Development of an electronic phase diagram and the predictions of plutonium alloy phase stability using electronic properties

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Abstract
Experimentally measuring electronic properties could have a significant impact in determining the kinetics of aged plutonium alloys. Phase stability of plutonium alloys can be assessed by using modified empirical electronic models in conjunction with measurements of electronic and magnetic properties of plutonium alloys. The issues surrounding the evaluation of aged plutonium alloys and the evolution of electronic-based alloy theories as applied to the prediction of the solubility of gallium in plutonium are presented. Using solid solution thermodynamics in combination with these electronic models, the phase diagram for dilute solid solutions can be estimated.

There are numerous measurements that could be used to determine the relationship between a material's phase stability and its electronic structure. The measured properties of interest here are the Seebeck coefficient (thermopower), Hall coefficient and electrical resistivity. Combining three property measurements (or three other phase sensitive properties) into a three-dimensional plot with a specific property on each axis, a region of space will be formed that describes the stability of the phase. Also, the implications of assessing electronic data with this methodology are discussed.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

1. Introduction

Physical and electrical property measurements of plutonium–gallium alloys can offer significant insight as to the extent of aging of the alloy. Pure plutonium has six allotropic phases between room temperature and melting under atmospheric conditions. Physical and crystal structural data for the six phases are shown in table 1 [1–3]. The phase of interest is the delta phase because it is very ductile, which makes it easy to machine and form. Because

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Table 1. Physical and thermodynamic data for plutonium phases [1–3].

Allotrope	Temperature range of stability (°C)	Space lattice and space group	Unit cell dimensions (Å)	Atoms per unit cell	X-ray density (g cm^{-3})
α	Below ~115	primitive monoclinic $P2_1/m$	(21 °C) $a = 6.183$ $b = 4.822$ $c = 10.963$ $\beta = 101.79°$	16	19.86
β	~ 115–~200	body-centred monoclinic I_1/m	(190 °C) $a = 9.284$ $b = 10.463$ $c = 7.859$ $\beta = 92.13°$	34	17.70
γ	~ 200–310	face-centred orthorhombic $Fddd$	(235 °C) $a = 3.159$ $b = 5.768$ $c = 10.162$	8	17.14
δ	310–458	face-centred cubic $Fm3m$	(320 °C) $a = 4.6371$	4	15.92
δ'	458–480	body-centred tetragonal $I4/mmm$	(465 °C) $a = 334$ $c = 4.44$	2	16.00
ε	480–641	body-centred cubic $Im3m$	(490 °C) $a = 3.6361$	2	16.51

the delta phase of pure plutonium is only stable at elevated temperatures, alloying elements, such as gallium, must be used to stabilize the delta phase at room temperature.

Unfortunately, consensus as to where the gallium-stabilized delta phase begins has not been reached. There are many different plutonium–gallium equilibrium phase diagrams in the literature. The equilibrium phase diagram, adapted from Ellingerr *et al* [4] and Peterson and Kassner [5], is shown in figure 1. Another equilibrium phase diagram, reported by Chebotarev *et al* [6], is shown in figure 2. The main difference between the two equilibrium phase diagrams is that the first diagram reports that the delta phase of alloyed plutonium is stable below room temperature, whereas the second diagram indicates that there is a eutectoid decomposition below 100 °C. Further experiments have refined the results, which are shown in figure 3 [7, 8].

The issues of phase stability are immediately recognized by the variations in the equilibrium phase diagrams. Microstructural conditions of the plutonium–gallium system that affect the stability between the alpha and delta phases are elemental segregation, homogeneity of the phase present and the amount of radiation damage.

The key issue with plutonium—1 wt% gallium is the microsegregation of gallium that occurs upon cooling to room temperature. Several studies [9–12] indicate that the microsegregation occurs during the solid-state phase transformation from $\varepsilon \rightarrow \delta$. A relatively large interdiffusion coefficient in the ε-phase limits segregation during solidification, but a decrease in the interdiffusion coefficient by approximately three orders of magnitude in the δ-phase sets the stage for gallium microsegregation.

An example of a typical microstructure for the plutonium—1 wt% gallium alloy is shown in figure 4 [13]. The low-gallium regions resulting from microsegregation contain
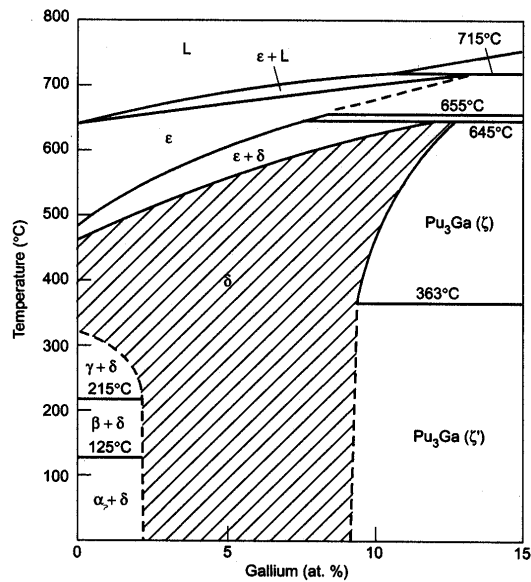
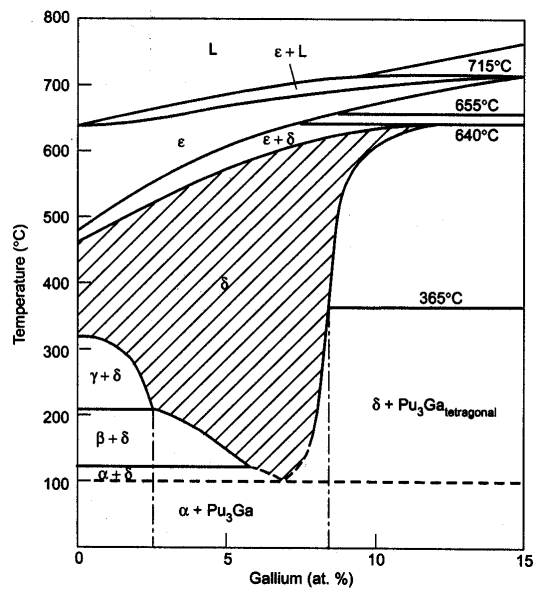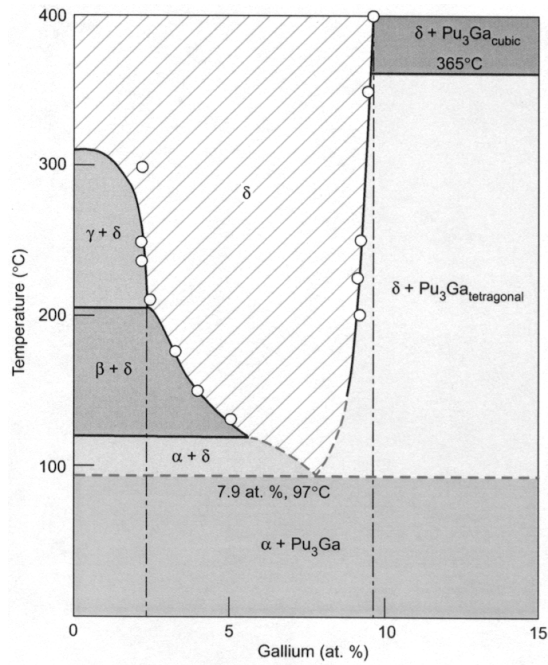**Figure 1.** Plutonium–gallium phase diagram [4, 5].

Figure 2. Plutonium–gallium equilibrium phase diagram by Chebotarev *et al* [6].

a metastable delta phase that undergoes multiple allotropic phase transformations, consistent with the phase diagram, ultimately reaching the room temperature alpha phase. The result is a brittle, high density, monoclinic alpha phase present in the grain boundaries. To eliminate these metastable regions, homogenization treatments are required for gallium to diffuse throughout the microstructure, resulting in an equilibrium concentration. Homogenization treatments will ensure full transformation of the face-centred cubic delta phase microstructure [9].

Figure 3. Plutonium–gallium equilibrium phase diagram by Chebotarev *et al* and Timofeeva [7, 8].
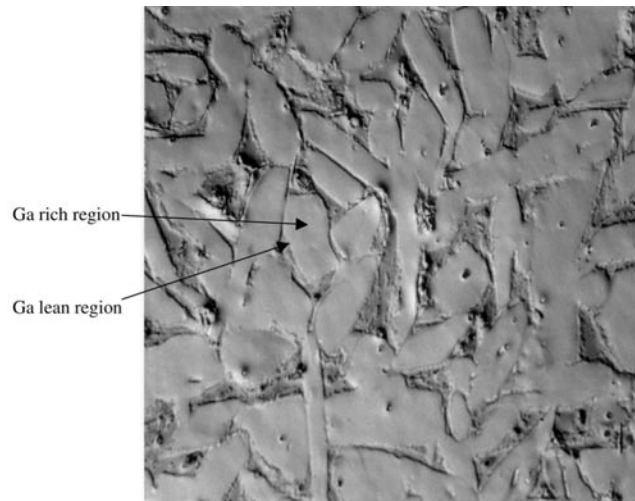
Figure 4. Typical microstructure of plutonium–1 wt% gallium alloy. Approximate core size is 30 μm [13].

To ensure that the homogenization treatments are successful, many experimental methods exist for determining the residual microsegregation present within an alloyed metal. However, assessing the present phases without destroying the material is preferred for plutonium–gallium alloys. Performing electronic property measurements is one way to non-destructively assess the phases present in a material.

To achieve new analytical methods of understanding and predicting plutonium alloy stability, it is important to revisit the empirical electronic concepts and analytical methodologies of the 1960s. Gschneidner [14–16], Waber [14–16], Brewer [17–19], Miedema [20], and others [21–24] introduced approaches to correlate electronic properties to phase crystal structure and transitions. Even though these models are qualitative by today's analytical and measuring practices [25–29], they bridged the essential gap between electronic interactions, solution thermodynamics and phase diagram construction.

The electronic properties of plutonium are dependent upon the phase or phases present because the electronic configuration of each phase is unique. Essentially, the electronic properties are a fingerprint of a particular phase. Utilizing this feature, the phases of aging plutonium alloys can be determined as a function of time. The electronic properties of interest are the Hall coefficient, the Seebeck coefficient (thermopower) and the electrical resistivity. The Hall coefficient determines the dominant electronic carrier type and the free charge carrier concentration in the material. The Seebeck coefficient describes how the effective mass or the curvature of the density of electronic energy states changes at the effective Fermi energy surface. It assists in identifying the position of the Fermi level relative to the band construction. Changes in the Seebeck coefficient will indicate when a phase transformation has occurred or should occur. Such transitions occur when the higher energy states are filling in one Brillouin zone configuration. This occurrence allows for the possibility of filling lower energy states in another specific Brillouin zone configuration. The electrical resistivity is affected by carrier concentration and the various scattering factors. With a material that experiences significant radiation damage, the electrical resistivity correlate better to the damage of the crystal structure.

Electronic properties can be utilized to calculate a plutonium–gallium phase diagram. An electronic analytical analysis will be presented, that calculates the boundaries of two-phase regions, and demonstrates the use of electronic property measurements to follow phase and microstructural changes. The electronic properties that can be used to determine the region of phase stability will be illustrated on phase stability diagrams.

2. Early approaches to electronic concepts

Empirical models developed by Hume-Rothery, Darken and Gurry, Engel and Brewer, and Miedema, coupled with the free electron theory, allow for correlation of electronic measurements to physical stability.

One of the first empirical methodologies for determining whether extended solid solutions existed between pure metals was proposed by Hume-Rothery *et al* [22, 23]. Their work identified general trends that occurred when alloying pure metals. These trends developed into the Hume-Rothery rules, which incorporated (1) a size factor, (2) the electrochemical factor and (3) the relative valence effect [14]. An additional criterion required the same crystal structure for both solute and solvent.

Darken and Gurry extended the Hume-Rothery rules by plotting electronegativity as a function of atomic radius. Figures 5 and 6 show Darken–Gurry maps that illustrate the elements that are favoured to form extended solid solutions with delta and epsilon plutonium, respectively [30]. Alloying plutonium with gallium can be assessed for gallium solubility by using Gschneidner's criteria that allow one to confidently use the Darken–Gurry model [14]. Plutonium is the solvent and is an fd-group element, while gallium is the solute and is an sp-group element. Applying Gschneidner's rule 3, which requires that extensively soluble solute and solvent atoms have a common metallic crystal structure, and recognizes that plutonium and gallium are face-centred cubic and orthorhombic respectively, then a gallium solubility of less than 5 at.% is expected. Since the face-centred cubic structure is a special case of
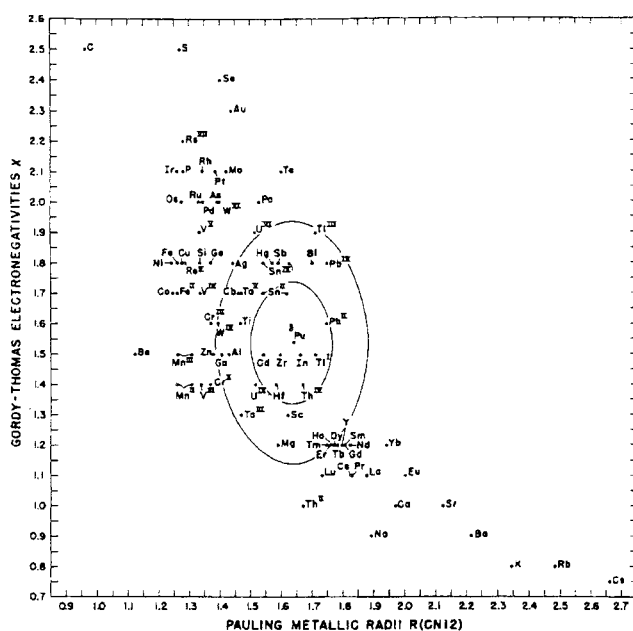
Figure 5. Darken–Gurry map for determining which elements are favoured for solution in delta plutonium [30].

Table 2. Predicting crystal structure from the number of unpaired s and p electrons [21].

Crystal structure	Elements	Alloys	Electronic configuration
BCC	1	< 1.5	$d^n s$
HCP	2	1.7 to 2.1	$d^n sp$
FCC	3	2.5 to 3.0	$d^n sp^2$
Diamond	4	> 3.0	$d^n sp^3$

the orthorhombic structure when the c/a ratio is 1.4, this rule is being applied at a boundary line case. It has been found that the delta phase of plutonium can be extended to 8 at.% with gallium additions. It is this face-centred cubic phase stabilizing effect of gallium that allows the delta phase to extend to room temperature.

The Engel–Brewer theory attempts to use the electronic configurations of metals and alloys to predict both the resulting crystal structure and the solute solubility limits for various phases of an alloy [21]. The numbers of unpaired s and p electrons that predict which crystal structure will occur for elements and alloys are shown in table 2. Shown in table 3 is the correlation of plutonium phases with specific excited electronic configurations [17]. Also given are the promotion energies for the transitions from ground state to excited states for a specific crystal structure.

Referring to table 4, the number of unpaired s and p electrons for each phase of plutonium metal exactly follows the predictions of Engel and Brewer for various crystal structures of plutonium phases [18]. For alloying delta plutonium with gallium, the gallium electronic configuration is sp^2. Because plutonium and gallium have the same number of unpaired s and p electrons, it is predicted that the gallium will stabilize the face-centred cubic phase of plutonium. From the plutonium–gallium phase diagram (figure 1), it can be seen that gallium does increase the range of the face-centred cubic phase field.
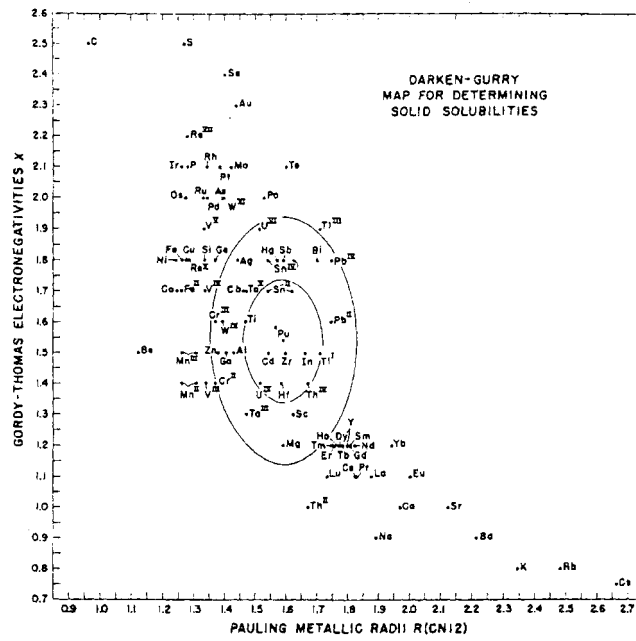
Figure 6. Darken–Gurry map for determining which elements are favoured for solution in epsilon plutonium [30].

Table 3. Plutonium electronic configurations [17].

State	Electronic configuration	Promotion energy ($\Delta E/R$)
Ground state	f^6s^2	—
BCC	f^5d^2s	21.45
HCP	f^6sp	22.23
	f^5dsp	29.97
FCC	f^5sp^2	34.0 ± 7

Table 4. Electron configurations for plutonium phases [18].

Plutonium phase	Electron configuration	Bravais lattice
Ground state	f^6s^2	—
α	—	Simple monoclinic
β	—	Body-centered monoclinic
γ	—	Face-centered orthorhombic
δ	f^5sp^2	Face-centered cubic
δ'	—	Body-centered tetragonal
ε	f^5d^2s	Body-centered cubic

Miedema developed an empirical equation based on Wigner–Sietz cells to determine the heat of formation of alloys. The Miedema model combines the cell interfacial electronic properties (using the difference in the electronic concentration of each Wigner–Sietz cell Δn_{ws}), and the differences in chemical potential of the electron (using the differences in work functions between solute and solvent metals $\Delta\phi$) between two adjacent cells. The heat

of mixing, ΔH, is shown below [20].

$$\frac{\Delta H}{N_o} = f(c) P \left[-e(\Delta \phi^*)^2 + \left(\frac{Q}{P} \right) (\Delta n_{ws}^{1/3})^2 - \frac{R}{P} \right]$$

where $f(c)$ is the solute concentration dependence for an alloy, and e is the charge of an electron. Note that Q/P and R/P are parameters determined from data correlation for various combinations of elements relative to the periodic table.

Miedema plotted the work function as a function of the density discontinuity for alloying plutonium with transition metals, alkaline metals, alkaline earths and noble metals. The Miedema parameters for plutonium and gallium are shown in table 5 and figure 7 illustrates how the Miedema model predicts the ability to form solid solutions [20].

Table 5. Values for the Miedema equation parameters [20].

Element	ϕ^x (V)	$\Delta n_{ws}^{1/3}$	$V_m^{2/3}$
Plutonium	3.8	1.44	5.2
Gallium	4.10	1.31	5.2
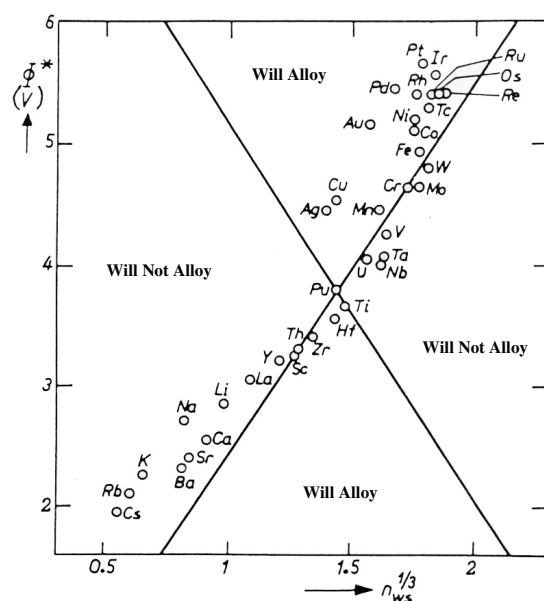
Figure 7. Prediction of elements that form solid solutions with plutonium using the Miedema model [20].

When reviewing the success of these empirical electronic-based models in predicting solubility, it is apparent that electronic measurements will give insight into the phase solubility. The electron is the significant entity to achieve bonding, crystal formations and phase equilibrium. The concept of treating the electron as a solute in a metal solution and equating the chemical potential of the electron in the various plutonium phases to achieve two-phase equilibrium offers a new approach to evaluating plutonium–gallium phase equilibrium and stability. The next section will apply the electronic concept to produce the plutonium–gallium phase diagram and thus illustrate the fundamental bridge between electronic energy states and phase stability and the validity of using electronic property measurements.

3. Electronic phase diagram

Phase diagrams typically display phase stability as a function of temperature and composition. By developing an analytical relationship between thermodynamic and electronic quantities, a new electronic phase diagram can be constructed. For example the new phase diagram would plot temperature as a function of electron concentration, thereby enabling a dialogue between physicists and metallurgists.

Referring to the 'alpha plus delta' two-phase region of figure 1, the chemical potential of gallium in the alpha phase is equal to the chemical potential of gallium in the delta phase. The chemical potential is equivalent to the solution free energy per mole of gallium in each phase for a specific composition. Therefore, the chemical potential can be represented as

$$\mu(T) = \Delta H(T) - T \Delta S(T)$$

where $\mu(T)$ is the chemical potential, $\Delta H(T)$ is the change in enthalpy per mole and $\Delta S(T)$ is the change in entropy per mole, and all are a function of temperature.

Treating the electron as a solute entity in the solution of the specific phase, these thermodynamic concepts can be applied to the electron. Using the free electron model, the chemical potential of the conduction electron at absolute zero equals the Fermi energy, E_F. The application of the chemical potential of the electron allows for the bridging from electronic measurements to the determination of phase equilibrium.

Since all values are on a per electron basis, then at absolute zero the enthalpy and entropy of an electron are

$$\Delta H(T = 0) = E_F = \frac{\hbar^2 3\pi^2}{2m} N^{2/3} \qquad \Delta S(T = 0) = 0.$$

The enthalpy of an electron at absolute zero is equal to the Fermi energy, and m is the electron mass and N is the electron concentration. The heat capacity at constant volume and pressure can be approximated as being equal for a solid, $C_p \approx C_V$. The heat capacity for the electron at constant volume is given by

$$C_V = \frac{\pi^2 k}{2} N \frac{T}{T_F}$$

where T_F is the Fermi temperature.

Substituting all equations in the chemical potential equation results in a general equation of

$$\mu(T) = E_F(T = 0) + \int_0^T C_V \, dT - T \left[\int_0^T \frac{C_V}{T} \, dT \right].$$

Integrating and simplifying the previous equation, the resultant equation for the chemical potential of an electron in a particular phase is

$$\mu(T) = E_F(T = 0) - \frac{\pi^2 k N T^2}{4 T_F}.$$

To obtain consistent units (Joules per electron), the previous equation must be modified to the following:

$$\mu(T) = E_F(T = 0) - \frac{\pi^2 k N T^2}{4 T_F} \frac{MW}{\rho N_A Val}.$$

The number of valence electrons for each atom has been used to predict phase stability. Valence of a phase is a macroscopic concept to incorporate a much more complex electronic situation. The specific number of valence electrons per atom in a given crystal structure can be

Table 6. Metallic radii and valences of plutonium atoms [3, 31].

Phase	Temperature (°C)	Radius (Å)	Radius at 25 °C (Å)	Valence
α	25	1.58	1.58	5
β	93	1.60	1.59	5
γ	235	1.601	1.589	5
δ	320	1.640	1.644	4.6
δ'	465	1.638	1.644	4.6
ε	490	1.622	1.594	5
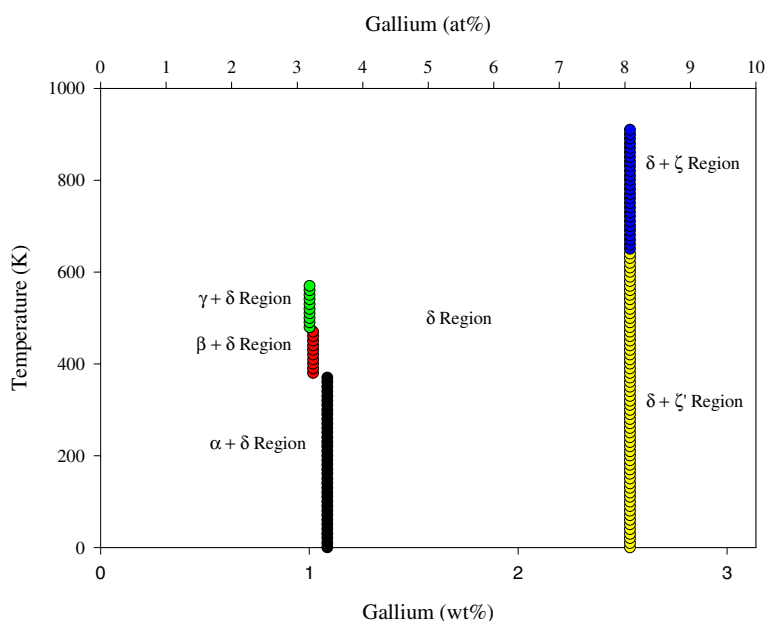
Figure 8. Calculated plutonium–gallium phase diagram.

related to the Fermi level using the free electron concept. When the Fermi level is in contact with a Brillouin zone boundary, it becomes potentially energetically favourable for a phase change. Therefore, the material tries to find a lower energy configuration into which it can transform.

Values for the valence of each plutonium phase are shown in table 6 [3, 31]. These valences are used to calculate physical and thermodynamic properties as suggested by the free electron theory. The valence electrons consist of s, p and unbonded d and f electrons. Only the number of s and p electrons, as suggested by Brewer, contributes to the identification of the crystal structure of a given phase. The electronic configurations that define BCC, HCP, FCC and diamond cubic crystal structures are $d^n f^m s$, $d^n f^m sp$, $d^n f^m sp^2$ and $d^n f^m sp^3$, respectively.

For each phase of a two-phase region, there will be a chemical potential equation. Setting the two equations equal to each other will result in obtaining the atomic percentage of gallium that divides the two-phase region from the delta phase region.

The results of using the chemical potentials to determine the phase diagram are shown in figure 8. Comparing the calculated phase diagram to the phase diagram in figure 1, one can see a very good correlation between the two diagrams. Notice the expected shift to the left with

increasing temperature in the delta–two-phase boundary in going from alpha to beta to gamma phase. These calculations include both enthalpic and entropic contributions to phase stability. Knowing that this analysis is based on the basic free electron model, further analysis could include more detailed electron models, even though the present analysis adequately models the alloying behaviour of gallium in plutonium, especially at the lower temperatures.

It has been determined that this analysis is very sensitive to the value of the valence of each phase. Also, this initial analysis did not consider the change in the latent heat for each phase transformation and the correction in the heat capacity due to electron–phonon interactions as a function of temperature.

4. Electronic property measurements

The above empirical electronic models for phase stability and the calculation of an electronic based phase diagram suggest direct electronic property measurements to determine phase stability and to nondestructively assess plutonium alloy aging.

Table 7. Electrical resistivity of plutonium [32].

Phase	Temperature ($^\circ$C)	Absolute resistivity ρ ($\mu\Omega$ cm)	Mean coefficient ($^\circ$C^{-1}) and temperature range ($^\circ$C)
α	-247	64.8	$+184.05 \times 10^{-4}$
	-223	128.0	$(-247$ to $-223)$
	-173	156.9	-4.18×10^{-4}
	-123	153.5	$(-147$ to $20)$
	0	146.45	
	$+107$	141.4	
β	147	108.5	-0.62×10^{-4}
			$(147$ to $197)$
γ	232	107.8	-0.50×10^{-4}
			$(232$ to $317)$
δ	352	100.4	$+0.72 \times 10^{-4}$
			$(352$ to $452)$
δ'	462	102.1	$+4.43 \times 10^{-4}$
			$(462$ to $474)$
ε	501	110.6	0.00
			$(488$ to $501)$

The electronic and magnetic properties have well defined functionality with electronic models. These properties are each dependent upon concentration and various phenomenological factors involving electrons. Therefore, correlations between the measured electronic property and phase stability can be difficult to analyse. To overcome the confusion due to numerous influencing factors, the data must be correlated by using more than one of the electronic properties. Electrical resistivity, Hall coefficient and Seebeck coefficient will be investigated. The reported electronic properties are for both pure plutonium and plutonium alloys. These data will illustrate how electronic properties can distinguish between the various plutonium phases.

4.1. Electrical resistivity

Electrical conductivity, the reciprocal of resistivity, is a function of electron concentration and a mobility factor. This mobility factor is correlated directly to scattering at various sites in the crystal. Resistivity can be primarily related to electron concentration at low temperature and fairly pure materials or it can assess the accumulated damage to the crystal structure from effects such as radiation. Electrical resistivity measurements have been performed on plutonium metal and plutonium alloys. Table 7 [32] and figure 9 [33] show the electrical resistivity of unalloyed plutonium metal as a function of phase (or temperature). One can see that the value of electrical resistivity changes within a single phase and between phases. This observation leads one to believe that when an alloy is cored, the value of electrical resistivity will be an average between the two phases present. Therefore, during homogenization treatments, the value of the electrical resistivity should move towards that of the homogenous phase. Figure 10 shows how the electrical resistivity of plutonium–gallium alloys varies as a function of temperature [33]. Comparing figure 10 to figure 9, one can see that gallium has a profound effect on smoothing out the variations in the electrical resistivity, and that phase changes in high gallium–plutonium alloys become difficult to observe. Using electrical resistivity measurements for phase identification of plutonium alloys is thus a relatively insensitive method. Consequently, electrical resistivity measurements may be a better indicator of the state of the accumulation of structural defects due to radiation during the aging of plutonium alloys.
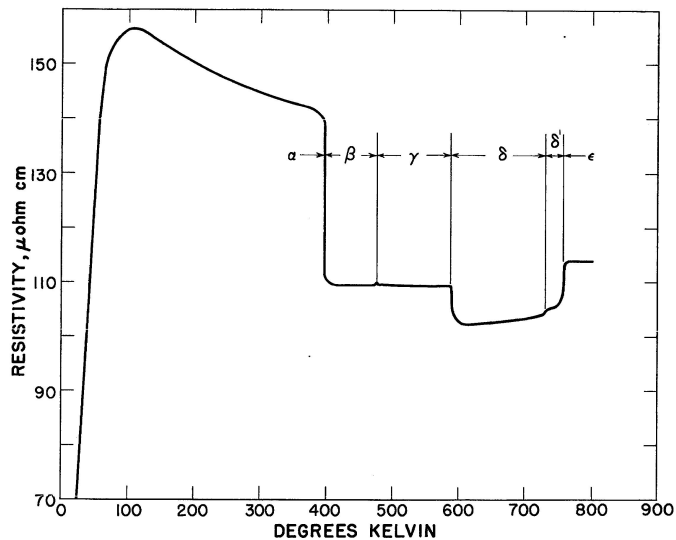

Figure 9. Electrical resistivity of plutonium as a function of absolute temperature [33].

4.2. Hall coefficient

The Hall coefficient, R_H, correlates the effect of a transverse magnetic field on an applied current resulting in a potential difference across the conducting material and can be given by the following expression:

$$E_H = R_H[J \times B].$$

For materials with a small electron concentration, like semiconductors, the actual electron concentration can be determined from the value of the Hall coefficient. In the case of a
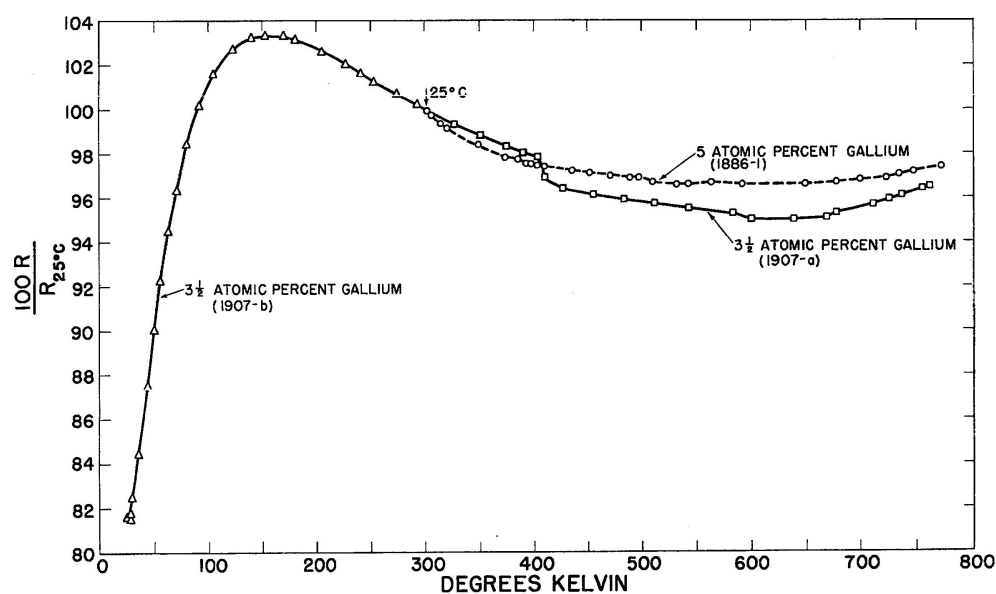
Figure 10. Resistivity as a function of absolute temperature for plutonium–gallium alloys [33].

metal with its high electron concentration, two difficulties arise. The first problem is the requirement to make very low voltage measurements across the material with such high electron concentrations. The second difficulty comes from the resulting circular electronic path in the conductor due to the applied magnetic field, which causes a magnetic field that opposes the applied magnetic field, resulting in a reduced effective magnetic field. The end result is a distorted value for electron concentration. However, the relative change in the value of the Hall coefficient with changing voltage is sufficient for monitoring the macroscopic changes in the material.

For pure plutonium, table 8 shows the Hall coefficient for specific temperatures [34]. The Hall coefficient has been measured for delta-stabilized alloys of aluminum and cerium. Figures 11 and 12 show the Hall coefficient as a function of temperature for aluminum- and cerium-stabilized delta phase plutonium, respectively [35].

The results for aluminum- and cerium-stabilized delta phase plutonium show that the Hall coefficient decreases with increasing alloy content. The Hall coefficient shows little dependence on temperature at higher temperatures, but a large dependence at lower temperatures. For delta-stabilized plutonium, the Hall coefficient is positive for the temperature range shown. This sign implies that delta-stabilized plutonium exhibits p-type conduction, suggesting a tight packing of the Fermi surface with the face-centred cubic Brillouin zone.

Table 8. Hall constant for alpha and delta plutonium [34].

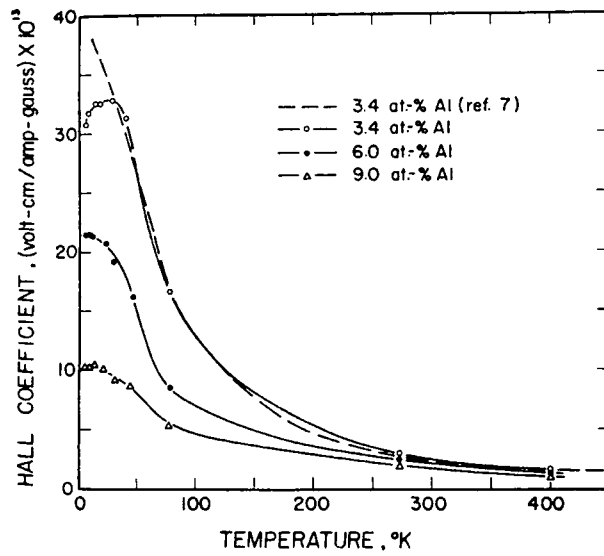| Temperature °K | R_H (m^3 C^{-1}) × 10^{11} | |
	Alpha plutonium	Delta plutonium
293	6.9 ± 0.5	11.1 ± 1.0
77	-9.5 ± 0.6	16.2 ± 1.5

Figure 11. Hall coefficient for aluminum-stabilized delta plutonium [35].
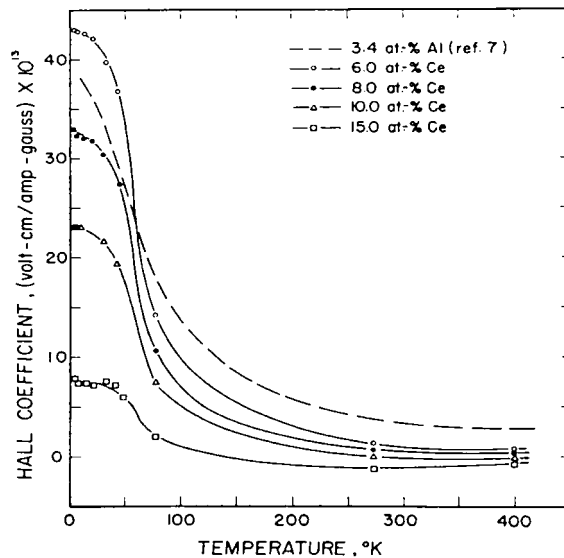

Figure 12. Hall coefficient for cerium-stabilized delta plutonium [35].

4.3. Seebeck coefficient

For metals, there are a high number of charge carriers, resulting in a high carrier concentration. The Seebeck coefficient for this case is given by [36]

$$S = \pm \frac{k}{e} 27.1 (r + 1.5) \left(\frac{m^*}{h^2} \right) kT n^{-2/3}$$

where k is Boltzmann's constant, e is the electron electrical charge magnitude, k/e is 86 μV K^{-1}, h is Planck's constant, r is the scattering parameter, m^* is the effective mass,
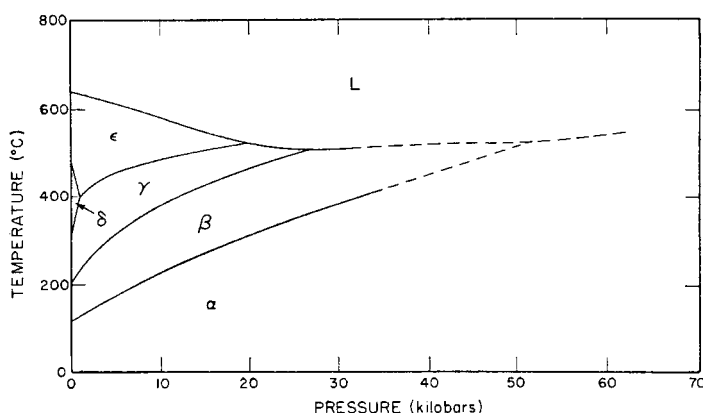
Figure 13. Effect of pressure on crystal structure in elemental plutonium [37].

Table 9. Seebeck coefficient of plutonium [34].

| Phase | Temperature (K) | Thermoelectric power ($\mu V\ K^{-1}$) | |
		Averaged values	Range
α	~ 20	1.75	~ 1.5–~ 2
	~ 80	10.1	8.6–11.6
	~ 100	9.8	8.2–11.5
	~ 293	~ 13	11.2–15.6
	300	11.5	7–15.5
β	400	9.1	7–10.7
γ	500	8.4	7.4–9.4
δ	600	3.0	2.3–3.7
δ'	725	2.32	—
ε	800	3.5	3.2–3.8

T is temperature and n is carrier concentration. The Seebeck coefficient is not influenced by the grain boundaries as long as the mean free path length of the carriers is much smaller than the grain size.

A strong deviation in the Seebeck coefficient is an indication that significant change in the filling of electronic energy states is occurring. For the material to minimize its energy, the material will undergo a transition to a different crystal structure that results in the lowest energy state available.

The Fermi surface for plutonium is known to be a very complex shape and does not resemble the spherical shape from the free electron model used to introduce the concept of the phase transition. Nevertheless, higher energy states will still be filled when plutonium is approaching a phase transition. Even though the shape of the plutonium Brillouin zone is not spherical, it should not distract one from using electronic measurements, such a Seebeck coefficient, to identify a transition. The shape of the Fermi surface does not matter in the case of measuring the Seebeck coefficient because the Seebeck coefficient will indicate the filling of higher energy states and the desire to have a phase transition.

The Seebeck coefficient has been measured for all six phases of pure plutonium. Shown in table 9 are the averaged values of the thermoelectric power of each phase of pure plutonium [34]. The data show that the Seebeck coefficient is positive for each phase of plutonium.
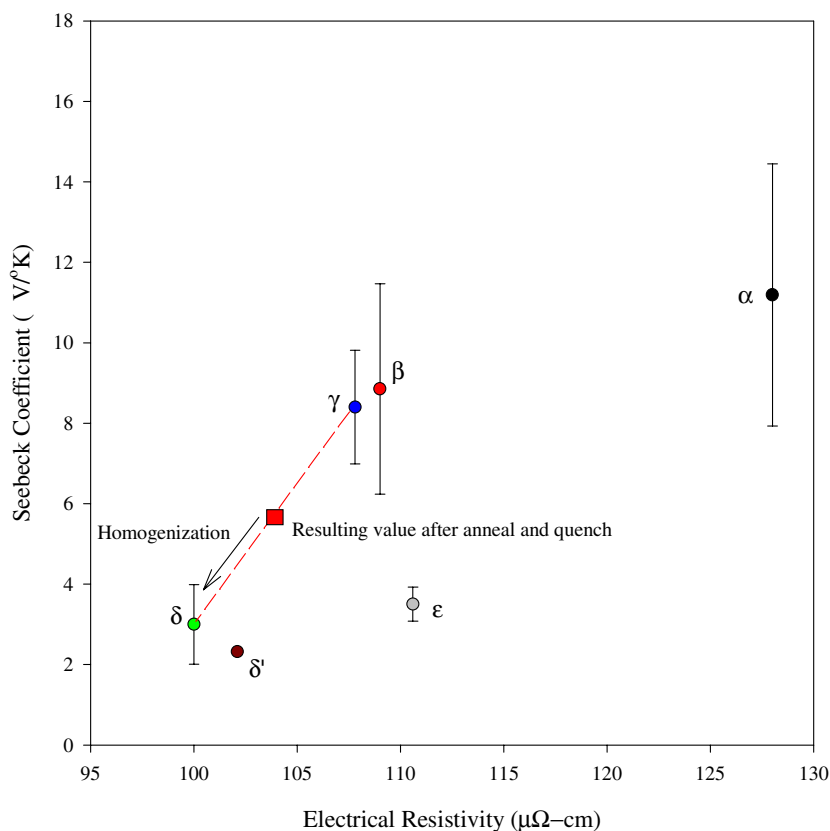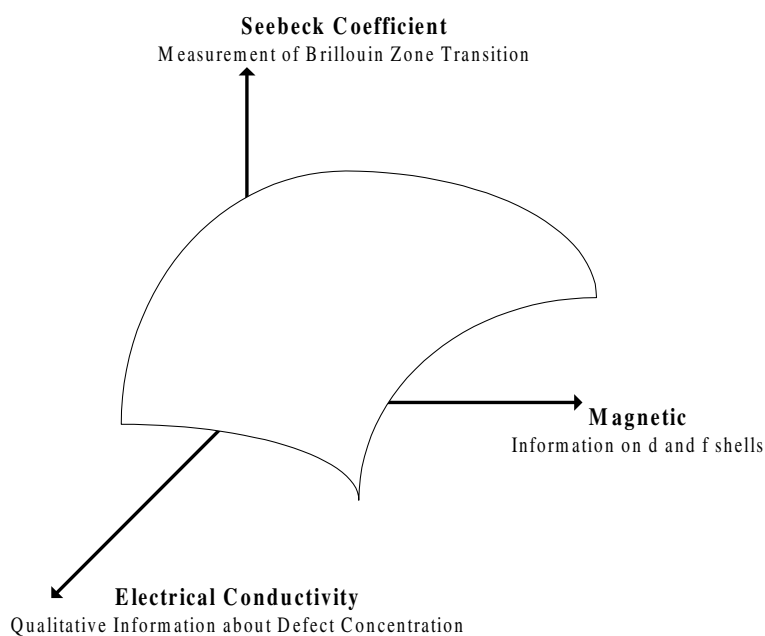

Figure 14. For example, if the resulting Seebeck coefficient and electrical resistivity values from a processing step are designated by red square, then upon homogenization the parameter values will eventually result in that of delta plutonium.

Pressure of the system can have a dramatic effect on the measured thermoelectric power, due to changes in phase structural parameters. In the case of elemental plutonium, the delta phase is very sensitive to the amount of pressure applied to the sample, as seen in figure 13 [37]. An increase in the pressure causes changes in the Brillouin zone size and electron concentration, resulting in electronic state filling where other plutonium phases with lower electronic energies become more energetically favourable, therefore causing a phase change in elemental plutonium from delta phase to either epsilon or gamma phase.

Radiation effects can dramatically change the electronic properties of materials. Some of the most significant interactions between radiation and atoms are transmutation of atoms, ionization of electrons, fission of atoms, production of thermal spikes, creation of interstitial atoms and vacancies and ordering or disordering of the atoms caused by recoil interactions. The result is structural changes, which influence the electron concentration and the Brillouin zone dimensions.

Therefore, depending upon the condition of the lattice after this type of interaction, the electronic properties could have been altered, which can affect the value of the Seebeck

Seebeck Coefficient
Measurement of Brillouin Zone Transition

Magnetic
Information on d and f shells

Electrical Conductivity
Qualitative Information about Defect Concentration

Figure 15. Zone designating a stable phase region according to these properties.

coefficient. With the resulting electronic changes occurring in the plutonium alloys during service, the use of electronic measurements should be able to correlate to structurally dependent properties, thus allowing assessment of ageing, homogenization and phase changes.

4.4. Multi-measurement analysis

The age of an unknown sample of plutonium can be determined by utilizing numerical data from electronic property measurements, such as the Seebeck coefficient and electrical resistivity. By experimentally obtaining electronic property data, the cost and difficulty of dealing with plutonium is greatly reduced. Using figure 14 as an example, the age of a plutonium sample can roughly be determined. The most relevant data points are those data for alpha and delta plutonium. If the Seebeck coefficient and electrical resistivity are low, then the sample is most likely delta-phase plutonium. For alpha-phase plutonium to be present, the Seebeck coefficient and the electrical resistivity must be relatively high. The error bars shown for the Seebeck coefficient do not represent the error in the measurement. They represent the difference in the Seebeck coefficient as a function of temperature. The data point is the average for each phase and the error bar is the minimum and maximum.

The practical use of figure 14 is as follows. If the resulting Seebeck coefficient and electrical resistivity values from a processing step are designated by the red square, then upon homogenization the parameter values will eventually result in that of delta plutonium. If after the homogenization treatment, the measured value of the Seebeck coefficient and electrical resistivity is not the value for delta plutonium, then one knows, without destroying the sample, that more heat treating is necessary.

Ultimately, expanding figure 14 into what is shown in figure 15 is needed. The additional axis will have magnetic property data associated with it. Considering Engel–Brewer theory

correlations of electronic hybrid states that specify crystal structure, the use of magnetic measurements can predict specific phase information because magnetic measurements give information about the d and f band filling. Then a region can be formed which designates an acceptable range of values.

The most beneficial aspect of utilizing electronic properties is to evaluate the quality of a material. If the time zero data and the allowed variance of that data are known, then the evaluation of the aged material can easily be performed. If the aged material property value falls outside the allowed variance, then the material would be taken out of commission. This concept is shown in figure 16. In this illustration, the value of the Seebeck coefficient and the electrical resistivity after some time falls outside of the allowed variance.
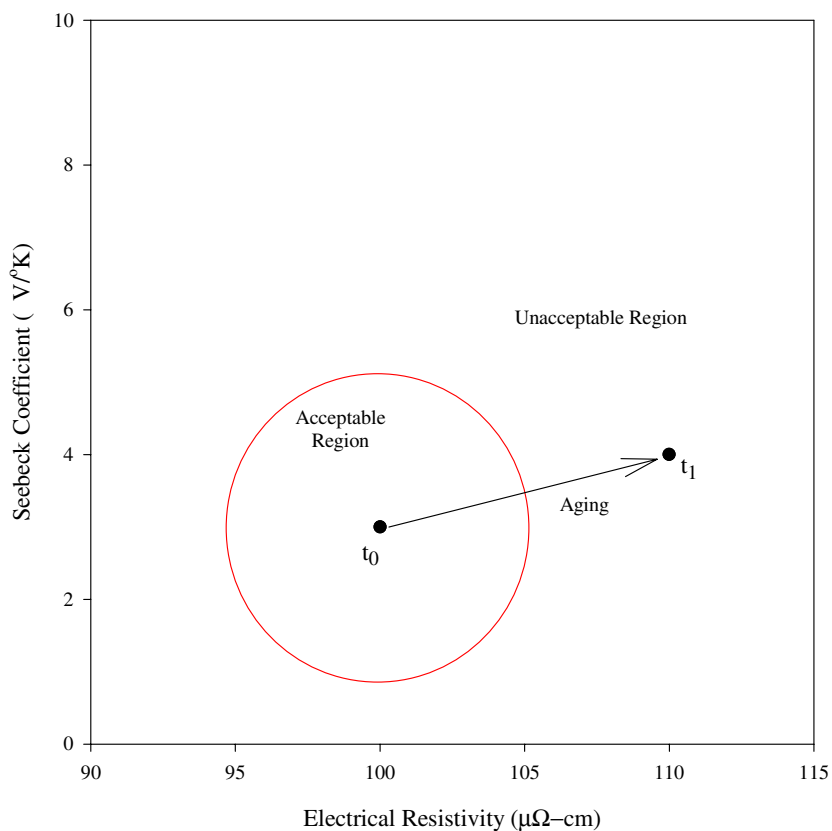
Figure 16. An arbitrary acceptable region is chosen and if the aged sample falls outside this region then the material is unsatisfactory relative to the Seebeck coefficient and the electrical resistivity.

5. Summary

After reviewing the electronic-based alloying models, it is apparent that electronic and magnetic measurements can offer insight into the degree of alloy phase stability (or ageing) of plutonium–gallium alloys. Also, the early electronic theories show that the phase of plutonium is dependent upon its electronic structure. The role of electrons in determining the phase stability has been demonstrated through the calculation of a plutonium–gallium phase diagram based on

the electron theory and thermodynamic relationships of the electron. Finally, the use of electronic property measurements was shown to be useful in observing differences in the alloying concentration, which reinforces the idea that electronic properties can determine the age of the material. Measurements have been initiated on surrogate material to demonstrate our philosophy.

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