

Invar model for δ -phase Pu: thermal expansion, elastic and magnetic properties

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We present a statistical mechanical model for the anomalous thermodynamic properties of fcc δ -phase Pu and Pu–Ga alloys. The model is based on the addition of a two-level ‘Invar’-like electronic energy structure to the ordinary Debye model for the lattice, there is no assumption of magnetic character of these electronic levels. Together with the usual Debye temperature Θ and lattice Grüneisen constant γ the model includes two additional parameters, the energy spacing ΔE and an electronic Grüneisen constant Γ . ΔE is 1400 K, and Γ is negative and depends strongly on the Ga content. The model accounts satisfactorily for thermal expansion, and it accounts for the anomalous decrease in the bulk modulus with temperature provided that one assumes *zero* elastic stiffness for the excited electronic state. This assumption is consistent with the results of the dynamic mean-field theory for Pu. We found some evidence for the hypothetical two-level structure using inelastic neutron scattering.

1. Introduction

Pu metal is famous for a wide range of highly unusual thermodynamic properties. We believe that these properties are expressions of electron correlation, but we do not yet know precisely how this connection works. In the periodic system, Pu is a focal point for a transition from itinerant to local 5f-electron behaviour, as suggested originally by Johansson [1]. One can see this transition in figure 1, a plot of the atomic volumes of the elements, which shows a striking discontinuity at the position of Pu in the periodic system. This discontinuity is reflected in the alloy phase diagram given by Smith and Kmetko [2], which shows in figure 2 the convergence of low melting point and crystal structure complexity precisely at Pu.

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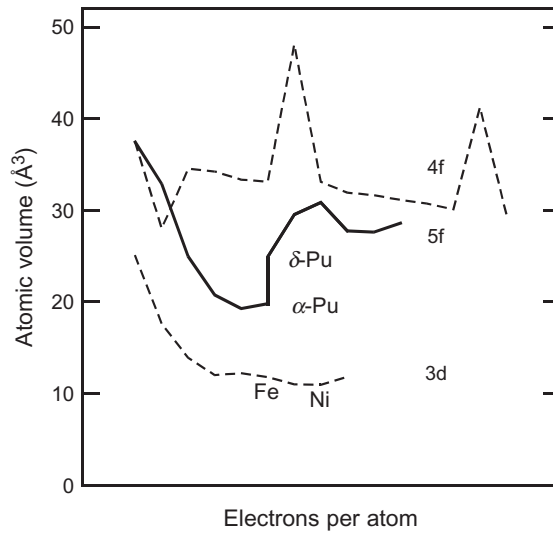


Figure 1. Atomic volume versus electrons per atom for the 5f actinide elements compared with the 3d and 4f elements. The increase in volume between α - and δ -phase Pu is thought to be a Mott transition [1]. The behaviour of the 5f series is similar to the 3d series at the beginning, and to the 4f series at the end. Traditional Invar alloys are found in the vicinity of Fe and Ni in the 3d series.

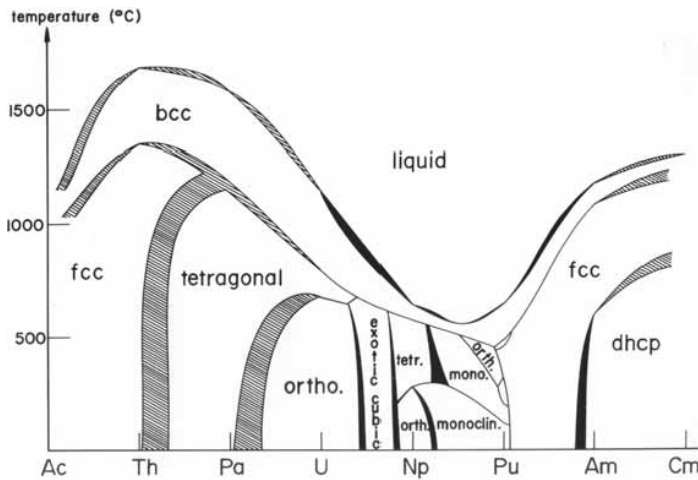


Figure 2. Composite phase diagram of the light actinides. (Reprinted from [2], copyright 1983, with permission from Elsevier.)

The extraordinary physical properties of Pu were gradually unveiled in the decades after the discovery of the element in the 1940s. The history of these discoveries is related by Jette [3], Smith [4] and Hammel [5]. The first discovery was that the metal appeared in a several phases, some of which had highly complicated crystal structures. A specific early discovery was that the fcc δ phase was stable only at high

temperatures, but also that this phase could be stabilized at room temperature and below by the addition of small amounts of specific solutes, for example Al and Ga. Another early discovery was that the thermal expansion of this fcc δ phase is *negative* in its pure form but is driven through zero to positive values by the alloying required for stabilization. Because of its anomalous negative value and the extreme sensitivity of this value to alloying, thermal expansion is one of the most characteristic properties of δ -phase Pu.

The elastic constants of δ -phase Pu also turned out to be unusual; they *decrease* strongly with increasing temperature in a way that is still not precisely quantified. From a simple point of view, the decrease with increasing temperature is inconsistent with the negative thermal expansion. The thermal softening measured by Debye–Waller factors is of great practical importance as it determines the low melting point [6] and hence the properties of Pu phase diagrams.

The application of theories descendant from Johansson's original insights has led to the widely held belief that the δ phase should be magnetically ordered as a result of the localization of the 5f electrons (see, for example [7]). However, there is *no* experimental evidence of magnetic order in *any* phase of Pu metal, and it now makes more sense to ask why Pu is *not* magnetically ordered [8].

The plan of this paper is to discuss the topics raised so far: thermal expansion, temperature-dependent elastic properties and the failure of magnetic order to appear as suggested by some of the current theories. We do this using an 'Invar' model developed for the thermal expansion of plutonium. Invar is an Fe–Ni alloy developed at the turn of the previous century by Guillaume [9], who was awarded the 1920 Nobel Prize in physics for the impact of his efforts on the art of metrology. The 'Invar' property for which the Fe–Ni alloys is named is 'invariant' thermal expansion. A related alloy, 'Elinvar', shows temperature-independent elastic properties. Fe–Ni alloys with similar compositions show definite magnetic properties, and the connection between magnetic and thermal properties was a lodestone for Guillaume's work on alloy development. This connection was exploited by Weiss in his development of an atomic theory of the Invar effect that is based on the magnetic properties of the iron atoms. As we shall explain in the next section, our own model for the thermal expansion in δ -phase Pu alloys is based on the Weiss model — but *without* the magnetism.

2. Thermal expansion

Volumetric data on the thermal expansion of some phases of Pu were first published by Jette [3], of which an outstanding feature was the negative thermal expansion of the δ phase. These results were corroborated by the X-ray diffraction data obtained by Ellinger [10]. The other phases of Pu have positive thermal expansions with unusually high values, as shown in figure 3.

It was subsequently found by Lee *et al.* [11] and by Elliott *et al.* [12] that the effect of almost every element that will dissolve in the δ phase is to enhance its stability to room temperature and below and to drive the thermal expansion of the δ phase from negative to positive values. We illustrate this behaviour by showing more recent lattice constant data for some Pu–Ga alloys determined by neutron diffraction over the

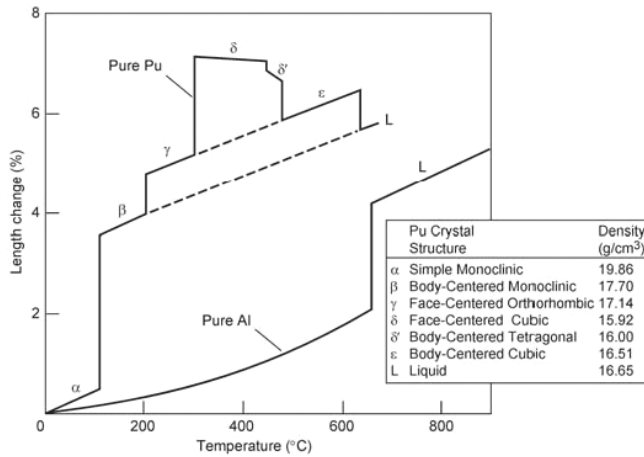


Figure 3. Thermal expansion of the phases of Pu compared with those of Fe.

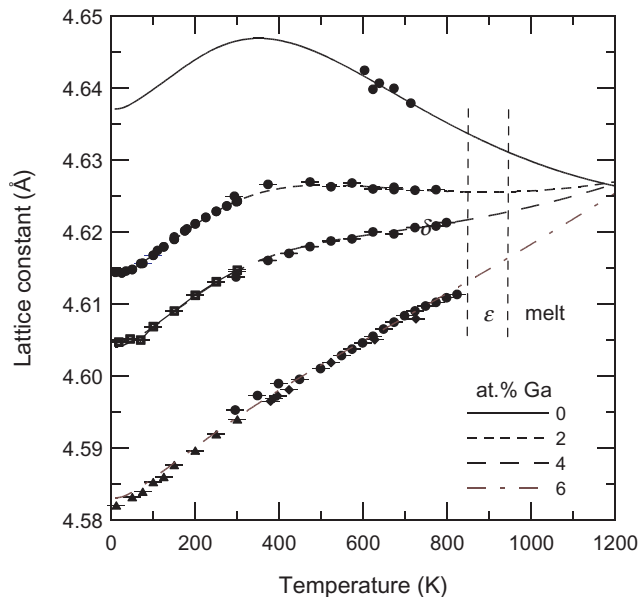


Figure 4. Lattice constants of Pu–Ga alloys measured by neutron diffraction. The curves through the data are fits by the ‘Invar’ model described in section 3 of this paper.

temperature range 15–800 K in figure 4 [13]. The change of expansion behaviour is especially clear at high temperatures, and figure 5 shows the coefficient of linear thermal expansion at 625 K plotted against the Ga concentration of Pu–Ga alloys [14].

From the Maxwell relation $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$ we learn that negative thermal expansion is associated with increasing disorder at higher pressures. For simple solids, which have only the lattice vibrational modes as degrees of freedom, the normal effect of pressure is to increase the order (and to decrease the entropy),

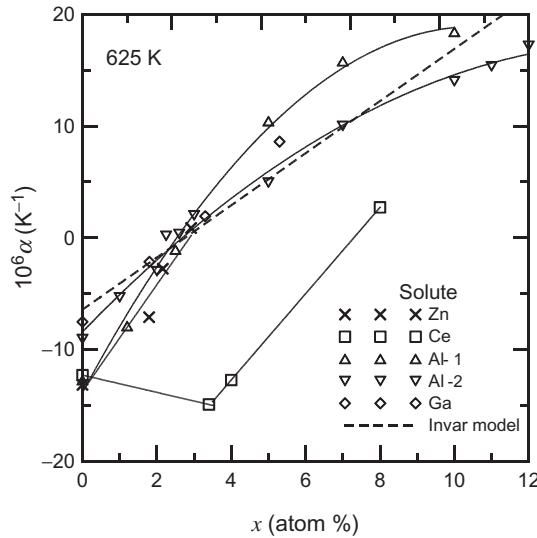


Figure 5. Coefficient of linear thermal expansion at 625 K for various Pu alloys. The dashed line is a fit by the 'Invar' model used to calibrate the Invar T value.

so that the thermal expansion is positive. For complex solids with negative thermal expansion, such as the recently discovered ceramic material ZrW_2O_8 [15, 16], the effect of pressure is to increase the vibrational entropy of the molecular modes, and this has been shown directly by neutron scattering under pressure by Mittal *et al.* [17]. For a simple fcc metal such as δ -phase Pu or fcc Fe–Ni Invar alloys, there are no internal vibrational modes; so we must look for an electronic degree of freedom whose entropy variation with pressure determines the thermal expansion. In the next section we shall discuss how this problem is addressed by the Weiss model for the Invar alloys.

3. Weiss two-level model for Invar

Weiss [18] developed a simple model for the thermal expansion for Fe–Ni alloys. He assumed that there are two distinct atomic states associated with the 3d atoms, namely a high-spin state and a low-spin state, as shown in figure 6. These atomic states are explicitly assumed to be of magnetic character. The states are assumed to be separated by some definite energy ΔE , say 1000 K. The higher-energy state is assumed to have a lower atomic volume than the lower-energy state. A system composed of such atoms would have negative thermal expansion because an increasing fraction of higher-energy lower-volume states would be occupied at higher temperatures. The Invar occupancy is given by

$$n_{\text{Invar}} = \frac{1}{1 + (g_1/g_2) \exp(\Delta E/k_B T)}. \quad (1)$$

g_1 and g_2 are the degeneracies of the lower and upper atomic levels respectively.

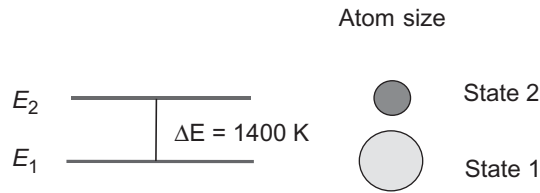


Figure 6. Schematic basis for the Invar model: two atomic energy states separated by energy ΔE are associated with different atomic volumes.

The formula for the Invar part of the thermal expansion is

$$a_{\text{Invar}} = a_1(1 - n_{\text{Invar}}) + a_2(n_{\text{Invar}}), \quad (2)$$

where a_1 and a_2 are the lattice constants associated with the two atomic states. For a real material, there is a competing effect from the lattice thermal expansion, which is usually positive. The Weiss two-level effect depends on the energy separation and the atomic volumes of the two levels, and the lattice expansion depends on the Debye temperature Θ and the Grüneisen parameter γ of the lattice.

On this basis it was possible to fit the thermal expansion of Pu–Ga alloys in figure 4 [13]; this fit is the line drawn through the measured data. An energy separation $\Delta E = 1400$ K is required to fit the data, and the atomic volumes for the lower and higher states are 25 \AA^3 and 21 \AA^3 respectively. For Pu, there is no reason to assume magnetic character for these two states.

4. Elastic properties of δ -phase Pu

From the single-crystal measurements made by Ledbetter and Moment [19] we know the three independent components of the elastic tensor at room temperature. From these measurements we have an accurate bulk modulus of $0.289 \times 10^{12} \text{ dyn cm}^{-2}$, and we know that δ -phase Pu is the most elastically anisotropic of all fcc metals with a Zener anisotropy of 7.

The ultrasound work of Taylor *et al.* [20, 21] was the first to show the temperature dependence of the bulk modulus of δ -phase Pu. Between 50 and 290 K, Taylor *et al.* obtained a linear decrease in the ultrasound Debye temperature $\Theta = 134 \text{ K} - 0.041 \text{ T}$ for Pu–5 at.% Al. These measurements were extended to nearly 800 K by Calder *et al.* [22]. Later, Lawson *et al.* used the Debye–Waller factors measured by neutron diffraction to show that this decrease in Θ with increasing temperature persists up to 800 K: $\Theta = 132 \text{ K} - 0.047 \text{ T}$ for Pu–5 at.% Al [23] and $\Theta = 131 \text{ K} - 0.047 \text{ T}$ for Pu–6 at.% Ga [6]. Most recently, Migliori *et al.* [24] have confirmed the decrease with increasing temperature using very precise ultrasonic measurements.

A third demonstration of the elastic softening came from the measurements of McQueeney *et al.* [25] of the phonon density of states between 15 and 300 K. They found pronounced softening at low frequency with the magnitude in agreement with the Debye–Waller factor measurements. Measurements were made with

a polycrystalline sample by McQueeney *et al.*, but they are in reasonable agreement with the single-crystal measurements by Wong *et al.* [26]. The actual phonon dispersion curves are quite unusual, especially a Kohn-like anomaly in the T1[011] branch and a large softening of the T1[111] mode. All the phonons except for the T1[111] branch were *predicted* quite well by Dai *et al.* [27] using dynamic mean-field theory (DMFT), and for this branch the prediction is qualitatively correct. The phonons have been discussed from a different point of view by Harrison [28].

Lawson *et al.* [6] showed that decrease in Θ with increasing temperature would account for the low melting point of Pu via the Lindemann rule. This demonstration was based on the behaviour of the δ phase, as the ε phase, from which Pu actually melts, exists over such a narrow temperature range that it is difficult to make an accurate determination of the temperature dependence of its elastic properties by neutron diffraction measurements. Ultrasonic elastic measurements of the ε phase are pending.

A crude estimate of the temperature dependence of Θ can be made by using the Invar occupancy to average over two values of Θ associated with the two Invar levels:

$$\Theta(T) = \Theta_1(1 - n_{\text{Invar}}) + \Theta_2(n_{\text{Invar}}). \quad (3)$$

As shown in figure 7, this works, provided that Θ_2 , the Debye temperature associated with the upper level, is taken to be zero! This is an interesting and surprising result, but the derivation [29] is not very convincing. Nadykto [30] has explained this behaviour of δ -phase Pu with a usual similar model that treats the δ phase as a mixture of atoms with δ and ε phases electronic structures.

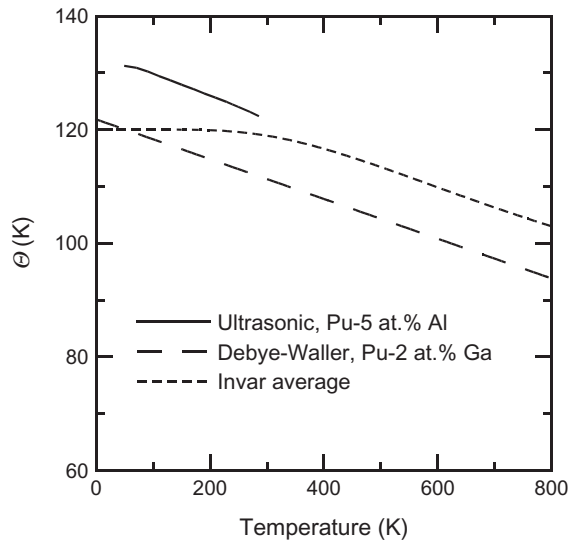


Figure 7. Debye temperature Θ for δ -phase Pu-Ga alloys measured by ultrasound and by Debye-Waller factors. The data sets are somewhat discrepant, and each is fitted by a different equation based on the Invar model.

5. Invar model for Pu thermodynamics

In this section we present a phenomenological thermodynamic model for the thermodynamic of δ -phase Pu. Various thermodynamic properties will be calculated from the free energy and compared with experiment. Agreement for most properties is good but is less so far a few properties.

We shall use the Helmholtz free energy $F(T, v)$, where T is the temperature and v is the volume normalized by its value at zero temperature and pressure, V/V_0 . The free energy has two parts: a Debye part that described the lattice dynamics, and an electronic part, based on the Weiss two-level model for Invar, that describes the peculiar electronic behaviour that seems to be responsible for the thermal expansion. Following Morse [31], the Debye part is given by

$$F_{\text{Debye}}(T, v, \Theta_0, \Delta E, \gamma, \Gamma) = \frac{1}{2}(v-1)^2 B_0 V_m + N_0 k_B T \left\{ \frac{9}{8} \frac{\Theta_0 v^{-\gamma}}{T} + 3 \ln \left[1 - \exp\left(\frac{-\Theta_0 v^{-\gamma}}{T}\right) \right] - D\left(\frac{-\Theta_0 v^{-\gamma}}{T}\right) \right\}, \quad (4)$$

where D is the Debye integral, and the electronic part is given by

$$F_{\text{Invar}}(T, v, \Theta_0, \Delta E, \gamma, \Gamma) = -\frac{1}{2}(v-1)^2 B_0 V_m n_{\text{Invar}} + N_0 k_B T \ln(1 - n_{\text{Invar}}) \quad (5)$$

with the Invar occupancy given in more detail than equation (1) by

$$n_{\text{Invar}}(T, v, \Delta, E, \Gamma) = \frac{1}{\exp(\Delta E v^{-\gamma}/k_B T)} \quad (6)$$

Ignorance has forced us to drop the g_1 and g_2 shown in equation (1). The total free energy is the sum of the Debye and the Invar free energies:

$$F_{\text{total}}(T, v, \Theta_0, \Delta E, \gamma, \Gamma) = \frac{1}{2}(v-1)^2 B_0 V_m (1 - n_{\text{Invar}}) + N_0 k_B T \left\{ \frac{9}{8} \frac{\Theta_0 v^{-\gamma}}{T} + h(1 - n_{\text{Invar}}) + 3 \ln \left[1 - \exp\left(\frac{-\Theta_0 v^{-\gamma}}{T}\right) \right] - D\left(\frac{-\Theta_0 v^{-\gamma}}{T}\right) \right\}. \quad (7)$$

The Invar free energy contributes a *negative* temperature dependence to the elastic constant, in agreement with experiment.

In addition to the thermodynamic variables T and v , the F values depend on four parameters that must be determined from experiment. Θ_0 , the Debye temperature, and γ , the lattice Grüneisen parameter, pertain to the lattice dynamics. According to [6], appropriate values are $\Theta_0 = 125$ K and $\gamma = 0.5$. ΔE is the energy level separation of the Invar levels introduced in section 3; it is 1400 K. Γ describes the volume dependence of ΔE according to

$$\Delta E = \Delta E_0 v^{-\Gamma} \quad (8)$$

by analogy with the lattice Grüneisen parameter defined by

$$\Theta = \Theta_0 \left(\frac{V}{V_0} \right)^{-\gamma} = \Theta_0 v^{-\gamma}. \quad (9)$$

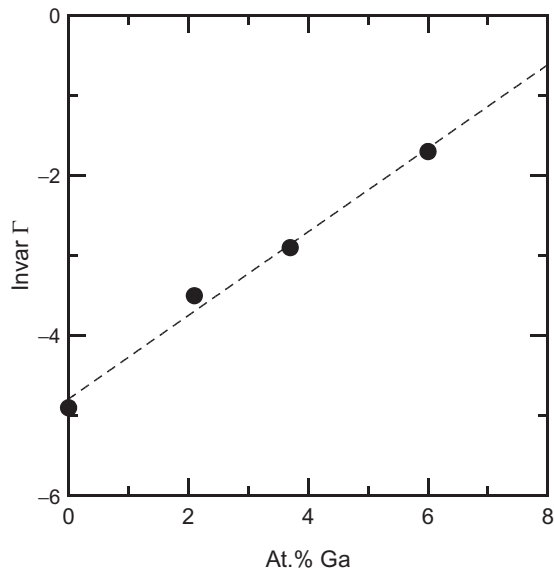


Figure 8. Invar Γ value versus Ga concentrated of Pu–Ga alloys obtained from the data in figure 4.

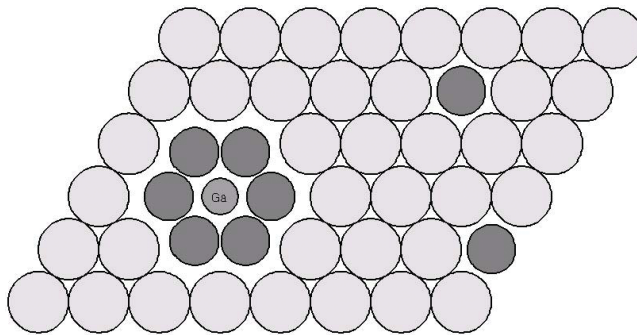


Figure 9. Atomic model for the effect of Ga on Pu–Ga lattice constants. Each Ga atom is assumed to force its 12 Pu neighbours into the smaller-volume excited Invar state.

Γ is the only parameter of the four that depends strongly on alloy composition, and its value can be determined from the high-temperature thermal expansion data in figure 5. The result of this calibration is shown in figure 8. Why does Ga have such a strong effect? We imagine that each Ga somehow forces all 12 of its Pu nearest neighbours into the excited small-volume Invar state, as shown schematically in figure 9.

The Invar free energy in equation (5) expresses surprising physics of great importance for the properties of Pu. The first term in the Debye free energy equation (4) is proportional to the square of the dilatation and provides a way to put the experimentally determined bulk modulus directly into the model. The corresponding term

in the invar free energy (equation (5)) works together with its partner in equation (4) to render every Invar-excited atom elastically neutral: *atoms in excited Invar states make zero contribution to the elastic properties of the material*. This term — or something like it — is required to obtain the correct elastic behaviour of δ -phase Pu without the artificial assumption of a temperature-dependent Θ that was used in earlier analysis, as reported in section 4, above.

Takke *et al.* [32] created a model for the lattice properties of intermetallic compounds with unstable 4f shells based on scaling. (See also the review by Thompson and Lawrence [33].) They used a general free energy with a single characteristic energy T_0 and an electronic Grüneisen parameter Ω_{el} , analogous to our ΔE and Γ respectively. The two-level model is a special case. They were able to rationalize negative contributions to thermal expansion and to $d\Theta/dT$ for CeSn₃ and CePd₃. This model does *not* work for δ -phase Pu because it predicts that the thermal expansion and the temperature derivative of the elastic constants should scale together, in disagreement with the available data for δ -phase Pu. It is exactly this failure that led to our more drastic assumption of zero elastic contribution from excited Invar states. Use of the Invar model in this form enabled an adequate description of the elastic properties of δ -phase Pu *without the introduction of any additional model parameters*.

6. Physical properties from the Invar model

The physical properties predicted by the model are derived by the usual process of computing various derivatives of the free energy. As a first step, the pressure is shown in figure 10. The lattice pressure is positive and rises with increasing temperature.

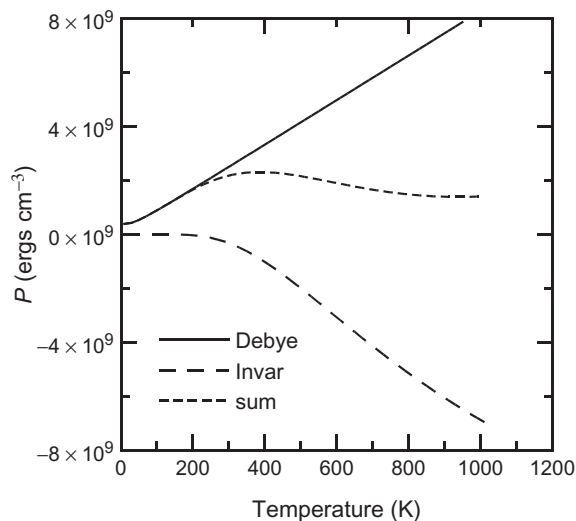


Figure 10. Calculated pressure versus temperature for the Invar model. The Invar pressure tends to cancel the Debye pressure. When the slope of the total pressure is negative, so is the thermal expansion.

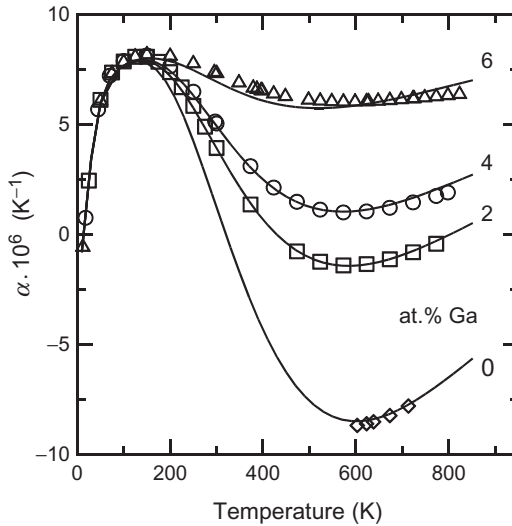


Figure 11. Calculated coefficient of linear thermal expansion for Pu–Ga alloys compared with the fitted data.

There is in this case a negative pressure from the Invar part of the free energy, and this pressure has a more complicated temperature dependence. The negative temperature slope for the sum of the two pressures already indicates negative thermal expansion through the mathematical identity $(\partial p/\partial T)_v = -(\partial p/\partial V)_T(\partial V/\partial T)_p$, as stability requires $B = V(\partial p/\partial V)_T > 0$.

The thermal expansion is shown in figure 11, where the calculated thermal expansion is compared with the experimental data. There is a trick involved in the comparison, as the experimental data shown in figure 4 are too sparse to permit a direct computation of thermal expansion. Instead, we have computed the experimental thermal expansion by differentiating the *fit* provided by the *atomic* Invar model and have compared this quantity with the thermal expansion obtained from model free energy. The evident discrepancies are well within experimental error. A very similar calculation led to the calibration of Γ versus Ga concentration that was shown in figure 9.

The calculated bulk modulus is plotted versus temperature in figure 12, together with both the Debye–Waller and the ultrasound data [6, 20, 22, 24]. The assumption of elastic cancellation by the excited Invar states is required to obtain the correct temperature dependence of the elastic modulus. The Debye–Waller elastic constants extrapolate to a value in accordance with the Lindemann melting criterion [6]. From both experiment [26] and theory [27], we have two candidates for anomalous phonons with energies below 4 meV whose temperature dependence could be associated with the anomalous temperature dependence of δ phase elastic properties, namely the Kohn-like anomaly in the T1[011] branch, and soft T[111] mode, and it would be most interesting to know their temperature dependences.

Figure 13 shows the calculated bulk modulus versus pressure, which is a *decreasing* function of pressure, contrary to the behaviour of most metals. However, it is

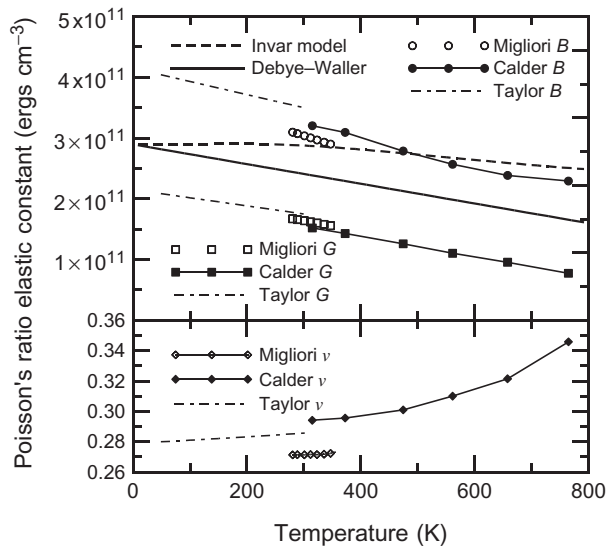


Figure 12. Calculated Invar model bulk modulus versus temperature, compared with the shear modulus G , bulk modulus B and Poisson's ratio ν from the ultrasonic experiments of Taylor *et al.* [20], Calder *et al.* [22] and Migliori *et al.* [24]. For the data from Migliori *et al.* every fifth point is shown. The bulk modulus estimated from the Debye–Waller factors [6] is also shown.

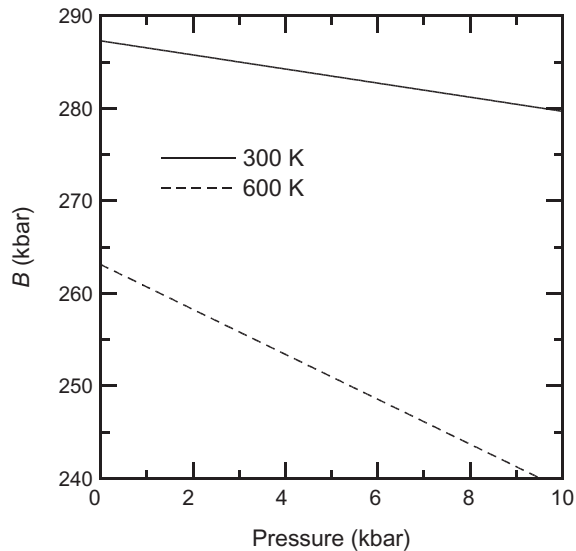


Figure 13. Calculated bulk modulus versus pressure for Pu-2 at.% Ga.

quite interesting to note that exactly this behaviour, decreasing stiffness with increasing pressure, has been observed for the low-density fcc phase γ -phase Ce by Voronov *et al.* [34] and most recently also by Jeong *et al.* [35]. In the case of Ce, the stiffness collapse is associated with the proximity of the pressure-induced γ - α transition

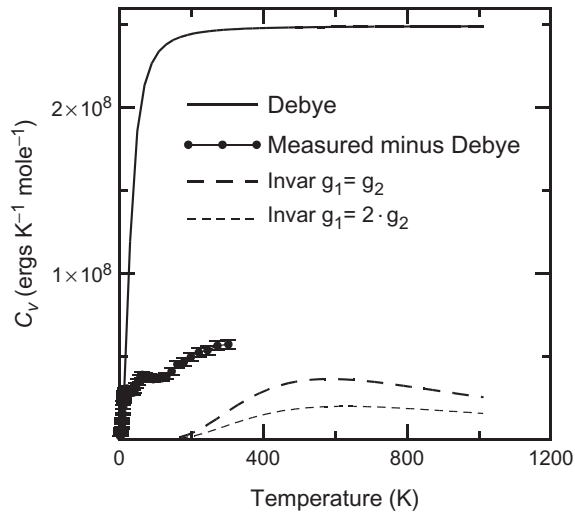


Figure 14. Measured heat capacity for Pu-5 at.% Al; the Debye contribution has been subtracted. The calculated curves are from the Invar model with different choices of Invar level degeneracies.

at 7 kbar; this transition is $\text{fcc} \rightarrow \text{fcc}$ [36]. For δ -phase Pu, similar pressures are sufficient to induce a transition to the much denser monoclinic α -phase [37, 38]. Experimental confirmation of the pressure effect on the elastic modulus of δ -phase Pu would be most desirable.

Figure 14 shows the measured and calculated heat capacities of Pu-5 at.% Al. The measurement is taken from the work of Lashley *et al.* [8]. In the figure, we have subtracted the appropriate lattice term from the measurements, for comparison with a calculated Invar term. The Invar term tracks the difference curve very well — so well that there could be no residual electronic term if it were also subtracted from the measurement! A smaller Invar term could be obtained by adjusting the Invar level degeneracies g_1 and g_2 , and this would require further adjustments to the Invar Γ values. More work on the δ -phase heat capacity problem is required before this analysis can be made.

7. Is δ -phase Pu magnetic?

In Weiss's original Invar model, *magnetic* atomic energy levels were supposed to be the origin of ΔE . There is today much discussion in the Pu literature about successful calculations of the expanded δ -phase volume achieved by allowing spin polarization of the 5f electrons, with resulting magnetic moments on the Pu atoms and even magnetic order. The papers by Söderlind [39] and by Söderlind and Sadigh [7] are typical of the calculations, while the experimental situation has been described in a recent paper by Lashley *et al.* [40]. However, magnetic order has never been observed experimentally: but by magnetic measurements, nor by neutron scattering, nor by heat capacity measurements to 9 T, nor by nuclear magnetic resonance measurements [41, 42].

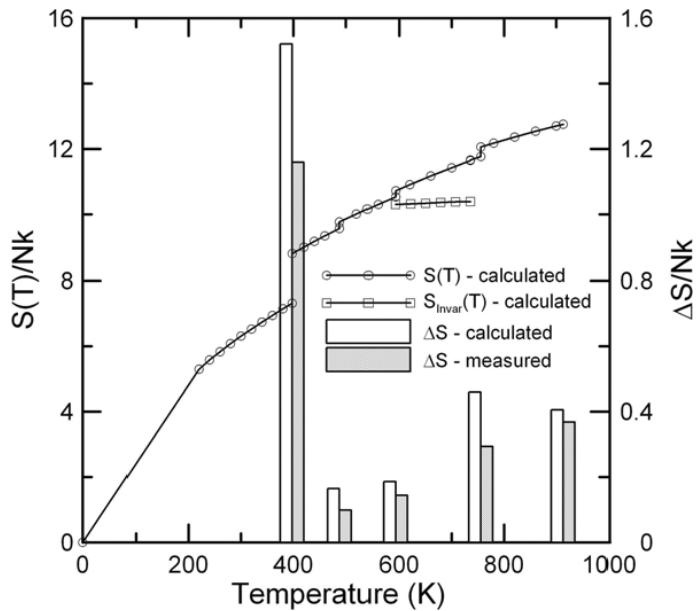


Figure 15. Measured latent heats of transformation between the phases of unalloyed Pu [43] and calculated entropy versus temperature [44]. The calculated Invar entropy is also shown.

Important information on magnetism is obtained from thermodynamics. By comparing the measured heats of transformation between the successive phase of Pu with calculated values based on lattice contributions to the entropies, we can search for any discrepancy that would be indicative of magnetic ordering. The expected discrepancy would be of order $k_B \ln(2)$ per atom. Measured values are available from the work of Foltyn [43], among others, and a calculation of the entropy that includes lattice, anharmonic and electronic effects has been made by Wallace [44]. Figure 15 shows a plot of Wallace's $S(T)$, the ΔS calculated from $S(T)$, and the experimental $\Delta S_n = H_n/NkT_n$ calculated from the measured enthalpies of transformation at each transformation n . For clarity, the ΔS values for $\delta \rightarrow \delta'$ and $\delta' \rightarrow \varepsilon$ have been combined in this plot, as there is a consensus that the ΔS for $\delta \rightarrow \delta'$ is quite small. The calculated entropy of melting has been taken rather arbitrarily as $\ln(3/2)$. The only serious discrepancy between the measurement and calculation occurs at $\alpha \rightarrow \beta$, and this may well be the result of the extreme sluggishness of this particular transformation. These thermal data would seem to exclude transformation from a magnetically disordered phase to an ordered phase at any temperature except perhaps $\alpha \rightarrow \beta$, and there is no magnetic order indicated for the α phase. The entropy associated with magnetic ordering is decisive for determining the complexity of phase diagrams in Fe systems, as pointed out by Acet *et al.* [45], but seems to play no part in the even more complex Pu phase diagram. As indicated in figure 15, the Invar entropy in the δ phase is very small and not expected to affect phase stability.

To a long list of experiments that show non-magnetism of δ -phase Pu, we add a recent neutron diffraction experiment. We looked for field-induced magnetic

diffraction in a sample of ^{242}Pu -2 at.% Ga prepared by the method described in [6]. Measurements were made at temperatures of 300, 165, 4.2 and 2.5 K and fields of 0 and 8 T with the field perpendicular to the diffraction plane, using the PHAROS spectrometer at the Los Alamos Neutron Science Center (LANSCE) configured as a powder diffractometer. There was no evidence of any magnetic signal under these conditions.

8. Connections with Pu theories

The success of the Invar model in fitting thermal expansion shows that there is a physically significant energy scale of $\Delta E = 1400$ K on the atomic length scale; this raises the question of whether a similar energy scale exists in the current Pu theories. Eriksson *et al.* [46], working in what has come to be called the *constrained* generalized gradient approximation (constrained GGA) found that the lowest energy state for δ -phase Pu occurred with the number of 5f electrons fixed at $N_f = 4$. This state is assumed to be fluctuating between localized and delocalized states, represented by $N_f = 5$ and $N_f = 0$ respectively. The results of the constrained GGA calculation are shown by solid curves in figure 16. Johansson's [1] concept of f-electron localization as a metal-insulator transition has been pursued by Kotliar and his collaborators in a series of DMFT calculations (see, for example, the paper by Savrasov *et al.* [47] and Kotliar [48]). The DMFT calculations give a double-well structure shown by dashed curves in figure 16. (Part of the discrepancy for the high-density phase may be due to the different choices of crystal structure; Eriksson *et al.* used the monoclinic α -Pu structure, while Savrasov *et al.* used the fcc δ -phase structure.)

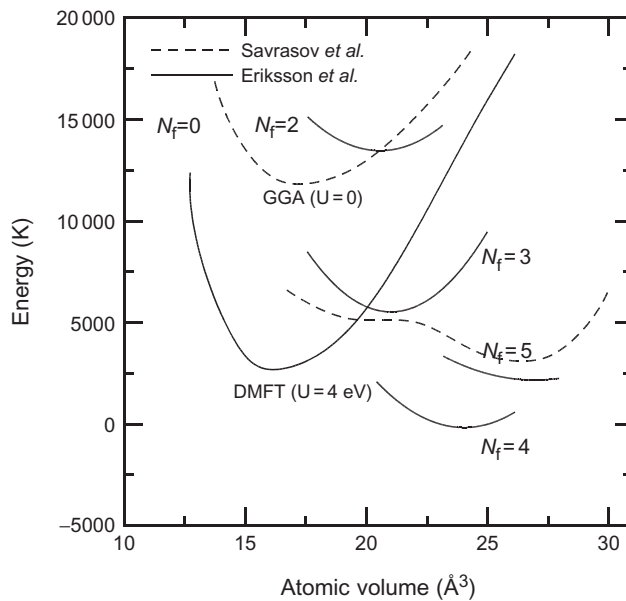


Figure 16. Calculated energy versus volume for atomic states of Pu. The solid curves are from Eriksson *et al.* [45] and the dashed curves from Savrasov *et al.* [46].

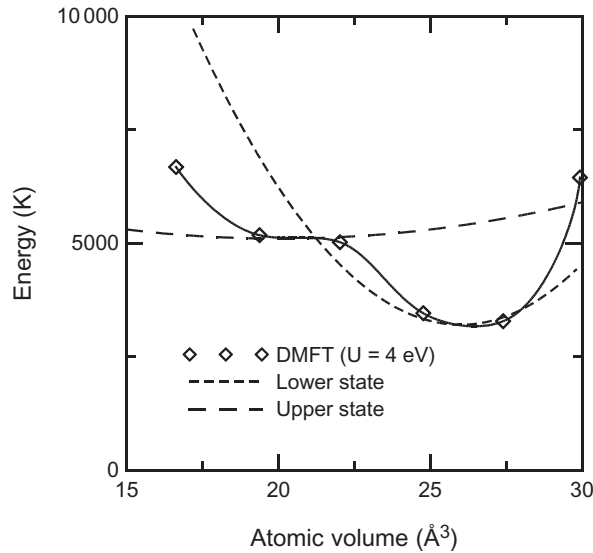


Figure 17. Two-level structure from the work of Savrasov *et al.* with schematic elastic fits to the separate levels. The levels are separated by 1900 K, rather than by the 1400 K suggested by thermal expansion, and the curvature of the lower level corresponds to a bulk modulus of about twice the experimental value δ -phase Pu. The fit to the upper level is notional only.

To match the Invar model, we are looking for atomic states that are separated by 1400 K in energy and 4 \AA^3 in volume. There is no exact match in figure 16, but the two minima given by the DMFT theory are fair matches in energy. (These appear to correspond to the $N_f=5$ and $N_f=3$ levels given by the constrained GGA calculation.) Both Eriksson *et al.* and Savrasov *et al.* indicated that the closely spaced levels given by their respective calculations could lead to an explanation of the negative thermal expansion of δ -phase Pu via the Invar effect. The higher minimum in the double-well structure in the work of Savrasov *et al.* seems to be flat, and this observation may explain why the assumption of zero elastic contribution from excited Invar levels is successful. The situation is illustrated in more detail in figure 17. The difference between the calculated levels is 1900 K, rather than 1400 K, and the bulk modulus used to fit the curvature of the calculated lower well is about twice the experimental value. Nevertheless, the agreement seems to be quite satisfactory at this stage of theoretical development. Calculations with higher accuracy and higher resolution are required to confirm the correspondence suggested here.

Finally, we mention two additional lines of theoretical effort. Cooper and co-workers [49, 50] described a model for Pu thermodynamics based on ‘self-induced Anderson localization’ that gives rise to distinct singlet and triplet states with an unspecified energy separation. It is tempting to identify the Invar level with this unspecified energy, but the model given by Cooper and coworkers remains undeveloped. Harrison [51] has shown that calculations of the mode Grüneisen constants, based on his interpretation of the phonon spectrum [28], can lead to a negative thermal expansion of the observed magnitude. As suggested by Harrison, one could test his theory with DMFT calculations at different volumes.

Harrison's calculation does not involve any characteristic energy of the order of our ΔE , and it is not clear that the correct temperature dependence for the thermal expansion can be obtained from this model.

9. Experimental search for Invar levels

We made an experimental search for the Invar levels using the PHAROS spectrometer at the LANSCE. We used high-energy incident neutrons (200 meV) to see whether any excitations corresponding to $\Delta E = 1400$ K (120 meV) could be found. These experiments are complicated by the presence of considerable scattering from the vanadium can required for radiological containment of the sample. In figure 18 we show scattering exceeding that of the empty can that appears at an energy of 90 meV = 1100 K, somewhat lower than expected. It is not clear whether there is any relationship between this observation and the Invar effect. Intermultiplet excitations [52] are known to give small cross-sections and 100 meV excitation energies consistent with our preliminary data. Much analysis remains to be carried out, and even then this observation not involve the Invar effect.

Another important aspect of the extra signal observed at about 90–100 meV is the momentum transfer (Q) dependence of the intensity. This is plotted for both the sample-plus-can and the can-only measurement in figure 19, where the signal is summed over the energy window from 84 to 104 meV. The lower Q limit of 3 \AA^{-1} is a consequence of the kinematic constraints imposed by the choice of incident energy. A qualitatively interesting feature of the form factor for the excitation in

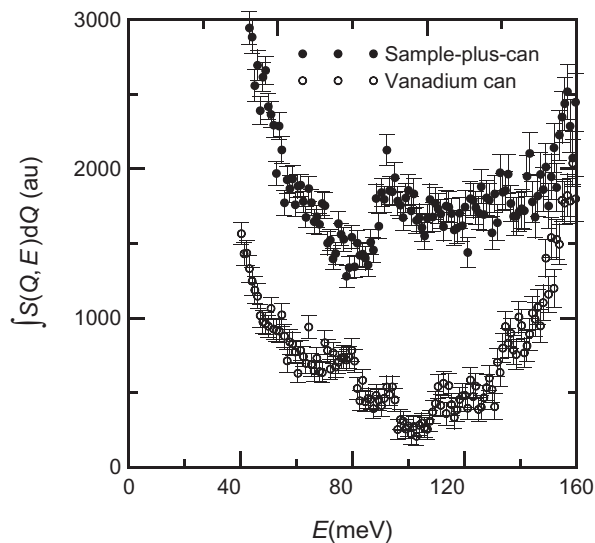


Figure 18. Scattered inelastic neutron signal for 200 meV neutrons incident on a Pu–2 at.% Ga sample at 300 K. The full circles indicate the signal from the sample plus the vanadium containment; the open circles indicate the signal from the empty containment. The two signals have been displaced by 1000 units for clarity.

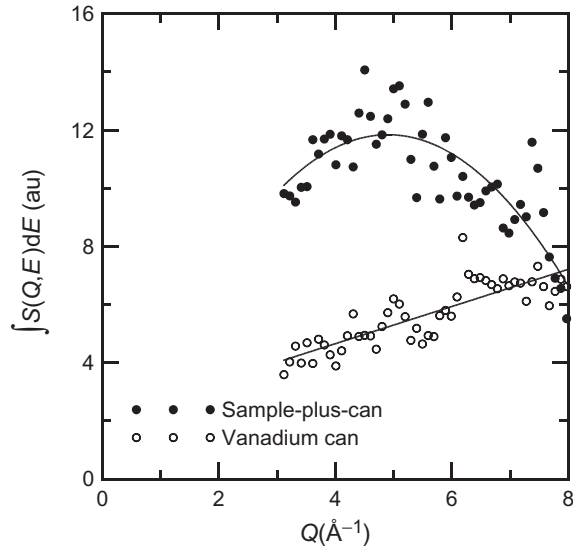


Figure 19. Dependence on momentum transfer Q of the inelastic neutron signals shown in figure 18.

δ -phase Pu is the lack of a minimum typically found at about 5 \AA^{-1} in form factors for excitations such as the ${}^6\text{H}_{5/2} - {}^6\text{H}_{7/2}$ transition in Sm metal. This places a significant constraint on any model that attempts to explain the nature of the transition. Further experiments are planned to explore the form factor in more detail, particularly at smaller momentum transfers that become accessible with a higher incident neutron energy.

10. Summary

We have developed a two-level Invar model for the thermal expansion of Pu–Ga alloys, and we have constructed a thermodynamic description of δ -phase Pu based on a free energy that includes the Invar model and the assumption of zero contribution from excited Invar states. The model depends on four parameters: two energies and their respective volume dependences expressed as two Grüneisen constants. The two energies are the Debye temperature Θ and the energy ΔE of the hypothetical excited Invar state. ΔE is 1400 K atom^{-1} , and the associated volume change is $4.2 \text{ \AA}^3 \text{ atom}^{-1} = 17\%$. When we look for corresponding energy structures in current theories, we find a good correspondence between the model and the double-well structure of results of calculations by Savrasov *et al.* [47] for ΔE , for ΔV and for the elastic softening of the excited Invar state. Our particular implementation of the Invar model shows that the thermal softening of the elastic constants is *independent* of thermal expansion, contrary to scaling models, but in agreement with experiment.

We looked for field-induced magnetic Bragg peaks in a polycrystalline sample of Pu–2 at.% Ga and were unsuccessful up to 8 T and down to 1.5 K. We did find

a small inelastic response at $\Delta E = 90$ meV that may be related to the Invar levels introduced to model the lattice properties, but it is too early to tell whether this correspondence is physically significant.

We conclude with a list of known problems or uncertainties associated with the Invar model for δ -phase Pu. The elastic contribution of the Invar free energy must be negative to explain the rapid decrease in the bulk modulus with increasing temperature, and this contribution must be investigated with more detailed DMFT calculations. We do not know in detail which soft phonons contribute to the temperature-dependent phonon density of states. The connection between the 100 meV structure found by neutron inelastic scattering and the Invar effect is not established, and further experiments are required. High-quality heat capacity data at higher temperatures are needed to validate the Invar model and to determine values for the degeneracies of the Invar levels. Finally, more detailed calculation is required to test the temperature dependence of the thermal expansion in Harrison's model.

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