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Conf-701001-2

UCRL - 72223

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Lawrence Radiation Laboratory
UNIVERSITY OF CALIFORNIA
LIVERMORE

MASTER

**THE DELTA AND EPSILON THERMAL EXPANSION COEFFICIENTS
AND THE DELTA-TO-EPSILON CONTRACTION FOR
SOME PLUTONIUM-RICH ALLOYS**

Alfred Goldberg
Robert L. Rose
David K. Matlock

June 17, 1970

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This paper was prepared for publication in the Proceedings of the
Fourth International Conference on Plutonium and Other Actinides, Santa Fe,
N. Mex., Oct. 5-9, 1970.

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THE DELTA AND EPSILON THERMAL EXPANSION COEFFICIENTS
AND THE DELTA-TO-EPSILON CONTRACTION FOR SOME
PLUTONIUM-RICH ALLOYS*

Alfred Goldberg and Robert L. Rose
Chemistry Department
University of California
Lawrence Radiation Laboratory
Livermore, California

David K. Matlock
Department of Materials Science
Stanford University
Stanford, California

Linear thermal expansion coefficients of the delta (δ) and epsilon (ϵ) phases and the $\delta \rightarrow \epsilon$ transition contraction were obtained by dilatometry for Pu and a series of Pu-Ga, Pu-Al, and Pu-Ce alloys. The expansion coefficients of the δ phase (α_δ) were plotted as a function of solute content and electron/atom concentration (e/a). The results are consistent with an electronic model that allows interband transitions to occur between the 5f band and the conduction band(s) during changes in both solute concentration and temperature. The expansion behavior of the ϵ phase (α_ϵ) for the different compositions was observed to be typical of many metals. The $\delta \rightarrow \epsilon$ contraction generally decreased with an increase in solute concentration. This was attributed to the relative extent to which the behavior of the δ and ϵ phases departed from that expected for a "normal" metal.

The correlations obtained for the Pu-Ga and Pu-Al series were similar in the three regions (δ , $\delta \rightarrow \epsilon$, and ϵ), but some variations from these results were obtained in the Pu-Ce series. Such differences are considered to be due to the effect of additional electronic interactions resulting from electronic transfer between Pu and Ce atoms. The similarity in behavior between data obtained from the Pu-Ga and the Pu-Al series is attributed in part to the similar valence behavior of the Ga and Al atoms.

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

Introduction

It is well recognized that the delta phase of plutonium and some of its dilute alloys exhibit a negative coefficient of expansion ($\bar{\alpha}_\delta$) over a wide temperature range. On alloying, the coefficient becomes less negative and changes to a positive value. Zachariassen(1) proposed a scheme whereby the distribution of electrons between the 5f and the 7s and 6d shells can be related to the atomic radius. On the basis of an anomalous radius of δ -Pu, he deduced values of the valence electron-to-atom concentrations (e/a) of 4.76 and 4.87 at 319 and 476°C, respectively. Using a mean value of 4.82 for e/a , Gschneidner et al.(2) attempted to correlate the average coefficient of expansion ($\bar{\alpha}_\delta$) over a temperature range generally from 300 to 440°C, for a number of solute elements — Al, Zn, Zr, In, and Ce. Although they show considerable scatter, the results can nevertheless be described by a linear relationship between $\bar{\alpha}_\delta$ and e/a , which led the authors to conclude that "the thermal expansion of delta plutonium alloys is strongly dependent upon electron concentration." A linear relationship between $\bar{\alpha}_\delta$ and e/a was also obtained by Taylor(3) for Ga additions to Pu. He used a value of 4.815 for e/a for Pu.

Gschneidner et al.(2) and Marples(4) discussed in some detail various electronic models that have been proposed to account for the negative values of $\bar{\alpha}_\delta$. In general, they consider the promotion of electrons from the 5f level to the 6d and 7s conduction bands as the temperature is raised, which results in a net contraction of the Pu atoms. According to Rocher and Friedel(5) such promotion is thermally activated and originates from the creation of electron defects (holes). The addition of solute increases the energy gap between the bands and thereby makes the thermal activation process more difficult. A different explanation, and probably one that is more generally accepted, is based on the high density of states and the rapid change in the density of states vs energy at the Fermi level in the 5f band. Overlapping of the 5f bands with the conduction bands permits promotion of electrons to the latter as the temperature is raised(1,2,4-7). The high specific heat obtained for the δ phase(8) supports the idea of the high density of states. To explain the above change from a negative to a positive coefficient of thermal expansion, the slope at the Fermi level must become less steep with alloying (for $e/a_{\text{alloy}} < e/a_{\text{Pu}}$) as the Fermi level is shifted with a change in e/a . Some modification in band configurations may also have taken place with alloying.

Zachariassen(1) indicated that the ϵ and γ phases of Pu exhibit a normal valence of 5, with the abnormal δ phase having a valence of less than 5. The ϵ phase of Pu has a relatively high coefficient of thermal expansion. Marples(4) reported values of $\bar{\alpha}_\epsilon$ as a function of Zr (valence 4) additions, which showed a decrease in the coefficient with an increase in Zr content. Thus, both the magnitude of the coefficient (for dilute additions) and the effect of alloying are apparently different for the δ (abnormal) and ϵ (normal) phases. However, Marples(4), in studying the effect of solute concentration on the lattice parameter of δ and ϵ phases for a large number of solute elements, noted that similar effects were observed for both δ and ϵ phases; and, in fact, the behavior obtained — deviation from Vegard's law — was opposite to that observed for the noble metals. He therefore suggested that the bonding in both δ and ϵ is not (entirely) metallic and that the positive deviation could perhaps be explained on the basis of a weakening in the (covalent) bonding due to a reduction in the e/a ratio. The lattice parameter results therefore suggest that both the δ and the ϵ phases behave abnormally.

The $\delta \rightarrow \epsilon$ transition for pure Pu is accompanied by a large contraction. On the basis of a hard-sphere model the transition from δ (fcc) to ϵ (bcc) should be accompanied by a volume increase, contrary to what is observed. Rudman⁽⁹⁾ considered the volume change associated with allotropic transitions for a number of metals involving fcc, hcp, and bcc crystal modifications. He observed that about half of the elements gave results that are in contradiction to the hard sphere model and showed that these exceptions could be explained generally in terms of magnetic and electronic transitions. Since the electronic behavior of (at least) δ -Pu is affected by alloying, it may be expected that the $\delta \rightarrow \epsilon$ volume change may also be altered by alloying. Data reported by Cope and Miller⁽¹⁰⁾ on several Pu-Ga alloys show that the $\delta \rightarrow \epsilon$ contraction is considerably reduced by alloying.

The present study was undertaken to obtain data that might show the influence of alloying on $\bar{a}_\delta$, $\bar{a}_\epsilon$ and on $\delta \rightarrow \epsilon$ contraction. In particular, we wished to determine whether any general trends exist for the $\bar{a}_\epsilon$ and $\delta \rightarrow \epsilon$ data and to compare such trends with results for $\bar{a}_\delta$. Additions of Al, Ga, and Ce were investigated using dilatometry.

Materials and Procedures

High-purity electrorefined Pu with less than 200 ppm impurities, excluding Am, was used as the base material. The Am content during the interval of testing was estimated to be between 220 and 300 ppm. A series of alloys ranging from approximately 3 to 12 at.% each of Ga, Al, and Ce were prepared by casting on a water-cooled copper hearth in the form of 200-g buttons. The cast buttons were heated for 24 hr at temperatures close to the solidus. Several dilatometer samples and a section for chemical analyses were cut from each button. To minimize alloy partitioning the machined samples were heated into the ϵ region and then rapidly cooled through the two-phase ($\delta + \epsilon$) region at rates above 400°C/sec by gas quenching with prechilled He. The samples were then annealed at 480°C for 16 hr, except for the 1-at.%-Ga alloy, which was held at 460°C.

A vertical-type dilatometer was used to obtain the expansion data. Several significant features of this apparatus may be noted. A counterbalance system permitted us to relieve the weight of the push rod. Any misalignment that may result during a run is avoided by having the bottom of the push rod tapered; it, in turn, sits in a conical indentation of a quartz disk that rests on the sample. Otherwise, due to the light load, any misalignment may cause binding. After various loads were tried, a net load of 5 g was used; this amounted to a stress of about 0.43 psi at the top of the sample. The sample weighed approximately 3 g and measured 0.500-in. high by 0.220-in. diam, with a 0.125-in.-diam bore. A 10-mil Pt/Pt-Rh thermocouple was intrinsically welded to the sample and led out through a clamp-type vacuum seal connected to the bottom of the outer quartz tube. The measuring system was calibrated prior to each run against a Boeckeler micrometer head. The dimensional change of the specimen causes a relative displacement between the outer tube and inner quartz rod, which are connected, respectively, to the body and core of a linear variable differential transformer (LVDT). Temperature-displacement output was obtained on an X-Y recorder.

The system was operated in vacuum under a pressure of less than 10^{-5} Torr. The dilatometer was calibrated with an Fe-30Ni-5Cr sample of known expansion characteristics obtained from the Bureau of Standards. These runs were highly reproducible. The experimental results were corrected using the deviations obtained for the standard specimen. Deviations would result from the quartz correction for the specimen length and from the temperature gradient between the quartz rod and tube. In all cases a constant heating rate of $4.5^{\circ}\text{C}/\text{min}$ was used.

An average value for $\bar{\alpha}_{\epsilon}$ was obtained by cycling a number of times in the ϵ range. The fact that, on the average, the slopes of the heating curves were approximately equal to those of the cooling curves indicated that creep was absent.

Results

Corrected dilatometric heating curves obtained for the Pu-Ga series are shown in Fig. 1. Because of the relatively large dimensional changes associated with pure Pu, the scale used for the pure metal is one-tenth that used for the alloys. Portions of the curve for the δ and ϵ regions of pure Pu are redrawn (dashed) on the same scale used for the alloys. The curves for the Al and Ce series are reasonably similar to those shown for the Ga series.

Figures 2, 3, and 4 show the $\bar{\alpha}_{\delta}$ values for the Pu-Ga, Pu-Al, and Pu-Ce series, respectively. The data for pure Pu were obtained for the $325\text{--}450^{\circ}\text{C}$ temperature range. Except where noted, the rest of the data represents average values for $300\text{--}450^{\circ}\text{C}$. The actual length of the specimens on reaching the δ phase was used as the base length for pure Pu. However, because of the negligible correction that would be required for the δ -stabilized alloys, the original starting length was used for these alloys. Also included in these figures are data obtained from the literature. The curves drawn are based only on our data.

A value of $-8.6 \times 10^{-6}/^{\circ}\text{C}$, obtained by Ellinger⁽¹¹⁾ using x-rays, is frequently taken as the most reliable for δ -Pu. By dilatometry we obtain a mean value of $-12.15 \times 10^{-6}/^{\circ}\text{C}$ ($+0.40 \times 10^{-6}$, -0.35×10^{-6}). Both values are plotted. Gschneidner⁽²⁾ points out that values ranging from -33×10^{-6} to $-6.0 \times 10^{-6}/^{\circ}\text{C}$ have been reported in the literature. Marples⁽⁴⁾ showed that the lattice parameter obtained for the δ phase of Pu may vary considerably depending on purity as well as on the technique of measurement (x-ray). In general, he obtained lower values for lower purity material. Using Marples' data on lattice parameters of Pu as a function of temperature for seven sets of curves, we calculated values of $\bar{\alpha}_{\delta}$ that vary from -6.5×10^{-6} to $-11.4 \times 10^{-6}/^{\circ}\text{C}$ between 300 and 450°C .

Our results agree reasonably well with those reported in the literature^(3,10) for the Pu-Ga series shown in Fig. 2. However, in contrast to the linear behavior suggested by Taylor⁽³⁾ in his Fig. 2, our data indicate a nonlinear relationship. The latter relationship is also exhibited for the Pu-Al and Pu-Ce alloys shown in Figs. 3 and 4. It may be noted that for these two series the data based on x-ray results generally fall above those obtained by dilatometry. This is opposite to what would be expected on the basis of an increase in vacancy concentration with increase in temperature.

Figure 5 is a plot of $\bar{a}_\delta$ as a function of c/a for the three series of alloys. The valences of Pu, Ga, Al, and Ce are taken as 4.80, 3, 3, and 3.64⁽²⁾, respectively. The value for Pu is obtained by interpolating to the average temperature (375°C) the values proposed by Zachariasen⁽¹⁾ (for 300 to 450°C). In contrast to the linear relationship proposed by Gschneidner et al.⁽²⁾ the relationships shown in Fig. 5 are nonlinear. In addition, three distinct curves are obtained. It may be argued on the basis of the corresponding phase diagram that the results for the highest Pu-Ga alloy may be affected by the presence of some zeta (ζ) phase. The ζ phase has a lower density than δ . Since the solubility limit of δ increases with temperature, a contraction would arise as a result of any dissolution of the ζ , thereby giving rise to an apparently low $\bar{a}_\delta$. However, no anomalous behavior indicative of the ζ phase was evident on the dilatometry curves. Again, the $\bar{a}_\delta$ value for pure Pu is taken as the average between 325 and 450°C; the corresponding mean valence accordingly should be 4.817. Although both of these factors may tend to straighten out the curves, they would still remain nonlinear.

Figure 6 shows the effect of solute concentration on the $\delta \rightarrow \epsilon$ contraction. Included in the figure are the results obtained by Cope and Miller⁽¹⁰⁾. Increased additions of either Ga or Al result in a decrease in the $\delta \rightarrow \epsilon$ contraction. For Ce additions a reversal in this trend is observed at about 7 at.% Ce. We were somewhat disturbed about the lack of good reproducibility in the magnitude of the $\delta \rightarrow \epsilon$ contractions. The possibility existed that transformation-induced creep may have taken place, although the load on the specimen was only about 0.4 psi (5 g). Accordingly, we made several dilatometric runs (on the same specimen of pure Pu), varying the load from 1 to 30 g. No systematic variation in the contraction could be seen as a function of load. However, for loads greater than about 20 g, creep of the ϵ phase was apparent. We also noted for the 3.3 at.% Ga addition that the $\delta \rightarrow \epsilon$ contraction could vary by a factor of two, depending on the heat treatment during homogenization. That all these samples were homogeneous was indicated by the constant start temperature of the $\delta \rightarrow \epsilon$ transition. Preferred orientation effects may also have contributed to the scatter. The relatively high contraction values obtained by Cope and Miller may be due to creep. Examination of their dilatometric heating curves show abnormally low expansion behavior for the ϵ phase, which probably resulted from too high a load on their specimens. The fact that the values for the high Ga contents correspond with our results may suggest that solid solution alloying has enhanced the creep resistance of the δ phase.

Figure 7 shows the variation of $\bar{a}_\epsilon$ with solute content for Ga, Al, and Ce additions and for Zr additions reported by Marples⁽⁴⁾. Considerable scatter may be seen in the data. In contrast to the effect of alloying on $\bar{a}_\delta$ for the δ phase, increasing amounts of Ga and Al (as well as Zr) result in a drop in $\bar{a}_\epsilon$. Small additions of Ce apparently have little effect, but an increase in Ce with amounts in excess of about 7 at.% results in a rise in $\bar{a}_\epsilon$.

Discussion

The $\bar{a}_\delta$ values obtained for the three series of alloys — Pu-Ga, Pu-Al, and Pu-Ce — are in reasonable agreement with those reported in the literature. The results are generally consistent with an electronic model that allows interband transitions to occur between a narrow and steeply sloping 5f band and a wide 6d band with a

change in both solute concentration and temperature. The correlations we observe, however, do not show the linear relationship between $\bar{\alpha}_\delta$ and c/a proposed by Gschneidner *et al.*⁽²⁾ nor that between $\bar{\alpha}_\delta$ and solute content obtained by Taylor. Furthermore, the fact that the three series of data do not superpose when $\bar{\alpha}_\delta$ is plotted vs c/a is inconsistent with the suggestion of Gschneidner *et al.*⁽²⁾ that "the coefficient becomes zero at essentially a single electron concentration value" for a number of solutes.

The electronic interaction between Pu and the different elements would not necessarily be expected to be the same in all cases. For example, Ce atoms, like those of Pu, can have the population of electrons between their inner and outer shells easily altered, depending on the temperature, structure, and solute concentration. The cubic $\rightarrow$ cubic' transition in Ce, which essentially involves a hydrostatic shrinkage of the lattice, has been attributed to the transition of one 4f electron to the conduction band⁽¹²⁾. Thus, one must not only consider the electronic contribution from Ce to Pu atoms but also the contribution from Pu to Ce atoms. As can be seen in Figs. 6 and 7, above about 7 at.% Ce there is a reversal both in the $\delta \rightarrow \epsilon$ contraction and in $\bar{\alpha}_\epsilon$. The divergence of the Ce data from the Al and Ga data in Fig. 5 becomes significant also at about 7 at.% Ce ($c/a \approx 4.72$). Thus, it would seem that at about this composition the specific influence of the Ce atoms begins to be felt. Aluminum and Ga, having similar valence behavior, may be expected to behave similarly. This may explain the relatively small divergence obtained in Fig. 5 for the two corresponding series.

Chalmers⁽¹³⁾ has shown that for many metals the value for $\bar{\alpha}$ is closely related to the melting point, namely, $\bar{\alpha} \times T(^{\circ}\text{K})_{\text{mp}} \times 10^3 \approx 20$. This relationship predicts a value of $21.4 \times 10^{-6}/^{\circ}\text{C}$ for Pu (mp 913°K), which falls within the range of values that we report. Alloying can either raise or lower the values reported for the pure metals⁽¹⁴⁾. Our results thus indicate that the ϵ phase behaves in a "normal" metallic manner. Variations in the $\delta \rightarrow \epsilon$ contraction perhaps may be explained on the basis of the difference in "normal" behavior between the two phases ("normal" refers here to the behavior typical for most metals, and does not imply normal behavior for the specific metal). This can be illustrated with reference to Fig. 1. Curve 2 shows the behavior obtained in going from the "abnormal" δ phase, in which dimensional changes are affected by electronic factors, to the "normal" ϵ phase. Curve 6 shows the behavior obtained between a more nearly "normal" δ and "normal" ϵ ; dimensional changes in both phases are relatively unaffected by electronic factors. The start of an expansion predicted on the basis of a hard-sphere model in changing from a more-densely to a less-densely packed crystal structure can be seen here. Curves 3-5 show intermediate conditions.

Summary

Linear thermal expansion coefficients in δ and ϵ phases and the $\delta \rightarrow \epsilon$ contraction were measured for Pu and a series of Pu-Ga, Pu-Al, and Pu-Ce alloys. The variations in expansion coefficients of the δ phase, obtained as a function of concentration for the different solutes, appear to be consistent with a general interpretation based on electronic effects. The expansion behavior obtained for ϵ is typical of that of most metals. Variations in the $\delta \rightarrow \epsilon$ contraction, as affected by solute concentrations, are related to the relative expansion behaviors of the two phases. Differences observed

for all three types of measurements between the Pu-Ce series and the Pu-Ga and Pu-Al series are attributed to the electronic interaction resulting from the contribution of electrons from Pu atoms to Ce atoms. The specific influence of Ce atoms is noticed for additions above about 7 at.% Ce.

Acknowledgments

The authors wish to thank Jack L. Robbins for his interest in supporting this work and his helpful comments in reading the manuscript. They particularly wish to thank Dr. T. B. Massalski of the Mellon Institute of Science, Carnegie-Mellon University, for his stimulating discussions and comments on the manuscript.

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Goldberg - Fig. 1

Goldberg-Fig. 2

Goldberg - Fig. 3

Goldberg-Fig. 4

Goldberg - Fig. 5

Goldberg-Fig. 6

Goldberg-Fig. 7