)$ between atoms. One contribution comes from the free-electron theory as

$$V_{fe}(d)=\frac{Z^2e^2\cosh^2\kappa r_c e^{-\kappa d}}{d}. \tag{1}$$

Here $Z=3$ is the valence of an f-shell metal, κ is the Fermi-Thomas screening parameter depending only upon the free-electron density, and r_c is the empty-core pseudopotential core radius. The f-shell contribution is (Ref. 5, following Ref. 3, p. 620)

$$V_f(d)=-\frac{1}{6}\frac{Z_f(1-Z_f/14)}{2}\left[\sqrt{\left(\frac{\hbar^2(6.49r_f)^5}{md^7}\right)^2+U_f^2}-U_f\right]+Z_f\frac{\hbar^2(3.98r_f)^{10}}{6md^{12}}. \tag{2}$$

The first term comes from a partial filling of the f band, and the second is a repulsion from overlap of neighboring f orbitals. It will be helpful as we treat plutonium to also consider a simple metal, aluminum, again $Z=3$ and for which $r_f=0$, eliminating the contribution of Eq. (2).

The calculation of vibration spectra in terms of such potentials is straightforward and was carried out in Ref. 5. For nearest-neighbor interactions the only parameters which entered are the first and second derivatives of $V(d)$, the sum of Eqs. (1) and (2), at the observed spacing, which we specify in terms of $V^{(1)}=d_0\,\partial V/\partial d$ and $V^{(2)}=d_0^2\,\partial^2V/\partial d^2$, evaluated at the nearest-neighbor distance $d=d_0$. This gives, for example, for longitudinal modes propagating in a [100] direction

$$\hbar^2\omega_{\mathrm{k}}^2=(\hbar^2/Md^2)E^{(2)}\sin^2(kd/\sqrt{8}), \tag{3}$$

where $E^{(2)}=8V^{(1)}+8V^{(2)}$ plays the role of a spring constant and $\hbar^2/Md^2=1.623\times10^{-6}$ eV for Pu_{238} and 18.76×10^{-6} eV for Al. The form is convenient since we shall be working with phonon energies.

The question of values for the parameters arises immediately. There are in fact many ways in which they can be obtained. For aluminum, values of r_c were given in Ref. 3 (p. 453) of 0.61 Å, obtained by fitting the pseudopotential form factors to full calculations, a value of 1.01 Å by adjusting the value appearing in a total energy for the metal (including some volume-dependent energies not discussed here) to be

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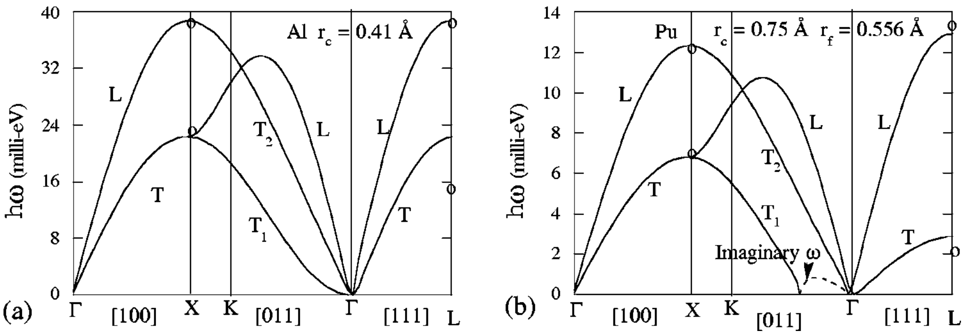

FIG. 1. To the left is the spectrum for aluminum, $d_0 = 2.86$ Å, obtained for nearest-neighbor interactions from Eq. (1). The circles at symmetry points are experimental values from Ref. 6. To the right is the corresponding spectrum for plutonium, $d_0 = 3.275$ Å. Experimental points are from Ref. 1. T_1 modes are polarized in a [01-1] direction; T_2 modes in a [100] direction.

minimum at the observed atomic spacing, and a value of 0.23 Å to obtain the observed bulk modulus in terms of the interactions in Eq. (1). This spread arises from the intrinsic approximate nature of the pseudopotential perturbation theory, from use of the approximate local empty-core form, and from the approximations used to calculate the property fit, as well as the local-density approximation to the electron-electron interaction. The spread in r_c is large because the properties are rather insensitive to its value, in contrast to the sensitivity of properties to the f-state radius, r_f. One radius is not more accurate than another, so it is appropriate to fit to a property such as that under discussion, and use that value to describe the entire area.

Thus for discussing the vibration spectrum of aluminum we could choose the $r_c = 0.23$ Å fit to the bulk modulus, which would assure that the speed of longitudinal sound was essentially correct, but we found that this gave peak frequencies at the zone face some 40% too small, exactly because the forms $\omega_k = \omega_0 \sin(kd/\sqrt{8})$, which follow from nearest-neighbor interactions, are not accurate. We choose to pick $r_c = 0.41$ Å, which gives the spectrum for aluminum shown in Fig. 1(a). These peak frequencies are in approximate accordance with experiments, but some slopes at $k=0$ are necessarily too large. The calculation of the spectrum itself, carried out in Ref. 5 and leading to formulas we shall give, is straightforward and only made intricate by the presence of a nonzero $d_0 \partial V/\partial d$.

For plutonium, $Z_f = 5$, $U_f = 4.61$ eV, $r_f = 0.58$ Å, and $r_c = 0.69$ Å (from Ref. 3, p. 605), and for the delta phase the equilibrium spacing is $d_0 = 3.275$ Å. r_f was fit to bandwidths from band calculations and r_c was obtained by including volume-dependent terms and adjusting r_c so that the minimum energy came at the observed spacing. We found in Ref. 5 that these values led to instability of the $T[111]$ (transverse modes with wave number in a [111] direction) and $T_1[110]$ modes, but that the r_f and r_c could be readjusted ($r_c = 0.67$ Å, $r_f = 0.40$ Å in Ref. 5) to give a fit to the experimental spectrum comparable to that for aluminum. We have since found that this failed, for example, to give the observed negative thermal expansion of δ-plutonium. We shall proceed with values, $r_c = 0.75$ Å and $r_f = 0.556$ Å, adjusted to give that negative expansion correctly. The resulting vibration spectrum, shown in Fig. 1(b), did not allow the stability we sought, but a lowering of energy as long-wavelength $T_1[110]$ mode amplitudes are introduced, showing up as imaginary frequencies. We shall see in the following section that this instability would almost be removed by the inclusion of second-neighbor interactions. Aside from this anomaly, the spectra of aluminum and plutonium are surprisingly alike. We noted in Ref. 5 that in the observed spectrum for plutonium, the slopes of the L and T spectra along [100] are almost identical, which can never be reproduced in our nearest-neighbor spectrum if the values at X are as different as they are. This is because Eq. (3) applies to both curves. The second-neighbor couplings discussed in the next section do not help and this remains a shortcoming of our description.

As we proceed to the thermal properties, we will also need higher derivatives, $V^{(i)} = d_0 \partial^i V/\partial d^i$, evaluated at the nearest-neighbor distance. It is these higher derivatives which lead to the extraordinary differences in the two metals. We have noted [5] that when we take derivatives of the total energy with respect to d, the factors in the phonon energy such as $\sin(kd/\sqrt{8})$ do not vary since kd simply indexes the state in question, with $kdN/(2\pi\sqrt{2})$ an integer between $-N/2$ and $N/2$ for N planes of atoms. In evaluating the higher derivatives another complication arises in that we will be calculating the shift in the phonon frequency as the total volume changes. Thus the derivative of the Fermi-Thomas screening parameter, $\kappa = (4e^2 k_F m/\pi\hbar^2)^{1/2}$ with $k_F = (3Z\sqrt{2}\pi^2)^{1/3}/d$, enters. Thus, $V^{(2)}$ is obtained holding κ fixed in the derivatives, and $V^{(3)}$ would come from another derivative holding κ fixed, but if we included the variation of κ in the last derivative we would write it as $V^{(3)\dagger}$. If the variation of κ were included in the last two derivatives, we would write it as $V^{(3)\dagger\dagger}$. The derivatives at $d_0 = 3.275$ Å, which enter our calculations for plutonium, based upon Eqs. (1) and (2) with $r_c = 0.75$ Å and $r_f = 0.556$ Å, are given in eV by

$$\begin{array}{llll} V^{(1)} = -2.28 & & & \\ V^{(2)} = 13.99 & V^{(2)\dagger} = 10.2 & & \\ V^{(3)} = -59.6 & V^{(3)\dagger} = -39.6 & V^{(3)\dagger\dagger} = -19.2 & \text{Plutonium} \\ V^{(4)} = -256 & & V^{(4)\dagger\dagger} = -454. & \end{array} \tag{4}$$

The $V^{(1)}$ and $V^{(2)}$ led to the dispersion curves in Fig. 1(b).

The derivatives at $d_0 = 2.86$ Å for aluminum, based upon Eq. (1) with $r_c = 0.41$ Å, are given in eV by

$$\begin{array}{llll} V^{(1)} = -1.66 & & & \\ V^{(2)} = 11.66 & V^{(2)\dagger} = 8.45 & & \\ V^{(3)} = -84.0 & V^{(3)\dagger} = -66.2 & V^{(3)\dagger\dagger} = -49.9 & \text{Aluminum} \\ V^{(4)} = 623 & & V^{(4)\dagger\dagger} = 432. & \end{array} \tag{5}$$

The $V^{(1)}$ and $V^{(2)}$ led to the curves given in Fig. 1(a).

The $V^{(4)}$ and $V^{(4)\dagger\dagger}$ for plutonium in Eq. (4) are anomalous relative to that for aluminum, but by examining the individual contributions, all of which grow with i, we saw that the f-bonding term, varying approximately as $-1/d^{14}$ when the Coulomb repulsion U_f is much larger that W_f, became dominant over the free-electron term just at the fourth derivative. The large negative values will make important differences in the properties.

This approximate first-principles description has an advantage, even with the adjustment of the two parameters r_c and r_f, over the much closer Born-von Kármán fourth-nearest-neighbor fit, in giving these higher $V^{(i)}$. With the additional $V^{(i)}$ we may obtain the Grüneisen constant for each mode and thus the thermal expansion and other properties. The same properties could be obtained, presumably more accurately, by repeating the calculation of the spectrum using Dynamical Mean-Field (DMF) Theory, as was done by Dai *et al.*,[7] but at different volumes. It could also be done by incorporating the correction $W_f/\sqrt{(W_f^2+U_f^2)} \sim 0.29$ for δ-plutonium (where W_f is the f-band width and U_f the Coulomb repulsion) in a traditional local density theory, as suggested in Ref. 4. That would be desirable, but the results are much easier to understand, and hopefully quite similar, in the simpler theory we use here. Further, we give the formulas, and the parameters in Sec. VII, which allow all of the estimates to be made also for other actinides.

II. SECOND-NEIGHBOR INTERACTIONS

We are using a description with only nearest-neighbor interactions, and indeed the interactions arising from the f electrons drop so rapidly that second neighbors at 4.63 Å are negligible, but one might ask about the free-electron term, Eq. (1). It may be directly evaluated for $r_c = 0.75$ Å for plutonium at the second-neighbor spacing as $V(4.63\text{ Å}) = 0.019$ eV, and contributes -0.10 eV to a $V^{(1)}(\text{2nd}) = d_0^2\,(1/d)\,\partial V/\partial d|_{d=\sqrt{2}d_0}$, for second neighbors and 0.95 eV to a $V^{(2)}(\text{2nd})$. Including these would add a second set of parameters, such as Eqs. (4) and (5), and a second set of contributions for each property we compute; and the use of Fermi-Thomas screening, rather than full quantum screening, is questionable at such distances in any case. In order to simplify the theory we drop these contributions, but we may check for any property how big they are. In particular, for the elastic constants, we found in Ref. 5 that $c_{11} = (V^{(1)} + V^{(2)})/\Omega_0$, with $\Omega_0 = d_0^3/\sqrt{2}$ the atomic volume. (The elastic constants, incidentally, were calculated from the speed of sound and thus at constant volume; the derivatives of the screening constant do not enter so the bulk modulus is a little different from that which would be obtained from modifying the total volume.) Nearest-neighbor interactions lead to the full set of elastic constants (energy per atom, or energy per volume if divided by the atomic volume)

$$c_{11} = V^{(1)} + V^{(2)},$$

$$c_{12} = -\tfrac{5}{2}V^{(1)} + \tfrac{1}{2}V^{(2)},$$

$$c_{44} = \tfrac{3}{2}V^{(1)} + \tfrac{1}{2}V^{(2)}. \tag{6}$$

The three values for plutonium are 11.72, 12.73, and 3.61 eV per atom, respectively. (1 eV per atom$=0.0645 \times 10^{12}$ergs/cm^3 for 2 δ Pu.) The second-neighbor contributions to c_{11} is $V^{(2)}(\text{2nd}) = 0.95$ eV/atom, to c_{12} it is $-V^{(1)}(\text{2nd}) = 0.10$ eV/atom, and to c_{44} it is $2V^{(1)}(\text{2nd}) = -0.19$ eV/atom, small enough to neglect. [These, again, were obtained from the speed of sound. Other approaches can change c_{11} and c_{12}, but leave $(c_{11}-c_{12})/2$ the same.] Further, they increase the difference between c_{11} and c_{44}, which were very nearly equal in experiment, but very different from two-body, central-force interactions.

On the other hand, the instability we saw for the $T_1[110]$ mode corresponds to a small negative shear constant, $(c_{11}-c_{12})/2 = 1/4[7V^{(1)} + V^{(2)}]|2/d^3 = -0.032 \times 10^{12}$ ergs/cm^3, and the second neighbors contribute positively to this shear constant, a value $\frac{1}{2}[V^{(1)}(\text{2nd}) + V^{(2)}(\text{2nd})]\sqrt{2}/d_0^3 = 0.027 \times 10^{12}$ ergs/cm^3, nearly sufficient to stabilize the lattice. This may be the only place where the second neighbors make an important difference and we proceed with nearest neighbors. This will mean that we cannot use the modes propagating in the $[110]$ direction in averaging over the Brillouin zone, but this will also considerably simplify the calculations since we will find that properties such as the Grüneisen constant are independent of wave numbers in the $[100]$ and $[111]$ directions, but they would vary with wave numbers along the $[110]$ direction.

III. AVERAGES OVER THE BRILLOUIN ZONE

In all of the properties we now explore we shall require averages of the frequency, or other functions of wave numbers, over the Brillouin zone. In principle we could redo the calculation which led to Eq. (3) for arbitrary wavenumbers and perform such averages. In view of the very considerable inaccuracies for the modes we have considered, that would not seem justified. The results will be much easier to write down and interpret if we reduce them to averages along symmetry lines, restricting them to $[100]$ and $[111]$ lines as indicated at the close of the last section. Many of these more accurate averages have been calculated for aluminum, [8] and it may be useful to test our simplified averaging for aluminum against the more complete studies.

We focus on averages over the Brillouin zone, $\langle \omega_{\mathbf{k}}^n \rangle$, with $n=1$ and 2, entering in this study, with $\mathbf{k}$ giving the wave number of the mode and also containing an index designating the three modes at that wave number. The average is obtained by dividing the Brillouin zone into pyramidal segments of equal volume centered on each of the $6+8=14$ symmetry lines, for each first averaging along the symmetry line. Since for each branch of the spectrum $\omega_{\mathbf{k}}$ is proportional to some $\sin(ks)$, and weighting by the cross section of the pyramid, $\langle\hbar\omega_{\mathbf{k}}\rangle$ becomes $\int_{0,\pi/2}\sin x\, x^2 dx/\int_{0,\pi/2}x^2\,dx = 24(\pi-2)/\pi^3 = 0.8836$ times the peak value, $[(\hbar^2/Md^2)E^{(2)}]^{1/2}$, for that branch [obtainable using Eq. (3) and, as we shall see, the denominators of Eq. (10)]. The average over the Brillouin zone becomes $6/42$ times this average for the $L[100]$ branch, plus $12/42$ times the average for the $T[100]$ branch, plus $8/42$ times the average for the $L[111]$ branch, plus $16/42$ times the average for the $T[111]$ branch. This yields 21.1 meV for aluminum [approximately what one would guess from Fig. 1(a)] and approximately equal to the[8] 25.3 meV obtained from numerical integrations over the entire Brillouin zone for a spectrum accurately fit to the measured spectrum.

The average of $1/(\hbar\omega_{\mathbf{k}})^2$ is $3\int_{0,\pi/2}dx\,x^2/\sin^2 x/\int_{0,\pi/2}x^2\,dx = 1.686$ times the reciprocal of the peak value squared, $[(\hbar^2/Md^2)E^{(2)}]^{-1}$, for that branch. Evaluating the weighted averages of the branches gives $\langle 1/(\hbar\omega_{\mathbf{k}})^2\rangle = 6.42\times 10^3/\mathrm{eV}^2$. It is in considerably poorer accordance with the[8] $2.49\times 10^3/\mathrm{eV}^2$ obtained from numerical integrations over the entire Brillouin zone. This is partially from inaccuracies of our spectrum but much more from an inaccuracy of this moment calculation where a major contribution, 5.10 of the 6.42, came from the $T[111]$ branches. Note that the value of $1/(\hbar\omega_{\mathbf{k}})^2$ for $T[111]$ is weighted by $16/42$, as above, since we are averaging over 42 branches. If we had included also the 36 [110] modes, there would have been more larger contributions, but we would have divided them by 78. We can expect errors on the scale of a factor of 2 in averages involving $1/(\hbar\omega_{\mathbf{k}})^2$, but they will be good enough to tell us which terms are important, and going beyond that average would be a major undertaking.

If we seek a representative value of the phonon energy as $\langle 1/(\hbar\omega_{\mathbf{k}})^2\rangle^{-1/2} = 12.5$ meV, we see that it is much less than $\langle\hbar\omega_{\mathbf{k}}\rangle = 21.1$ meV because of its heavy weighting of low frequencies. One must be careful in using Debye temperatures Θ_D, or Debye energies $k_B\Theta_D$ which attempt to give representative phonon energies.

IV. THERMAL EXPANSION

Thermal expansion arises because the energy ($(n_{\mathbf{k}}+1/2)\hbar\omega_{\mathbf{k}}$ in a mode, in the $n_{\mathbf{k}}$th excited state) varies with volume Ω, giving a contribution to a pressure of $(n_{\mathbf{k}}+1/2)\hbar\,\partial\omega_{\mathbf{k}}/\partial\Omega$. Summing this over all the modes for a given volume gives the total pressure, which when divided by the bulk modulus B, gives the negative of the dilatation, $\delta\Omega/\Omega = -\Sigma_{\mathbf{k}}B^{-1}(n_{\mathbf{k}}+1/2)\hbar\,\partial\omega_{\mathbf{k}}/\partial\Omega = \Sigma_{\mathbf{k}}(n_{\mathbf{k}}+1/2)\hbar\omega_{\mathbf{k}}\;\gamma_{\mathbf{k}}/B\Omega$, where $\gamma_{\mathbf{k}}$ is the mode-Grüneisen constant,

$$\gamma_{\mathbf{k}} = -\,(\Omega/\omega_{\mathbf{k}})\,\partial\,\omega_{\mathbf{k}}/\partial\,\Omega, \tag{7}$$

for each mode. It may be helpful to think of this pressure as arising from a "phonon gas" since the second derivative of the energy of this gas with respect to volume will give a thermal contribution to the (adiabatic) bulk modulus arising from $\partial^2\omega_{\mathbf{k}}/d\Omega^2$. Due to the anisotropy of the system, there will even be contributions to the shear constant from the phonon gas, and at one point we thought that this might remove the instability of the $T_1[110]$ modes shown in Fig. 1(b). It did not, which caused us to look at second neighbors in the preceding section. We return in the following sections to these further properties of the phonon gas.

The $n_{\mathbf{k}}$ that enters in all cases, is $n_{\mathbf{k}} = 1/[\exp(\hbar\omega_{\mathbf{k}}/k_BT)-1]$, and we sum over all $3N$ modes for the N atoms so the result can be written in terms of the volume per atom, $\Omega_0 = d^3/\sqrt{2}$, as

$$\frac{\delta\Omega}{\Omega} = \frac{1}{B\Omega_0}\left\langle\frac{3\hbar\omega_{\mathrm{k}}\gamma_{\mathrm{k}}}{2\tanh(\hbar\omega_{\mathrm{k}}/2k_BT)}\right\rangle \approx \frac{3k_BT}{B\Omega_0}\langle\gamma_k\rangle. \tag{8}$$

The expectation value $\langle\rangle$, indicates an average over all modes. The final expression obtains at high temperatures where the hyperbolic tangent approaches $\hbar\omega/(2k_BT)$. The linear expansion $\delta d/d$ is one-third of this $\delta\Omega/\Omega$, and taking the derivative with respect to temperature at high temperature, gives the linear thermal expansion coefficient,

$$\alpha_{\mathrm{TE}} = \frac{\mathrm{k}_B\langle\gamma_k\rangle}{B\Omega_0}. \tag{9}$$

Obtaining the Grüneisen constant from Eq. (7) is quite direct. For the $L[100]$ mode we take the derivative with respect to d of both sides of Eq. (3) (first writing out $E^{(1)}$ in terms of $\partial V/\partial d$ and $d^2V/\partial d^2$) to obtain $2\hbar\omega_{\mathbf{k}}\partial\hbar\omega_{\mathbf{k}}/\partial d = 8(\hbar^2/M)\sin^2(kd/\sqrt{8})\,\partial(1/d\,\partial V/\partial d + \partial^2V/\partial d^2)/\partial d = 8(\hbar^2/Md^3)\sin^2(kd/\sqrt{8})(-V^{(1)}+V^{(2)\dagger}+V^{(3)\dagger})$, noting as we indicated that $\sin^2(kd/\sqrt{8})$ does not vary in the derivative, but that in the derivative for the change in volume the screening constant changes, so a † appears. Noting that $\Omega\,\partial/\partial\Omega = 1/3\;d\,\partial/\partial d$ we obtain for $L[100]$ and the other modes

$$\gamma_{L[100]} = -\frac{1}{6}\frac{-8V^{(1)}+8V^{(2)\dagger}+8V^{(3)\dagger}}{8V^{(1)}+8V^{(2)}},$$

$$\gamma_{T[100]} = -\frac{1}{6}\frac{-12V^{(1)}+12V^{(2)\dagger}+4V^{(3)\dagger}}{12V^{(1)}+4V^{(2)}},$$

$$\gamma_{L[111]} = -\frac{1}{6}\frac{-4V^{(1)}+4V^{(2)\dagger}+8V^{(3)\dagger}}{4V^{(1)}+8V^{(2)}},$$

$$\gamma_{T[111]} = -\frac{1}{6}\frac{-10V^{(1)}+10V^{(2)\dagger}+2V^{(3)\dagger}}{10V^{(1)}+2V^{(2)}}. \tag{10}$$

Note that in each case the expression in the denominator is $E^{(2)}$ so formulas for the frequencies in each mode (given in Ref. 5) can be obtained from the denominators and comparison with Eq. (3), using the $\sin(kd/\sqrt{6})$ for the sine factor in the case of [111].

Using values for δ-Pu from Eq. (4) we obtain $\gamma_{L[100]} = 0.38$, $\gamma_{T[100]} = 0.05$, $\gamma_{L[111]} = 0.43$, and $\gamma_{T[111]} = -1.49$, applying to each entire symmetry line. The weighted average over symmetry lines is $\langle\gamma\rangle = (6\gamma_{L[100]} + 12\gamma_{T[100]} + 8\gamma_{L[111]} + 16\gamma_{T[111]})/42 = -0.42$. The negative sign came entirely from the $T[111]$ branch. Substituting this in Eq. (9), using the experimental bulk modulus[9] of $B = 0.289 \times 10^{12}$ ergs/cm^3, yields $\alpha_{\mathrm{TE}} = -8.1 \times 10^{-6}$/K, close to the experimental value [9] of about -7.7×10^{-6}/K because, as we indicated, we adjusted r_c and r_f not only to fit the vibration spectrum but to give the appropriate negative thermal expansion. The use of our inaccurate bulk modulus predicted in the next section, $B = 0.800 \times 10^{12}$ ergs/cm^3, yields $\alpha_{\mathrm{TE}} = -2.9 \times 10^{-6}$/K.

We may note in passing that the corresponding evaluation of $\langle \hbar\omega_{\mathbf{k}} \rangle$, as described in Sec. III, gives 6.42×10^{-3} eV for plutonium, or a Debye temperature of $\Theta_D = \langle \hbar\omega_{\mathbf{k}} \rangle / k_B = 75$ K. Also, the $\langle \gamma_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \rangle$ which enters the low-temperature $\delta d/d$ [obtainable from the first form in Eq. (8)] is 0.171×10^{-3} eV, positive in contrast to the negative $\langle \gamma_{\mathbf{k}} \rangle \langle h\omega_{\mathbf{k}} \rangle = -2.70 \times 10^{-3}$ eV because the only negative $\gamma_{\mathbf{k}}$ in $\langle \gamma_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \rangle$ is weighted by such low frequencies.

It is also possible to calculate the full temperature dependence, as opposed to the high-temperature limit, of δd by evaluating the expectation value in Eq. (8) by integrating over wave numbers [using Eq. (3) or its counterpart] for each branch and taking the weighted average over branches. It yields a $\delta d(T)$, which is nearly horizontal (but with a slightly positive $\partial \delta d(T)/\partial T$ at $T = 0$, and then at 20 or 30 K turns down to approach a linear curve described by the linear coefficient given above. The experimental curves from Ref. 9, in contrast, suggest a positive peak at some 400 K then turning over to the negative linear coefficient in the range of stability, 592–794 K, discussed here. There are uncertainties of a few thousandths of an angstrom (Lawson, private communication) due to specimen position, which may be at least partly responsible for the discrepancy.

We may note that a zero-temperature shift in the lattice distance, which arises from the pressure due to zero-point fluctuations, depends upon the isotopic mass as $1/\sqrt{M}$, and therefore causes a difference in the zero-temperature spacing for different isotopes. However, the total shift is only $\delta d = \langle \gamma_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \rangle d/(2B\Omega_0) = 6.2 \times 10^{-5}$ Å (evaluated as above), so the difference between Pu_{239} and Pu_{242} is only $\delta d = 5 \times 10^{-7}$ Å. There has been discussion of an experimental difference (Lawson, private communication) considerably larger than this.

The behavior of aluminum is quite different. The $\gamma_{\mathbf{k}}$ for the four branches are quite close, and positive, at 0.94, 0.90, 0.98, and 0.78, respectively, and the weighted average of $\langle \gamma_{\mathbf{k}} \rangle = 0.865$ yields (again using the experimental B) a thermal expansion coefficient of $+10.0 \times 10^{-6}$/K, positive, and in very rough agreement with the experimental 25×10^{-6}/K. The fuller calculation based upon Eq. (8) again gives a $\delta d(T)$, which starts out horizontal at low temperature and bends to the linear positive slope, for aluminum at 100 or 200 K.

V. TEMPERATURE DEPENDENCE OF THE BULK MODULUS

Lawson *et al.*[9] have also noted that the bulk modulus of plutonium (and its alloys), as well as the Debye temperature, decreases rapidly with temperature, $dB/dT = -150 \times 10^6$ ergs/(cm^3 K) over the temperature range 50–300 K. The experiments are done with alloys, since pure plutonium is stable only in the narrow range of 592–724 K. The alloys at this lower temperature range show a positive thermal expansion of about $\alpha_{\mathrm{TE}} = +9 \times 10^{-6}$/K (Ref. 9, Fig. 2), in contrast to the negative expansion of pure plutonium discussed in the preceding section.

In discussing this temperature dependence, there are two contributions to the bulk modulus which we must consider. The first arises from the dependence of the bulk modulus (at $T = 0$) on the lattice constant combined with the temperature dependence of the lattice constant. The second arises from the thermal energy of the phonon gas, $k_B T$ in each mode at high T, and the second derivative of that energy with respect to volume (holding the excitation quantum number for each mode constant as in calculating the pressure).

For the first contribution, we need the dependence of the bulk modulus on spacing $(d/B)\partial B/\partial d$, with $B = (c_{11} + 2c_{12})/3$. We gave forms for the elastic constants in Sec. II, leading to $B = \left[-\frac{4}{3}V^{(1)} + \frac{2}{3}V^{(2)}\right]/\Omega_0 = 0.50$ eV/Å$^3 = 0.80 \times 10^{12}$ ergs/cm^3, higher than the experimental value of 0.29×10^{12} ergs/cm^3. Taking the derivative with respect to spacing as for Eq. (10) leads to

$$\frac{d}{B}\frac{\partial B}{\partial d} = \frac{4V^{(1)} - 2V^{(2)\dagger} - V^{(2)} + V^{(3)\dagger}}{-2V^{(1)} + V^{(2)}} = -4.48 \qquad (11)$$

for plutonium from the parameters of Eq. (4). The negative sign is the same as in most materials, corresponding here to a positive Grüneisen constant for the bulk modulus of plutonium because it is dominated by longitudinal modes. Using the experimental B and $\alpha_{\mathrm{TE}} = +9 \times 10^{-6}$/K (for the alloys tested, Ref. 9) gives a negative contribution to $\partial B/\partial T = -4.48 B\alpha_{\mathrm{TE}} = -12 \times 10^6$ ergs/cm^3 K, a contribution of the same sign, but a factor of 12 smaller than the observed $\partial B/\partial T$.

The same analysis for aluminum yields $B = 0.97 \times 10^{12}$ ergs/cm^3, compared to the experimental 0.72×10^{12} ergs/cm^3, $(d/B)\partial B/\partial d = -6.77$ from Eq. (11), to be compared with an experimental -12.9 obtained from the pressure dependence of the bulk modulus.[10] This -6.77, with the experimental a_{TE} and B, gives a contribution to $\partial B/\partial T$ of -122×10^6 ergs/cm^3 K or $[-232 \times 10^6$ ergs/cm^3 K using the experimental $(d/B)\partial B/\partial d = -12.9]$ to be compared with the experimental [10] $\partial B/\partial T = -175 \times 10^6$ ergs/cm^3 K. All estimates are comparable to the experiments for aluminum.

The second contribution to $\partial B/\partial T$ requires a sum over all modes of $(\Omega^2/\hbar\omega_{\mathrm{k}})\partial^2\hbar\omega_{\mathrm{k}}/\partial\Omega^2$. The evaluation is a little intricate; first, writing this in terms of the derivatives of $(\hbar\omega_{\mathrm{k}})^2$ with respect to d. Then, for a mode (in the [100] or [111] directions) for which $(\hbar\omega_{\mathrm{k}})^2 = (\hbar^2/M)[A_1V^{(1)} + A_2V^{(2)}]\sin^2 ks$, we may evaluate $(\Omega^2/\hbar\omega_{\mathrm{k}})\partial^2\hbar\omega_{\mathrm{k}}/\partial\Omega^2$ in terms of the constants A_1 and A_2, obtaining

$$\frac{\Omega^2}{\hbar\omega_k}\frac{\partial^2\omega_k}{\partial\Omega^2} = \frac{2A_1V^{(1)} - 2A_1V^{(2)\dagger} + A_1V^{(3)\dagger\dagger}/2 - A_2V^{(3)\dagger} + A_2V^{(4)\dagger\dagger}/2}{9(A_1V^{(1)} + A_2V^{(2)})} - \left\{\frac{-A_1V^{(1)} + A_1V^{(2)\dagger} + A_2V^{(3)\dagger}}{6[A_1V^{(1)} + A_2V^{(2)}]}\right\}^2. \qquad (12)$$

In fact, the magnitude of $V^{(4)\dagger\dagger}$ is so much greater than the other $V^{(i)}$ that the numerator in the first term is essentially $A_2V^{(4)\dagger\dagger}/2$, and $V^{(2)}$ is so much larger than $V^{(1)}$ that the denominator is essentially $9A_2V^{(2)}$, so the first term may be taken as $\frac{1}{18}V^{(4)\dagger\dagger}/V^{(2)}=-1.80$ for all modes. Similarly, the largest term in the second term of Eq. (12) is $-[V^{(3)\dagger}/6V^{(2)}]^2=-0.22$. This same constant total value of -2.02 applies to all modes with wave numbers along the two sets of symmetry lines ([100] and [111]), and we may take it to be the average for all modes. Then, noting that the excitation number for each mode at high temperatures is $k_BT/\hbar\omega_{\mathrm{k}}$, the contribution to the bulk modulus is a sum over the modes of $(k_BT/\hbar\omega_{\mathrm{k}})\Omega\ \partial^2\hbar\omega_{\mathrm{k}}/\partial\Omega^2=-2.02k_BT/\Omega$. There are three modes per atomic volume Ω_0 so the contribution to $\partial B/\partial T$ is $3\times2.02k_B/\Omega_0=-33.7\times10^6$ ergs/cm^3 K. This is much larger than the contribution of -12×10^6 ergs/cm^3 K obtained from the thermal expansion of plutonium alloys, leading to a total $\partial B/\partial T=-46\times10^6$ ergs/cm^3 K, considerably smaller than the experimental -150×10^6 ergs/(cm^3 K). The sign is correct and perhaps the magnitude is close enough that the origin may be the correct one, recalling that even our estimate of the low-temperature bulk modulus was in error by a factor of 2.8. The thermal contribution to the bulk modulus is seen here to be dominated by the second derivative of the phonon-gas energy with respect to volume. Lawson *et al.*[9] noted that the variation of the bulk modulus with temperature is quite independent of the alloy concentration. The dominance of the phonon-gas term explains how this can be so although the thermal expansion coefficient changes sign with very small alloy concentrations.

Repeating the analysis of the phonon-gas term for aluminum, Eq. (12) yields +1.16 rather than −2.02, and a contribution to $\partial B/\partial T$ of 29.2×10^6 ergs/cm^3 K. This is of the opposite sign of our prediction of the contribution from change in volume, but in this case is much smaller, within the scatter of our estimates of the contribution from thermal expansion. This is the anticipated behavior for metals, a decrease in B due to thermal expansion, but in the case of plutonium, with negative expansion, it is dominated by the phonon-gas contribution.

There are analogous contributions to the elastic constant $(c_{11}-c_{12})/2$ due to the shift in phonon frequencies under strain. The calculation is particularly intricate because we introduce a small strain, e, and then phonon amplitudes u, and must calculate the change in energy including the terms e^2u^2, which are of fourth order in the displacements. A convenient strain is to expand the lattice in the z direction by a factor $1+e$ while contracting it in the two lateral directions by $1/(1+e)^{1/2}$, so that the volume is rigorously conserved. With this shear the modes are no longer purely longitudinal and transverse, except for propagation in the ±[100]], ±[010], and ±[001] directions, and one would need to solve for the modes at every wavenumber. For these six simple directions it is again sufficient to evaluate the frequency for the zone-boundary mode. We treated these, finding the $L[001]$ frequencies shifted by a factor $1-3.09e^2$, the two $T[001]$ frequencies by $1+1.28e^2$, the $L[100]$ and $L[010]$ frequencies by $1-1.15e^2$, the $T[100]$ and $T[010]$ polarized along the [001] frequencies by $1-5.83e^2$, and the $T[100]$ polarized along [010] (as well as the $T[010]$ polarized along [100]) shifted by $1-3.72e^2$. Using just these six cube directions gives the average frequency shift as $\langle\delta\omega_{\mathrm{k}}/\omega_{\mathrm{k}}\rangle=-2.44e^2$, and a negative contribution to $\frac{1}{2}(c_{11}-c_{12})$ due to the thermal phonons (with a value of $-6.9k_BT/d^3=-0.008\times10^{12}$ ergs/cm^3 at room temperature). This still leaves the second-neighbor contribution and the corresponding calculation gave $\langle\delta\omega_{\mathrm{k}}/\omega_{\mathrm{k}}\rangle=-0.033e^2$, a much smaller contribution, but still negative. It would have been very interesting if the phonon gas had led to a positive contribution to the elastic constant. It would mean that the structure, and the phonon spectrum, could be stabilized self-consistently by the phonon gas itself. It appears not to be the case in plutonium or aluminum, but might be in some other metal.

VI. THE DEBYE-WALLER FACTOR

Lawson *et al.*,[9] indicated that there is a temperature dependence of another measure of lattice rigidity, rather than the bulk modulus, obtained from the Debye-Waller factor from neutron diffraction. The property which is measured is the intensity of the Bragg reflection of neutrons from the lattice, reduced by the Debye-Waller factor[11] $\exp[-\langle(\mathbf{q}\cdot\delta\mathbf{r})^2\rangle]$, where $\mathbf{q}$ is the wavenumber of the diffraction and $\delta\mathbf{r}$ is the displacement of each atom from its equilibrium position. In order to treat it, we write the displacement of each atom in terms of the normal coordinates $\mathbf{u}_k$ ($\mathbf{k}$ is the wave number of the normal coordinate but again includes an index for the three polarizations for each wave number) such that the displacement of the ith atom is given by

$$\delta\mathbf{r}_i=\sqrt{1/N}\Sigma_{\mathbf{k}}\mathbf{u}_k\exp(i\mathbf{k}\cdot\mathbf{r}_i), \tag{13}$$

with N the number of atoms present (e.g., Ref. 11, p. 407ff). In terms of these normal coordinates, we may obtain the $\langle(\mathbf{q}\cdot\delta\mathbf{r})^2\rangle$ for one atom by writing out $(\mathbf{q}\cdot\delta\mathbf{r})^2=(1/N)\Sigma_{\mathbf{k}\mathbf{k}'}\mathbf{q}\cdot\mathbf{u}_{\mathbf{k}}\mathbf{q}\cdot\mathbf{u}_{\mathbf{k}'}\exp(i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_i)$, averaging over i so that only the terms with $\mathbf{k}'=-\mathbf{k}$ and of the same polarization contribute, leading to

$$(\mathbf{q}\cdot\partial\,\mathbf{r})^2=\frac{1}{3N}q^2\Sigma_{\mathbf{k}}u_{\mathbf{k}}u_{-\mathbf{k}}, \tag{14}$$

with the $\frac{1}{3}$ coming from the angular average of the component along $\mathbf{q}$ and the sum is over all $3N$ normal coordinates This expression does not depend upon the displacements being small. Note that the squared displacement of one atom is obtained from an average, $(1/3N)q^2\Sigma_{\mathbf{k}}$, of $u_{\mathbf{k}}u_{-\mathbf{k}}$ over all normal coordinates.

We made an intricate derivation of the thermal averages over all modes, including anharmonic terms, but the result is much more easily obtained by considering a single normal coordinate and then generalizing the result as an average over all. The notation will best match if we consider the coordinate corresponding to the highest-frequency longitudinal mode in the [100] direction, with alternate atoms having displacements $\pm u$ in opposite directions on alternate planes, or relative x displacements of $2u$ between neighboring planes. Then we evaluate the change in energy per atom by summing the interaction energies between atoms in neighboring planes and write the result as an expansion $E(u)=E^{(1)}(u/d)+\frac{1}{2}E^{(2)}(u/d)^2+\frac{1}{3!}E^{(3)}(u/d)^3+\frac{1}{4!}E^{(4)}(u/d)^4+\ldots$. When we sum over neighbors the odd terms sum to zero for the mode and we obtain as before for the second-order term $E^{(2)}=8V^{(1)}+8V^{(2)}$. We return later to the fourth-order term. We could use this $E^{(2)}$ to obtain the normal-mode frequency for this mode by equating the potential energy per atom $\frac{1}{2}E^{(2)}(u/d)^2$ to the kinetic energy per atom $\frac{1}{2}M\omega_k^2u^2$ leading to the value given in Eq. (3) [for the $\sin(kd/\sqrt{8})=1$ for this mode].

For high temperatures we could proceed by letting the potential energy in each mode equal $\frac{1}{2}k_BT$, but it will generalize to the nonharmonic case, in which we keep the fourth-order term, if we note that the probability at high temperatures of a particular value of u with potential energy $E(u)$ is proportional to $\exp[-E(u)/k_BT]$, with $E(u)=\frac{1}{2}E^{(2)}(u/d)^2$ in the harmonic case. Then the expectation value, in thermal equilibrium, of u^2 becomes

$$\begin{aligned}\langle u^2\rangle &= \frac{\int \exp[-E(u)/k_BT]u^2du}{\int \exp[-E(u)/k_BT]du}\\ &= d^2\frac{\int \exp[-E^{(2)}(u/d)^2/2k_BT](u/d)^2d(u/d)}{\int \exp[-E^{(2)}(u/d)^2/2k_BT]d(u/d)}\\ &= d^2k_BT/E^{(2)} = k_BT/M\omega_k^2. \end{aligned} \tag{15}$$

The final form remains correct for any mode, and as in Eq. (14) it ends up being averaged over modes as

$$\langle(\mathbf{q}\cdot\delta\mathbf{r})^2\rangle/(q^2d^2) = \langle u_{\mathbf{k}}u_{-\mathbf{k}}\rangle/3d^2 = (\hbar^2k_BT/Md^2)\langle 1/(\hbar\omega_k)^2\rangle, \tag{16}$$

where again the expectation value $\langle 1/(\hbar\omega_{\mathbf{k}})^2\rangle=(1/3N)\Sigma_{\mathbf{k}}1/(\hbar\omega_{\mathbf{k}})^2$, an average over all modes, is to be distinguished from the expectation values such as $\langle u^2\rangle$ in Eq. (15), which are thermal averages.

One may associate a Debye-Waller temperature Θ_{DW} with this expression (Lawson *et al.*[12]), but it is a different average from the $k_B\Theta_{\mathrm{D}}=\langle\hbar\omega_{\mathbf{k}}\rangle$ which we evaluated near the end of Sec. IV. By comparing Eqs. (1) and (3) of Ref. 12 with the final form in Eq. (16) here, we see that this Θ_{DW} is defined by

$$3/(k_B\Theta_{\mathrm{DW}})^2 = \langle 1/(\hbar\omega_{\mathbf{k}})^2\rangle. \tag{17}$$

This is one of the averages obtained for aluminum in Sec. III. For plutonium it leads to $\Theta_{\mathrm{DW}}=\sqrt{3}/[k_B\langle 1/(\hbar\omega_{\mathbf{k}})^2\rangle^{1/2}]=67$ K, half the experimental value of $\Theta_{\mathrm{DW}}=117$ K, extrapolated to pure δ-Pu from the data for alloys given by Lawson *et al.*[12] We saw in Sec. III that our average over the Brillouin zone, $\langle 1/(\hbar\omega_{\mathbf{k}})^2\rangle$, for aluminum was more than a factor of 2 too large, corresponding to a comparable underestimate of Θ_{DW}, so this is not a serious discrepancy for plutonium.

Lawson *et al.*[12] have also given the temperature dependence of this Debye-Waller temperature as $\partial\Theta_{\mathrm{DW}}/\partial T\sim -0.043$. As for the bulk modulus, there is a contribution due to thermal expansion. The volume dependence of $1/(k_B\Theta_{\mathrm{DW}})^2$ is described by a constant $(\Omega/k_B\Theta_{\mathrm{DW}})\,\partial(k_B\Theta_{\mathrm{DW}})/\partial\Omega=-\langle\gamma_{\mathbf{k}}/\omega_{\mathbf{k}}^2\rangle/\langle 1/\omega_{\mathbf{k}}^2\rangle=1.24$, with $\langle\gamma_{\mathbf{k}}/\omega_{\mathbf{k}}^2\rangle$ evaluated as in Sec. III. This is the opposite sign and of similar magnitude to the $(\Omega/B)\,\partial B/\partial\Omega=1/3(d/B)\,\partial B/\partial d=-1.49$ obtained for plutonium from Eq. (11). These two measures of rigidity have the opposite dependence on volume, just as the sign varied among the $\gamma_{\mathbf{k}}$ for different modes. This gives a contribution to the temperature dependence of $\partial\Theta_{\mathrm{DW}}/\partial T=\partial\Theta_{\mathrm{DW}}/\partial\Omega\times\partial\Omega/\partial T=(-\langle\gamma/\omega_{\mathbf{k}}^2\rangle/\langle 1/\omega_{\mathbf{k}}^2\rangle)\times 3\alpha_{\mathrm{TE}}\Theta_{\mathrm{DW}}$. Using again the experimental value for the alloys tested (Ref. 9) of $\alpha_{\mathrm{TE}}=9\times10^{-6}$ K and $\Theta_{\mathrm{DW}}=67$ K this gives $\partial\Theta_{\mathrm{DW}}/\partial T=0.0022$. This is of opposite sign and very much smaller than the experimental $\partial\Theta_{\mathrm{DW}}/\partial T\sim -0.043$. Such a discrepancy is what suggested the invarlike effect to Lawson *et al.*[9] We consider here an alternative origin, arising from the lack of harmonicity of each mode, deviations of the potential energy of each mode from u^2.

We return to the first form in Eq. (15) with $\frac{1}{2}E^{(2)}(u/d)^2$ replaced by $\frac{1}{2}E^{(2)}(u/d)^2+\frac{1}{4!}E^{(4)}(u/d)^4$. The calculation of $E^{(4)}$ for each branch is carried out as in Sec. V, expanding the change δd in spacing for each neighbor to the fourth order in the difference, $2u$, in relative displacement of the planes for the highest-frequency mode, and then carrying out a Taylor expansion of the potential energy to the fourth order in δd. The $E^{(2)}$'s are the same as the denominators in Eq. (10), as we found for the $L[100]$ mode after Eq. (3). The $E^{(4)}$'s for the four branches are

$$\begin{aligned}E^{(4)}(L[100]) &= 16[9V^{(1)} - 9V^{(2)} + 6V^{(3)} + V^{(4)}] = -12\,230\ \mathrm{eV},\\ E^{(4)}(T[100]) &= 8[-3V^{(1)} + 3V^{(2)} + 6V^{(3)} + V^{(4)}] = -4550\ \mathrm{eV},\\ E^{(4)}(L[111]) &= 16[7V^{(1)} - 7V^{(2)} + 4V^{(3)} + 4/3V^{(4)}]\\ &= -10\,200\ \mathrm{eV},\\ E^{(4)}(T[111]) &= -30V^{(1)} + 30V^{(2)} + 36V^{(3)} + 2V^{(4)}\\ &= -2177\ \mathrm{eV}, \end{aligned} \tag{18}$$

with numerical values for plutonium obtained using Eq. (4). The four values of $E^{(2)}$, obtained from the denominators in Eq. (10) using Eq. (4) for plutonium, are 93.8, 28.6, 102.9, and 5.12 eV, respectively.

We may expand the $\exp\left(-\frac{1}{4!}E^{(4)}(u/d)^4/k_BT\right)\sim\left(1-\frac{1}{4!}E^{(4)}\times(u/d)^4/k_BT\right)$ in both integrals now in Eq. (15) and change variables to x, with $x^2=\frac{1}{2}E^{(2)}(u/d)^2/(k_BT)$ to obtain

$$\langle u^2\rangle = \frac{2k_BTd^2}{E^{(2)}} \times \frac{\displaystyle\int \exp(-x^2)\; x^2\{1-[E^{(4)}k_BT/6E^{(2)2}]x^4\}dx}{\displaystyle\int \exp(-x^2)\{1-[E^{(4)}k_BT/6E^{(2)2}]x^4\}dx}$$

$$= \frac{2k_BTd^2}{E^{(2)}}\frac{1/4-(15/16)[E^{(4)}k_BT/6E^{(2)2}]}{1/2-(3/8)[E^{(4)}k_BT/6E^{(2)2}]}$$

$$\approx \frac{2k_BTd^2}{E^{(2)}}\left(1-\frac{E^{(4)}k_BT}{2E^{(2)2}}\right). \tag{19}$$

This again is for the highest frequency mode for each branch and, as in the final form of Eq. (15) for modes of smaller wave number, the u^2 becomes $u_{\mathbf{k}}u_{-\mathbf{k}}\sin^2 ks$ (with $s=d/\sqrt{8}$ for [100] modes) which leads to the form

$$\langle u_k u_{-k}\rangle = \left\langle \frac{k_BT}{M\omega_k^2}\left(1-\frac{E^{(4)}k_BT}{2E^{(2)2}}\right)\right\rangle \tag{20}$$

for each branch, with the leading factor averaging to $1.686d^2k_BT/E^{(2)}$ for that branch. The factors of $\sin^2 ks$ canceled in the ratio $E^{(4)}/E^{(2)2}$ in the final factor. The net effect is to multiply the $1/(\hbar\omega_{\mathbf{k}})^2=1.686Md^2/[\hbar^2E^{(2)}]$ for each branch appearing in Eqs. (16) and (17) by $1-E^{(4)}k_BT/[2E^{(2)2}]$ for that branch.

There are then two terms in the expression for $3/(k_B\Theta_{\mathrm{DW}})^2$. The first, which comes from the harmonic approximation, is proportional to an average of $1/E^{(2)}$ and the second, which arises from anharmonicity, to an average of $E^{(4)}k_BT/E^{(2)3}$. The value for $E^{(2)}$ [given after Eq. (18)] is so small for the transverse [111] mode that with a $1/E^{(2)3}$ it almost completely dominates the second term, although multiplied by 16/42 because it appears in 16 of the 42 branches included in the average, and although the corresponding $E^{(4)}$ from Eq. (18) is the smallest. Thus the expression for Θ_{DW} can be taken as

$$\frac{3}{[k_B\Theta_{\mathrm{DW}}(T)]^2} = \frac{3}{[k_B\Theta_{\mathrm{DW}}(0)]^2} - \frac{16\times 1.686Md^2E^{(4)}k_BT}{42\times 2\hbar^2E^{(2)3}}, \tag{21}$$

with $E^{(2)}$ and $E^{(4)}$ for the $T[111]$ mode. Again using $\Theta_{\mathrm{DW}}=67$ K, this leads to a contribution of $\partial\Theta_{\mathrm{DW}}/\partial T=0.054(Md^2/\hbar^2)(k_B\Theta_{\mathrm{DW}})^3E^{(4)}/E^{(2)3}=-0.11$, even more negative than the experimental −0.043 given by Lawson *et al.*,[12] and completely dominating the term from thermal expansion. However, the same fact that the average is dominated by a single term, which simplified Eq. (21), also led us to overestimate $\langle 1/\omega_{\mathbf{k}}^2\rangle$ by a factor of 2.6 in Sec. III. To go beyond this is a major undertaking, so we conclude simply that it is not difficult to understand the large negative $\partial\Theta_{\mathrm{DW}}/\partial T$ in plutonium and that it comes from a source completely different from that which causes the large negative $\partial B/\partial T$.

TABLE I. Parameters for other trivalent metals from Ref. 3, for simple metals from p. 453 and for the actinides from p. 605. r_0 is the atomic sphere radius, related to the spacing d in fcc crystals by $d^3/\sqrt{2}=4\pi r_0^3/3$.

	Z_f	r_0 (Å)	r_c (Å)	r_f (Å)	U_f (eV)
Al	0	1.58	0.23		
Ga	0	1.67	0.31		
In	0	1.84	0.46		
Ac	0	2.10	0.85	1.11	3.00
Th	1	1.99	0.88	0.87	3.20
Pa	2	1.80	0.79	0.70	3.35
U	3	1.69	0.74	0.64	4.09
Np	4	1.66	0.71	0.60	3.90
Pu(δ)	5	1.81	0.69	0.58	4.61
Am	6	1.91	0.76	0.58	4.96
Cm	7	2.03	0.82	0.61	5.10

Applying the same formulas to aluminum gives a $\Theta_{\mathrm{DW}}=251$ K and $-\langle\gamma_{\mathbf{k}}/\omega_{\mathbf{k}}^2\rangle/\langle 1/\omega_{\mathbf{k}}^2\rangle=-0.081$, which with the experimental thermal expansion gives a contribution to $\partial\Theta_{\mathrm{DW}}/\partial T=(-\langle\gamma/\omega_{\mathbf{k}}^2\rangle/\langle 1/\omega_{\mathbf{k}}^2\rangle)\times 3\alpha_{\mathrm{TE}}\Theta_{\mathrm{DW}}=-0.0152$. The contribution from anharmonicity is $\partial\Theta_{\mathrm{DW}}/\partial T=0.054(Md^2/\hbar^2)(k_B\Theta_{\mathrm{DW}})^3E^{(4)}/E^{(2)3}=-0.13$, from an $E^{(2)}=6.7$ eV and $E^{(4)}=-1382$ eV. Even in aluminum the temperature dependence of the Debye-Waller factor, in contrast to that of the bulk modulus, seems to be dominated by anharmonicity of the [111] transverse modes, rather than the softening of the modes (especially the $T[111]$ modes) due to thermal expansion. This could be tested by measuring the change in the Debye-Waller factor under pressure. We would expect $(\Omega/\Theta_{\mathrm{DW}})\,\partial\Theta_{\mathrm{DW}}/\partial\Omega=-\langle\gamma_{\mathbf{k}}/\omega_{\mathbf{k}}^2\rangle/\langle 1/\omega_{\mathbf{k}}^2\rangle=-0.081$, a factor of 10 smaller than a value which would be inferred from the variation due to thermal expansion.

VII. APPLICATION TO OTHER ACTINIDES

All of the formulas here are applicable to other trivalent metals and actinides (which is why they were included), but different values for the parameters are appropriate. We list in Table I the values for the other actinides and other trivalent metals. It may well be appropriate to adjust these in accordance with some property for each of these elements, as we did for plutonium, but then all other properties can be directly and simply predicted.

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