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The Anomalous Thermal Expansion, Specific Heat, Magnetic Susceptibility and Band Structure of Delta Plutonium *

by

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Abstract

A rigid, multiple band model, some features of which were suggested by the calculated eigenvalue of the plutonium atom, was assumed for delta plutonium. By finding conditions under which the model accounts for various properties of the metal, some details of the band structure were determined. The outstanding feature is the small breadth of the $5f_{5/2}^2$ band, around 0.4 eV. The system consisting of this narrow band superimposed upon a much broader 6d band accounts for the negative expansion coefficient as well as for its dependence upon electron concentration as alterable by alloying, the most satisfactory agreement occurring for a 5f-band population of no more than four or five electrons per atom. The contraction is the result of atomic size reduction due to the loss of 5f electrons, as proposed by Zachariasen. The high electronic specific heat (3 cal/mole-°K) and the large magnetic susceptibility, assumed to consist entirely of spin paramagnetic and diamagnetic terms, are also accounted for by the model.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

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THE BAND STRUCTURE, SPECIFIC HEAT, MAGNETIC
SUSCEPTIBILITY, AND ANOMALOUS THERMAL EXPANSION OF DELTA PLUTONIUM*

By

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A rigid, multiple band model, some features of which were suggested by the calculated eigenvalues of the plutonium atom, was assumed for delta plutonium. By finding conditions under which the model accounts for various properties of the metal, some details of the band structure were determined. The outstanding feature is the small breadth of the $5f_2$ band, around 0.4 eV. The system consisting of this narrow band superimposed upon a much broader 6d band accounts for the negative expansion coefficient as well as for its dependence upon electron concentration as alterable by alloying, the most satisfactory agreement occurring for a 5f-band population of around four or five electrons per atom. The contraction is the result of atomic size reduction due to the loss of 5f electrons, as proposed by Zachariasen. The high electronic specific heat (3 cal/mole-°K) and the large magnetic susceptibility, the latter assumed to consist entirely of spin paramagnetic and diamagnetic terms, are also accounted for by the model.

1. Introduction

1.1 Very little quantitative treatment of the band structure of the metals in the 5f series of elements exists. So far only treatments of gamma uranium have appeared. Ridley⁽¹⁾ computed the lowest levels of the various

*Work performed under the auspices of the U. S. Atomic Energy Commission.

bands by the Wigner-Seitz method. Then, by forcing the wave functions to vanish at the Wigner-Seitz radius, she obtained the upper limits of exaggerated energy ranges for each state. A similar computation for copper gave ranges that were about three times greater than the energy bands obtained by Howarth⁽²⁾ via the cellular method. Application of the same factor of three to the results for uranium gives 0.6 to 1.2 eV for the width of the 5f band, depending upon the electron configuration, and about 6.0 eV for that of the 6d band. The very broad 7s band lies too high in energy to be at all occupied. Lehman,⁽³⁾ using a statistically derived potential for which the Dirac equation was numerically solved, has estimated the bands to be about 20 per cent larger than Ridley found; the 7s band in his work is also too high in energy to be occupied. In addition, Lehman⁽⁴⁾ has indicated the spin-orbit splitting to be of the order of the 5f-band width, so that it cannot be treated as a small perturbation.

1.2. Lee and Hall suggested that a similar picture might apply to plutonium metal, but that, since the 5f charge distribution contracts with increasing atomic number, the respective band should be narrower than in uranium.⁽⁵⁾ The small breadth of the 5f band indicated for uranium and the fact that curium, which lies only two steps beyond plutonium, acts chemically as a typical rare-earth element, suggests that plutonium and its immediate neighbors reside in a twilight region between the transition metals on one hand, and the rare-earth metals on the other.*

* Two independent treatments of the band structure of delta plutonium appear in a paper presented at this conference, "Electronic Band Structures of Plutonium and its Monocarbide" by E. A. Kmetko and J. T. Waber.

1.3. Delta plutonium, one of six allotropes, crystallizes in the F.C.C. form. It is stable, when pure, only between 592 and 724°K. This phase can be stabilized over a much greater temperature range by alloying with comparatively small amounts of aluminum or cerium, among several other elements.⁽⁶⁾ An alloy containing 2.5 at.-% aluminum, for example, is stable in the delta form between 0 and 900°K. Recently americium was added to the list of delta retainers.⁽⁷⁾ All of the solute atoms having smaller valencies than plutonium act to reduce its electron concentration. On the other hand, uranium⁽⁶⁾ and neptunium,⁽⁸⁾ both of which exhibit higher valencies than does plutonium, diminish the stability range of the delta phase.

1.4. Perhaps the most striking feature of delta plutonium, also characteristic of the neighboring delta-prime phase, is a negative thermal expansion coefficient. For nominally pure delta it is $-8.6 \times 10^{-6}/^{\circ}\text{C}$ as reported by Ellinger.⁽⁹⁾ That for delta prime appears to be several times larger, though considerable uncertainty arises because of the narrowness of the stability range, which lies between 724 and 753°K.⁽¹⁰⁾ The same elements which stabilize delta also cause its thermal expansion coefficient to increase algebraically. Concentrations of aluminum greater than about 3 at.-%, for example, cause the coefficient to become positive over the original stability range.⁽¹¹⁾ The large effects of relatively small amounts of solute upon the thermal expansion and the stability range of delta plutonium suggest that these effects have an electronic origin.

1.5. Negative expansion coefficients have been reported for several rare-earth metals. These anomalies occur in the neighborhood of Curie and Néel points, however, and are, therefore, probably associated with magnetic transitions, as proposed by Zener⁽¹²⁾ and Chandrasekhar.⁽¹³⁾ The delta and delta-prime phases so far have not been found to exhibit

any magnetic anomalies; their temperature ranges of stability are, after all, rather high. Consequently, it is improbable that the anomalous thermal expansion has anything to do with magnetic transitions.

1.6. According to Varley⁽¹⁴⁾ the entropy of an electron gas S_e can decrease with increasing volume if both the density of states $g(E)$ and its rate of change with energy dg/dE are sufficiently great at the Fermi level. This, of course, means that the electron gas pressure must have a negative temperature dependence. The volume thermal expansion coefficient α_v , compressibility χ , and $(\partial S/\partial V)_T$ are related as follows:

$$\alpha_v/\chi = (\partial S/\partial V)_T = (\partial S_L/\partial V)_T + (\partial S_e/\partial V)_T \quad (1)$$

where the subscript L denotes the lattice component. The thermal expansion can be negative, therefore, if the second term on the extreme right is the larger. Lee and Hall rejected Varley's proposal of this as the mechanism responsible for the existence of a negative thermal expansion coefficient in delta plutonium, however.⁽⁵⁾ Their argument was that the thermoelectric power, which according to the simple theory⁽¹⁵⁾ is proportional to dg/dE , is not large enough. There is some question, however, as to the applicability of this relationship to the present case.⁽¹⁶⁾

1.7. Zachariasen cautiously suggested a completely independent explanation of the negative thermal expansion coefficient.⁽¹⁷⁾ His analysis of the dependence of atomic radii upon electronic configuration for various series of elements indicates that in delta and delta-prime plutonium the 5f bands contain more electrons than they do in the other phases. Furthermore, he concludes that the number decreases by approximately 0.1 electron/atom as the temperature increases from 320 to 473°C, a range which encompasses all of the delta and delta-prime stability ranges. Thus, the atoms shrink as the temperature increases,

the result possibly being an overall contraction of the crystal. He did not attempt to clarify the mechanism by which the loss of 5f electrons occurs. Other proposed mechanisms are described by Lord in a review article on plutonium.⁽¹⁸⁾

1.8. The electronic specific heats of all the plutonium phases above room temperature are large.⁽¹⁹⁾ For delta it is 3.0 cal/mole-deg and is very nearly temperature independent.

1.9. All of the phases of plutonium are paramagnetic. The susceptibility of pure delta is 520×10^{-6} emu/mole at the bottom of the stability range and decreases very slightly with increasing temperature.⁽²⁰⁾ It is somewhat higher and has a more pronounced negative temperature dependence in a 3.5 at.-% aluminum alloy in the temperature range 20-300°K.⁽²¹⁾

(These results are shown in Fig. 8, discussed below). So far, there is no information indicative of either ferromagnetic or antiferromagnetic ordering in delta plutonium. The total susceptibility, therefore, seems to be largely the sum of the Pauli spin paramagnetic and diamagnetic types.

1.10. In the present work a simple, rigid, electronic band model is assumed for delta plutonium. A simplification to merely two bands follows mainly from the very sizable spin-orbit splitting of the 5f levels calculated for the plutonium atom.⁽²²⁾ A rather narrow $5f_{5/2}$ band rests upon a comparatively broad 6d band which has a relatively low density of states, the Fermi level at 0°K lying in the vicinity of the narrower band. Smoluchowski has discussed the anomalous temperature dependence of the electrical resistivity of plutonium metal in terms of a similar model.⁽²³⁾ Should the Fermi level at 0°K lie above the middle of the narrower band, it must rise with increasing temperature; the population of the narrower band, therefore, decreases. The rate at which the electron loss occurs depends upon electron concentration,

being a maximum, at lower temperatures, when the narrow band is just fully occupied at absolute zero. A mechanism is thus supplied which accounts for the diminution in the 5f electron concentration observed in Zachariasen's work. In addition, it provides a means of explaining the effects of alloying upon the thermal expansion.

1.11. The electronic specific heat and the interband electron transfer rate both depend upon the widths of the individual bands. Thus, by determining band widths for which these properties, as calculated from the model, are in accord with experiment, some knowledge of the band structure is obtained. The 6d band is very broad in units of the thermal energy kT , so that only the average density of state in the vicinity of the Fermi level is provided. However, where the band width and kT are comparable, as would be the case for the 5f band of delta plutonium were its width of the order of 0.1 eV, it is possible to obtain an estimate of the width. As it turns out the physical properties also depend to a marked degree upon the number of electrons in the 5f band at 0°K. This introduces some arbitrariness into the matter of determining the band width, which can be reduced, however, by considering the estimated valency, temperature dependence of the specific heat, and effects of alloying upon the thermal expansion coefficient.

2. Band Model

2.1. Self-consistent solutions of the Dirac equation, for which exchange was included by a variation of Slater's $\rho^{1/3}$ correction scheme, have been obtained by Waber, Liberman and Cromer.⁽²²⁾ In addition to the boundary condition for the free atom, Wigner-Seitz boundary conditions corresponding to the various crystalline forms of the metal were imposed upon the solutions. The $5f_{7/2}^1$ state lies about 1.2 eV above the $5f_{5/2}^5$ state. This spin-orbit splitting depends only slightly upon the electron configuration and the extent to which the atom is "compressed".

2.2. As mentioned earlier, Ridley's result for the band structure of gamma uranium implies that the 5f band in plutonium metal could have a breadth of the order of 0.1 eV, in the absence of spin-orbit splitting. Thus, if the center-to-center distance of the sub-bands corresponding to $j = \frac{5}{2}$ and $j = \frac{7}{2}$ is larger than about an electron-volt, the bands will not interact appreciably even at temperatures in the delta range. According to Zachariasen's work⁽¹⁷⁾ there is little likelihood that the 5f band in the metal could have more than 5 or 6 electrons per atom. We can ignore, therefore, the upper sub-band and consider only the $5f_{\frac{5}{2}}$ sub-band which contains 6 states per atom. It is hereinafter called simply the f band, unless specified otherwise.

2.3. An important result of this study is that for the likely range of the f band width the band shape is immaterial at temperatures above about room temperature. This is of particular importance inasmuch as each sub-band is split, by interactions between wave functions of various symmetry types, into lesser sub-bands, thus complicating the shape. A symmetric parabolic f band was used throughout most of this work, however. Its state density $g(E)$ is given below:

$$\text{For the upper half: } g(E) = C(E_2 - E)^{1/2} \quad (2-a)$$

$$\text{For the lower half: } g(E) = C(E - E_1)^{1/2} \quad (2-b)$$

$$\text{where } C = 0.75 \times N \times [2/(E_2 - E_1)]^{3/2} \quad \text{and} \quad (2-c)$$

E is the energy in electron-volts. E_1 and E_2 are the lower and upper f band edges, respectively. N is the number of states in the f band, taking spin degeneracy into account.

2.4. Not only is spin-orbit splitting in the 6d band ignored, but the density of states in that band is taken to be constant. This is tantamount to having the density of states in the actual band change negligibly over the width of the f band plus several kT on either side. The average density of states in the 7s band is much smaller than in

the 6d band (hereinafter referred to as the d band), and thus was completely ignored. Furthermore, it probably lies far above the other bands, as it did in Ridley's results.

3. Computation

3.1. A program was written in the FORTRAN II language for a band system which is more general than the one described above. The more general system accommodates up to 26 bands, each having as many states as desired. The shape of a band may be specified as rectangular, symmetrical linear, or symmetrical parabolic. An arbitrary number of rectangular bands may be combined to give a stepwise approximation to any desired band structure.

3.2. The program provides: 1) the electronic specific heat C_v^e , 2) the interband electronic transfer rate R , and 3) the height of the Fermi level, all as functions of temperature T and the Fermi level height at 0°K ζ_j^0 . To accomplish this, the following integrals are evaluated and tabulated as part of the program:

$$N(0, \zeta_j^0) = \sum_i \int_{E_{l_i}}^{\zeta_j^0} g_i(E) dE \quad (3-a)$$

$$N(T_l, \zeta'_k(T)) = \sum_i \int_{E_{l_i}}^{E_{u_i}} g_i(E) f(E, \zeta'_k(T)) dE \quad (3-b)$$

$$U(T_l, \zeta_j(T)) = \sum_i \int_{E_{l_i}}^{E_{u_i}} g_i(E) E f(E, \zeta_j(T)) dE \quad (3-c)$$

where N is the total number of electrons in all bands; U is the internal energy; g_i , E_{l_i} and E_{u_i} are the density of states, the lower and upper limits of the i th band, respectively. $\zeta'_k(T_l)$ is the value of the Fermi level used in constructing the tables of values $N(T_l, \zeta'_k(T_l))$. $f(E, \zeta_j(T_l))$ is the Fermi-Dirac distribution function. The integrations are performed numerically, by means of an adaptive Simpson's rule subroutine, or by

evaluating an appropriate analytic function, whichever method is required for the particular case. For a given ζ_j^0 and $N(0, \zeta_j^0)$, $\zeta_j(T_l)$ is found by an Aitken polynomial interpolation subroutine, using the table for $N(T, \zeta_k(T_l))$ and $\zeta_k(T_l)$ under the condition that $N(0, \zeta_j^0)$ must equal $N(T_l, \zeta_j(T_l))$. The values of $\zeta_j(T)$ thus obtained are then inserted into expression (3-c) for the evaluation of the internal energy. The rate of interband electron transfer, R , is found by using a table $N_i(T_l, \zeta(T_l))$ which gives the population of the i th band at temperature T_l . The specific heat is derived similarly from the table $U(T_l, \zeta_j(T_l))$.

3.3. The energy of an electron with magnetic moment $\pm \beta$ in a magnetic field, H , is $\pm \beta H$. The Pauli spin susceptibility χ_p of an electron gas associated with a mole of atoms is, therefore:

$$\chi_p = \frac{1}{2} L \beta / H \sum_i \left[\int_{E_{l_1} - \beta H}^{E_{2_1} - \beta H} g_1(E, E_{l_1} - \beta H, E_{2_1} - \beta H) f(\zeta, E - \beta H) dE \right. \\ \left. - \int_{E_{l_1} + \beta H}^{E_{2_1} + \beta H} g_1(E, E_{l_1} + \beta H, E_{2_1} + \beta H) f(\zeta, E + \beta H) dE \right] \quad (4)$$

where L is Avogadro's number, and the density of states is, as before, given on a per atom basis. ζ in the above expression is dependent upon H as well as upon T and ζ_j^0 as above. It is obtained in a manner similar to that already described except that

$$N(0, \zeta_j^0) \rightarrow N(0, \zeta_j^0, H) = \frac{1}{2} \sum_j \left[\int_{E_{l_1} - \beta H}^{\zeta_j^0} g_1(E, E_{l_1} - \beta H, E_{2_1} - \beta H) dE \right. \\ \left. + \int_{E_{l_1} + \beta H}^{\zeta_j^0} g_1(E, E_{l_1} + \beta H, E_{2_1} + \beta H) dE \right] \quad (5-a)$$

and

$$N(T, \zeta_k') \rightarrow N(T, \zeta_k', H) = \frac{1}{2} \sum_1 \left[\int_{E_{1-} - \beta H}^{E_{1+} - \beta H} g_1(E, E_{1-} - \beta H, E_{1+} - \beta H) f(\zeta_k', E - \beta H) dE \right. \\ \left. + \int_{E_{1-} + \beta H}^{E_{1+} + \beta H} g_1(E, E_{1-} + \beta H, E_{1+} + \beta H) f(\zeta_k', E + \beta H) dE \right] \quad (5-b)$$

The parametric arguments in the g_1 denote the shifts which H causes in the limits of the two spin bands.

3.4. The diamagnetic contribution to the susceptibility of a crystal usually consists of two parts. One is associated with the bound electrons in the ion, while the other, the Landau diamagnetism, is due to the conduction electrons. However, where the effective masses of the current carriers are large, as they very probably are for plutonium metal, the Landau term reduces to that for bound electrons.⁽²⁴⁾ The diamagnetic moment of an electron in a particular state is proportional to ρ^2 , the average of the square of the perpendicular distance of the electron from the field axis. Using Hartree wave-functions Waber and Boyd⁽²⁵⁾ have computed the matrix elements of ρ^2 for the free plutonium atom having the configuration $(5f)^6(7s)^2$. The totality of such matrix elements yields a molar susceptibility of -72×10^{-6} emu. The total magnetic susceptibility obtained in this work consists simply of the Pauli and diamagnetic terms obtained as described above.

4. Results and Discussion

4.1. Specific Heat. Fig. 1 illustrates the dependence of the electronic specific heat C_v^e upon temperature and electron concentration for the case where the parabolic f band and the rectangular d band, respectively, are 0.1 and 2.5 eV wide. The maximum occurring at $\sim 120^\circ K$ grows more pronounced as ζ_0 descends toward the middle of the f bands. As the f band broadens the maximum shifts toward higher temperatures all the while becoming broader. When the f band is

~ 0.3 eV wide the maximum becomes only a vestige giving rise to a plateau-like region.

4.2. The existence and behavior of the maximum are associated with the entropy S which is related to the specific heat at constant volume C_v in the following manner:

$$C_v = T (\partial S / \partial T)_V \quad (6)$$

For an isolated band of states both S and the derivative, at any temperature, are largest when the band is just half occupied by electrons but approach zero as the band becomes either full or empty. Furthermore, the entropy reaches a specific maximum value proportional to the average density of states for any degree of occupancy as the temperature increases without bound so that C_v tends asymptotically to zero. The behavior is modified by the presence of available states outside the band, such as those in the d band, so that instead of falling to zero the specific heat reaches a minimum and steadily rises thereafter. For a very narrow band, therefore, the specific heat at low temperatures can exhibit a peak which resembles the Schottky anomaly.

4.3. The specific heat is linear to only about 60°K when the f band is 0.2 eV wide. The extent of the linear range is about proportional to the band width. Consequently, in substances wherein the Fermi level lies within a very narrow band, the customary analysis of the low-temperature specific heat into linear and cubic terms may not be valid over as wide a range as one would like.

4.4. Fig. 2 indicates how the electronic specific heat C_v^e in the delta range depends upon the f and d band widths when the f band is just fully occupied at 0°K. Fig. 3 corresponds to the case where the f band is only 82.3% occupied at 0°K. These figures show that C_v^e depends upon the widths of both bands. The temperature dependence is smaller as ζ^0 descends toward the center of the f band as a consequence of the change

in height and position of the peak. Approximate agreement between the experimental result and the predictions of the two-band model is provided under a rather broad range of conditions as the figures show. It is thus impossible to specify the widths solely on the basis of agreement between the experimental and calculated specific heats.

4.5. Interband Electron Transfer. Figs. 4 and 5 show the dependence of the interband electron transfer rate R upon ζ^0 and temperature for parabolic and rectangular f bands having the same widths as in Figs. 2 and 3. At lower temperatures, the maximum rate occurs when ζ^0 lies at, or close to, the upper edge of the f band. Similar behavior, except for the sign of R , is found when ζ^0 roams through the lower half of the band. The range of ζ^0 in the figure is too restricted to show the maxima at high temperatures. As ζ^0 moves below the band edge, the interband transfer rate decreases. This is consistent with the observed effects of alloying upon the thermal expansion coefficient of delta plutonium when the solutes reduce the electron concentration.

4.6. The dependence of R upon the breadths of the f and d bands for the delta stability range is given in Fig. 6 for the case where the f band is 100 per cent occupied at 0°K . The curves in Fig. 7 correspond to the case where the f band at 0°K is 82.3 per cent occupied.

4.7. The expansion coefficient of delta plutonium is expressible as the sum of (1) a negative term which reflects the radial contraction of the atoms, (2) a lattice expansion term and (3) an electronic term, the latter two being given by Eq. (1). In spite of the large electronic heat of delta plutonium the electronic term is probably not more than a sixth as large as the lattice term. The absolute magnitude of the negative term must exceed that of the sum of the other terms by an amount numerically equal to the observed expansion coefficient.

4.8. The lattice expansion coefficient probably has a value in the neighborhood of $30 \times 10^{-6}/^{\circ}\text{K}$ (this will be justified below). Therefore, since the metallic radius of the plutonium atom decreases by $\sim 0.020\text{\AA}$ for each electron vacating the 5f band, the electrons must depart from that band at a rate of $\sim 30 \times 10^{-5}/\text{atom-deg K}$ in order to account for the observed negative expansion coefficient.

4.9. The curves presented in Figs. 6 and 7 show that a transfer rate of this general magnitude is realizable over a rather broad range of values for the width of the f band inasmuch as it depends upon the f band population as well as upon the density of states in the d band.

4.10. Because the specific heat of delta plutonium is approximately independent of temperature,⁽¹⁹⁾ the f band, in the model assumed, cannot be fully occupied, otherwise the total specific heat would increase by ~ 10 per cent over the delta range. Furthermore, this implies that the atoms would have a valence of only ~ 2 , which is unlikely. The accord between the experimental and calculated specific heats, consistent with the required value for R, is most favorable when the f band is between ~ 70 and 85 per cent occupied at 0°K . The lower boundary of this range is a consequence of R becoming smaller and ultimately changing sign as ζ^0 descends below the midpoint of the band. Thus, if the two-band model corresponds to delta plutonium, there are between 4 and 5 electrons in a $5f_{\frac{5}{2}}$ band which cannot be much wider than about 0.4 eV. Correspondingly, the density of states in the d band, in the vicinity of the $5f_{\frac{5}{2}}$ band, is approximately 4 states/atom-eV. Considerations to be described below indicate that the f band cannot be appreciably smaller than indicated above.

4.11. Thermal Expansion and Alloying Effects. The linear expansion coefficient for delta plutonium and its alloys may be expressed as:

$$\alpha = A + XB \quad (7)$$

where A is the expansion coefficient given by Eq. 1, and is described in

section 1 (the lattice expansion is the major component of this term). B is the negative term associated with the shrinkage of the atoms and refers to the pure metal. X is the relative rate of interband electron transfer with respect to the unalloyed metal. As Fig. 5 shows, for each per cent change in f band population, X will decrease by about 2 per cent when the band is 100 per cent occupied. When it is 75 per cent occupied, however, X decreases by about 6 per cent for each percentage change in band population.

4.12. Gschneidner et al ⁽²⁶⁾ determined the effects of solutes having various valencies upon the thermal expansion coefficient of delta-phase alloys in the range from ~ 300 to $\sim 440^\circ\text{C}$. Zinc and aluminum both cause the coefficient to vanish at the same concentration, 3 at.-%. This is somewhat surprising considering that these elements are typically divalent and trivalent, respectively. For cerium, with an assigned valency of 3.64, ⁽²⁷⁾ and zirconium, which is commonly tetravalent, the corresponding concentrations are 6.0 and 9.5 at.-%, respectively. There appears to be an inconsistency in that, with the valencies assumed, the total electron concentration in the two bands is reduced by 2.25, 1.87, 3.27 and 4.75 per cent for the four elements in the order named. The change in electron concentration in each band is proportional to the density of states at the Fermi level. For the case pertaining to Fig. 5, where the f band is rectangular, very close to 90 per cent of the change in electron concentration occurs in the 5f band regardless of the occupancy. Where the f band is parabolic (see Fig. 4), the occupancy must be between 20 and 80 per cent for a correspondingly large percentage change to occur in that band. When the changes in electron concentration for the various solutes as listed above in conjunction with the results presented in Fig. 5 are used, Eq. (7) gives -40×10^{-6} to -71×10^{-6} for the range of the contraction term B. This is in substantial agreement with the range

of values obtained for B from the values for R shown in the same figure. The corresponding range for the lattice thermal expansion coefficient differs from the above in magnitude by the amount of the observed thermal expansion coefficient of the unalloyed metal. It is $+ 31 \times 10^{-6}$ to $+ 62 \times 10^{-6}/^{\circ}\text{C}$.

4.13. The lattice expansion coefficient can be estimated by using Grueneisen's law. For rare-earth metals, the Grueneisen constant, γ , lies between 0.50, for cerium, and 2.26 for europium, the average being very nearly unity.⁽²⁸⁾ This, together with values for the compressibility of delta alloys^{(29),(30)} indicate, therefore, that the lattice expansion coefficient can be between 10×10^{-6} and $50 \times 10^{-6}/^{\circ}\text{C}$. Quite likely the electronic character of A amounts to less than 20 per cent. Inasmuch as the sum of A and B must equal $-8.6 \times 10^{-6}/^{\circ}\text{C}$, the results are in good agreement with those obtained from the alloying behavior. The values of A and B obtained above by the various means are summarized in Table I.

4.14. The lattice thermal expansion coefficient for a soft metal such as delta plutonium should probably compare with those of lead and tin. A likely value for the coefficient A would then lie between 25×10^{-6} and $50 \times 10^{-6}/^{\circ}\text{C}$. Thus the two-band model appears to be not unsuccessful in providing a rather plausible estimate of the experimentally indeterminate lattice expansion coefficient for delta plutonium. It is tempting to compare the coefficient thus obtained with those of the alpha, beta and gamma phases of plutonium which are 55×10^{-6} , 38×10^{-6} and $34 \times 10^{-6}/^{\circ}\text{C}$, respectively. However, it seems likely that the electron populations in the 5f levels of these phases also depend upon temperature. Thus the actual lattice expansion coefficients would be obscured as it is in the case of delta plutonium. The very large value of the coefficient for the alpha phase suggests that the f band is less

than half occupied so that electrons enter it as the temperature rises.

4.15. Curves showing the lattice constant vs temperature for delta alloys are concave downward,⁽¹¹⁾ indicating that the contraction term B grows larger as the temperature rises. According to the two-band model this cannot happen unless the f band is greater than 0.2 eV wide. For bands smaller than this the interband transfer rate R, and hence also B, clearly decreases above 400°K for all values of ζ^0 inside the upper half of the f band. Fig. 4, corresponding to the parabolic f band, shows that R rises with temperature as long as the band is not more than about 90 per cent occupied at 0°K. This behavior is also clearly indicated by the curves in Figs. 6 and 7. Thus, the allowable range for the breadth of the 5f band lies between about 0.2 and 0.4 eV if the two-band model is to account for the negative thermal expansion coefficient and for its dependence on alloying.

4.16. According to Eq. (1), the term A must vanish as the temperature goes to absolute zero. The term B, however, depending as it does upon the interband electron transfer rate and temperature, not upon the specific heat as does A, will change with temperature in a different manner. The Debye temperature for an 8 at.-% aluminum-plutonium alloy is reported as 138°K.⁽³¹⁾ Below this temperature, A must fall rather steeply as the temperature drops in a manner more or less independent of the composition. On the other hand, the value of B can remain quite high down to rather low temperatures, the actual behavior being strongly composition dependent. Thus the thermal expansion coefficient, which is the sum of these two differently varying terms, can become anomalous at lower temperatures. Solente⁽³²⁾ has observed anomalies in the dependence of the lattice constant upon temperature for two stable delta alloys. For the alloy containing 5 at.-% aluminum a plateau occurs between approximately 50 and 150°K. The plateau appears to have degenerated

into merely an inflection point at around 150°K in the alloy containing 8 at.-% aluminum. These anomalies are in qualitative agreement with the behavior predicted by the two-band model. The plateau observed for the 5 at.-% alloy implies the existence of a slightly lower, but overlapping, temperature range in which the expansion coefficient is negative in alloys containing less than 5 at.-% of the solute. It is unwise to attempt more than a qualitative account at this time inasmuch as the quantities C_v^e and R depend directly upon the density of states in the very low temperature range, and the present work is incapable of elucidating the actual band shape. The curves for R vs T and ζ^0 for a parabolic band differ markedly from those for a rectangular band at lower temperatures.

4.17. Magnetic Susceptibility. The sum of the Pauli paramagnetic susceptibility and the diamagnetic susceptibility as it depends upon temperature and electron concentration, computed as indicated earlier, appears in Fig. 8. Available experimental results are presented in the same figure. The curve at high temperatures corresponds to nominally pure delta plutonium,⁽²⁰⁾ while the three points at approximately 20, 80, and 300°K are for a 3.5 at.-% aluminum alloy.⁽²¹⁾

4.18. As ζ^0 passes through the upper 5f-band edge, the temperature dependence changes sign. The negative dependence of the alloy, therefore, corresponds to an incomplete f band at 0°K. There is obviously a need for an extensive study of the susceptibility at low temperatures for a series of alloys having as broad a range of solute concentration as possible.

4.19. The agreement between the computed and experimental values of the susceptibility seems to be quite good. There are hardly any discernible differences at high temperatures, i.e., above ~ 300°K, among the results computed for the various shaped bands.

5. Conclusions

5.1. Some features of the delta-plutonium band structure were determined by finding the conditions under which the assumed two-band model could simultaneously account for the specific heat, magnetic susceptibility, and the negative thermal expansion coefficient and its dependence upon alloying. The most important feature is the breadth of the f band, roughly 0.4 eV. This is an order of magnitude narrower than the d bands in the transition metals but still much broader than the 4f levels in the rare earths. The peculiarities of the delta phase are attributable to the narrowness of this band and its interactions with other bands sharing the same energy range.

5.2. For the d band only the average density of states in the vicinity of the $5f_{\frac{5}{2}}$ band was determinable. The magnitude, 4 states/atom-eV, is consistent with what one would ordinarily expect for a d band heavily involved in the binding and transport properties of a crystal.^{(1),(2)}

5.3. Rather reasonable values for the coefficients associated with the lattice expansion and radial contraction of the atoms occur when the f band contains between 4 and 6 electrons at absolute zero. This is somewhat more than the 3.4 indicated by Zachariasen.⁽¹⁷⁾ It is, therefore, tempting to speculate on the shape of the charge distribution of the electrons associated with the 5f band. For, were the centers of the $5f_{\frac{5}{2}}$ and $5f_{\frac{7}{2}}$ sub-bands sufficiently far apart and were 6 electrons to populate the lower sub-band, then the squares of their wave functions in the unperturbed states would add up to give a spherical charge distribution. This is more or less a requirement for atoms of a F.C.C. crystal.

5.4. The complete rigidity of the band system is doubtful, of course. When the electrons are redistributed among bands whose associated charge distributions grossly differ, as they most certainly do for 5f and 6d

electrons, the bands would be expected to move relative to each other, in order to accommodate the changing potential. As electrons are moved from 5f into 6d states, however, the computed levels for the free atom move downward with some relative shift.⁽²²⁾ The comparatively large thermally induced change in relative band populations suggests that band instability causes the many phase changes in plutonium metal. However, alloying that can considerably reduce the 5f band population stabilizes the delta phase. This may be indicative of a rigid band system in delta plutonium. Phase changes and stabilization in plutonium appear to be related to the rather large electronic free energy and the way it depends upon temperature and electron concentration.⁽³³⁾

5.5 At high temperatures the behavior of the specific heat, magnetic susceptibility and interband electron transfer rate are remarkably independent of the shape of the $5f_{5/2}^2$ band. At low temperatures, however, the properties are strongly dependent upon the shape. It is not possible to resolve the structural details of a band whose breadth is of the same order of magnitude as the thermal energy, any more than it is possible to use a large broom to paint meaningful detail upon a small canvas. The further elucidation of the band structure of delta plutonium awaits experimental studies of various properties, for example the low-temperature magnetic susceptibility of a broad spectrum of stable delta alloys.

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Table I. The positive thermal expansion term (involving the lattice expansion and an electronic term) and the negative term reflecting the radial shrinkage of the atoms (obtained by various means).

Method	$A \times 10^6$	$B \times 10^6$
From interband transfer rate, R, for 82% occupancy	--	-30 to -50
From alloying behavior, i.e., the change in R vs electron concentration for 80% occupancy	+31 to +62	-40 to -71
From Grueneisen's law $A = 1.19 \times$ lattice expansion coefficient	+12 to +60	--

CAP TIONS

- Fig. 1. Specific heat vs temperature for a two-band model consisting of a symmetric parabolic band containing 6 states 0.1 eV wide centered at 0.375 eV superimposed upon a rectangular band containing 10 states and extending from 0.0 to 2.5 eV. The Fermi level at 0°K is indicated for each curve.
- Fig. 2. Specific heat over the stability range of delta plutonium for a two-band system. The symmetric parabolic band with 6 states is centered at 0.375 eV; its width is indicated along the abscissa. The Fermi level at 0°K coincides with the top of this band. A rectangular band extends from 0.0 eV to the energies indicated parametrically adjacent to each shaded band. As Fig. 1 indicates, the temperature dependence within each band is approximately linear.
- Fig. 3. Specific heat over the stability range of delta plutonium for a two-band system. The symmetric parabolic band with 6 states is centered at 0.375 eV; its width is indicated along the abscissa. The band is 82.3 per cent occupied at 0°K. A rectangular band extends from 0.0 eV to the energies indicated parametrically adjacent to each shaded band. As Fig. 1 indicates, the temperature dependence within each band is approximately linear.
- Fig. 4. The interband electron transfer rate for a two-band system. The parabolic band containing 6 states is 0.3 eV wide; it rests upon a rectangular band having 10 states and extending from 0.0 to 2.5 eV. The Fermi level ζ° at 0°K is indicated parametrically. In the cases shown the electrons leave the narrower band inasmuch as ζ° lies above the center of that band.
- Fig. 5. The interband electron transfer rate for a two-band system. The rectangular band containing 6 states is 0.3 eV wide; it rests upon a rectangular band having 10 states and extending from 0.0 to 2.5 eV. The Fermi level ζ° at 0°K is indicated parametrically. In the cases shown the electrons leave the narrower band inasmuch as ζ° lies above the center of that band.
- Fig. 6. The interband electron transfer rate in the stability range of delta plutonium for a two-band system as it depends upon the width of the two bands. The width of the narrower parabolic band containing 6 states corresponds to the abscissa while that of the rectangular band with 10 states is indicated parametrically adjacent to each shaded band. The Fermi level at 0°K coincides with the top of the parabolic band.
- Fig. 7. The interband electron transfer rate in the stability range of delta plutonium for a two-band system as it depends upon the width of the two bands. The width of the narrower parabolic band containing 6 states corresponds to the abscissa while that of the rectangular band with 10 states is indicated parametrically adjacent to each shaded band. The parabolic band is 82.3 per cent occupied at 0°K.

Fig. 8. Sum of the Pauli spin paramagnetic susceptibility and diamagnetic susceptibility for a two-band model for delta plutonium. The width of the parabolic $5f_5^2$ band centered at 0.375 eV (6 states) is 0.3 eV while the 6d band extends from 0.0 to 2.5 eV. The dashed lines and points indicate experimental results so far published and referred to in the text.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8