STEP-DR
68-0344

*J. Phys. Chem. Solids* Pergamon Press 1968. Vol. 29, pp. 815–821. Printed in Great Britain.

# PHASE DIAGRAM, COMPRESSIBILITY AND RESISTANCE OF AMERICIUM AS A FUNCTION OF PRESSURE

**D. R. STEPHENS, H. D. STROMBERG and E. M. LILLEY**
Lawrence Radiation Laboratory, University of California, Livermore, California 94550, U.S.A.

(*Received* 26 *September* 1967; *in revised form* 8 *December* 1967)

**Abstract**—The compressibility at room temperature and pressure-temperature phase diagram of americium were measured to 35 kbar, and the electrical resistance at room temperature was measured to 120 kbar. Americium exhibits a higher compressibility than other actinides; in general, the physical properties of americium resemble rare earths more closely than the other actinides.

The melting curve of americium obeyed the Kraut and Kennedy melting relation. Details of the phase diagram were in good agreement with recent work of Wade and Wolf. The melting point at 1 atm is 1173°C.

There was an anomaly in the curve of resistance vs. pressure at 90 kbar; the effect may be due to a phase transition.

## 1. INTRODUCTION

As a part of a continuing study of high-pressure properties of actinide elements, we measured the compressibility, pressure-temperature phase diagram, and electrical resistance of americium as a function of pressure. McWhan and coworkers [1,2] have studied the physical properties of americium in detail. Their work showed that the stable phase of americium at room temperature is d.h.c.p., which is the same structure as the rare-earth elements lanthanum, praseodymium, and neodymium. They reported evidence that americium transforms from d.h.c.p. to f.c.c. at 600–700°C and then melts at 994°C. All the work of McWhan and coworkers indicates that the properties of americium are quite similar to the rare earths. Their magnetic studies showed that americium is trivalent, as are most rare earths; americium is close-packed, like the rare earths and unlike the other actinides; the thermal expansion, atomic volume, heat of vaporization, and melting point of americium are all much closer to those of the rare-earth series than those of the actinides. McWhan and coworkers also showed that the properties of the actinides thorium through plutonium are intermediate to the transition elements and rare earths. They concluded from the above evidence that americium is the first actinide to be properly described as a rare-earth element.

## 2. EXPERIMENTAL

### 2.1. *Samples*

The americium samples were estimated to be 99·5+ per cent pure. Our samples were Am-241. Metallic impurities were present to 0·1 per cent. The remainder of the impurities were oxide and nitride and were estimated by metallographic examination. The crystal structure was d.h.c.p. and the metal was ductile.

Two samples of americium of lower purity, 99·0 per cent, were also used in the compression studies and are described in Section 3. These two samples contained both d.h.c.p. and f.c.c. phases.

All samples were prepared by Wade and Wolf [3].

### 2.2. *Measurements*

Since americium emits both $\alpha$ and $\gamma$ rays and in addition is easily oxidized, all measure-

ments were performed under inert atmosphere in a glove box. Specific measurement techniques are discussed below.

2.2.1. *Compressibility studies.* The compressibility measurements were basically the same as described previously[4]. The dies were not end-loaded, and the maximum pressures were about 30 kbar. All measurements were at room temperature, which was about 23°C.

The samples were cylindrical, of about 0·29 in. dia. by 0·6 in. length. They were wrapped with lead and run in an 0·313 in. bore die in the usual manner.

2.2.2. *Phase diagram.* The pressure-temperature phase diagrams were determined by use of differential thermal analysis[5, 6]. The samples were contained in tantalum capsules which were welded in an argon atmosphere.

As in previous work, transition data could not be obtained at 1 atm. Thus, the transition data were extrapolated back to 1 atm to obtain this information.

Platinum, platinum – 10 per cent rhodium thermocouples were used. All temperatures were corrected for pressure effects of thermocouple e.m.f. by the results of Hanneman and Strong[7].

2.2.3. *Resistance.* The resistance measurements were essentially the same as described previously[8] except that the samples were not hoop-shaped; they were slivers cut from foil and placed across the Bridgman anvil flat. Data were taken at room temperature, or about 23°C. The anvils were automatically calibrated as before; the bismuth calibrating samples were also placed across the flat. We estimate that the pressure gradient across the sample in such geometry was approximately 10 per cent. Some data were obtained in girdle anvil dies in the same manner as described previously[8].

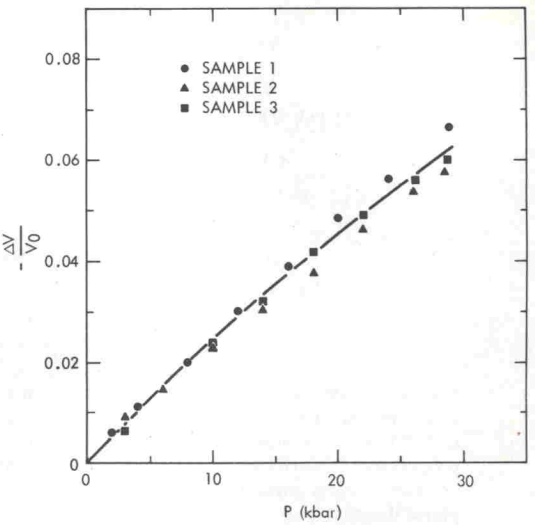



Fig. 1. Compression of americium vs. pressure.

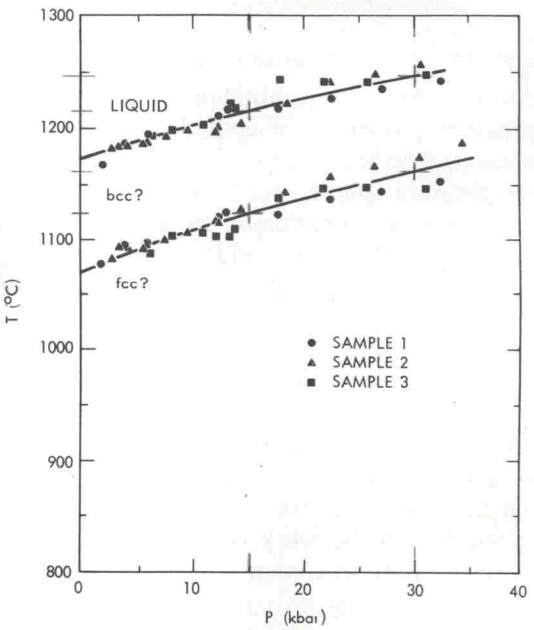



Fig. 2. Phase diagram of americium.

## 3. DISCUSSION

### 3.1. *Results*

The compressibility of americium is shown in Fig. 1, phase diagram in Fig. 2 and resistance in Fig. 3. The data are discussed below.

### 3.2. *Compressibility studies*

Three different samples were run. In Fig. 1, only sample 3 was 99·5 per cent pure and completely in the d.h.c.p. phase. This material

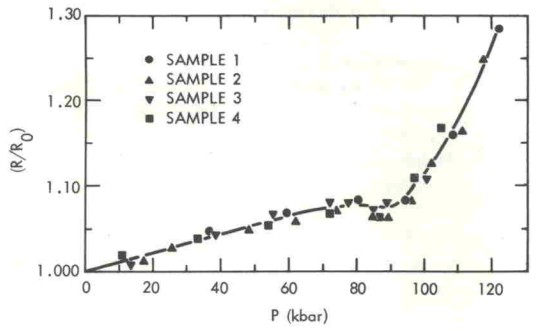



Fig. 3. Resistance of americium vs. pressure.

was also used for the phase diagram studies. The other two samples were about 99·0 per cent pure and contained some f.c.c. phase in addition to the d.h.c.p. However, all three sets of data agreed with ±5 per cent and the results seem representative of d.h.c.p. americium of 99·5 per cent purity.

Table 1 presents the smoothed compression curve and initial compressibility for americium. The data were taken at 23°C. Compressibilities at $P = 0$ for $4d$, $5d$, $4f$, and

*Table* 1. $\Delta V/V_0$, *and compressibility for americium*

| $P$ (kbar) | $-\frac{\Delta V}{V_0}$ | Compressibility<br>Compressibility at 1 atm (kbar$^{-1}$) |
|---|---|---|
| 5 | 0·0131 | 0·00277 |
| 10 | 0·0248 | |
| 15 | 0·0354 | |
| 20 | 0·0455 | |
| 25 | 0·0552 | |
| 29 | 0·0627 | |

actinide series are shown in Fig. 4. The data were taken from [4] and [9], and unpublished work of Stephens and Lilley. The data of Stephens and coworkers for the $4f$ series are shown as solid points. The peak in compressibility at europium is due to its abnormal +2 valence. The properties of europium are more similar to the alkaline earths than to

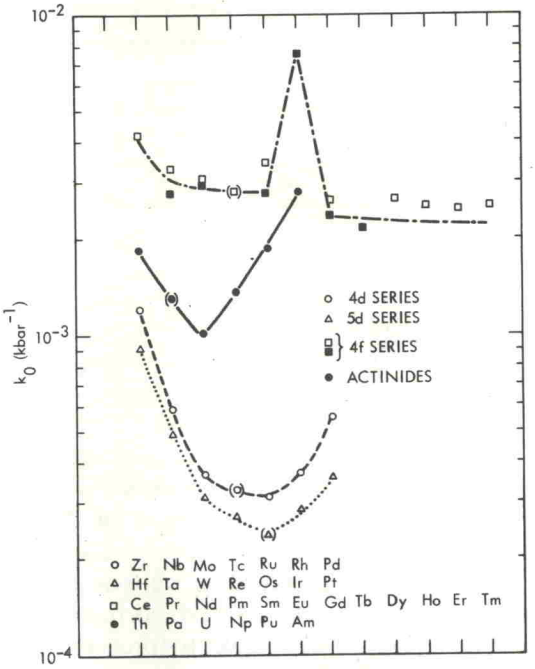



Fig. 4. Comparison of compressibilities for transition metals, rare earths, and actinides.

the rare earths [10]. As mentioned in Section 1, McWhan concluded from a study of several physical properties that americium is the first actinide to exhibit true earth properties, and that U, Np, and Pu were intermediate between the transition elements and rare earths. As may be seen from our data for Am, compressibility values confirm McWhan's conclusions. Our previous value for neptunium [11] is intermediate to the curves for the transition elements and rare earths, while our compressibility for americium is in good agreement with those of the rare earths.

### 3.3. *Pressure-temperature phase diagram*

Phase transformation data for americium are shown in Table 2. Our phase diagram for americium is in very poor agreement with the work of McWhan *et al.*[1].

Their measurements indicated a transition from d.h.c.p. to f.c.c. between 600 and 700°C. They reported that this evidence was marginal, and they determined the melting point to be

*Table 2. Transition curves and initial slopes for americium*

| Transition data T(°C) | | | Initial slope of transition line (°C/kbar) | |
|---|---|---|---|---|
| Pressure (kbar) | Solid–solid curve f.c.c. → b.c.c.? | Fusion curve b.c.c.? → liquid | Solid–solid curve | Fusion curve |
| 0 | 1072 | 1173 | 4·4 | 4·0 |
| 5 | 1091 | 1188 | | |
| 10 | 1108 | 1203 | | |
| 15 | 1123 | 1216 | | |
| 20 | 1137 | 1227 | | |
| 25 | 1150 | 1238 | | |
| 30 | 1162 | 1248 | | |
| 35 | 1174 | | | |

994 ± 7°C. Our data extrapolated to 1 atm indicate a solid–solid transition at 1072°C and a melting point of 1173°C.

It is unlikely that our data were in error as much as 180°C. The largest correction we previously have had to make to force a melting curve to extrapolate to a correct value, for six elements, is 25°C; the average value is 10°C. We believe that a more plausible explanation is that the transition McWhan measured at *ca.* 995°C was not the melting point. Americium is definitely rare-earthlike in all its properties. One of the properties that all rare earths seem to exhibit is that they are close-packed at room temperature, but transform b.c.c. before melting. Even Pu, which is rare-earthlike at high temperatures, transforms to b.c.c. before melting. Therefore, it is possible that the transition McWhan detected at 994°C may have been from f.c.c. to b.c.c. Our value of 1072 vs. McWhan's 995°C could be explained in terms of relative sample purity. The method used by McWhan was as follows: two tantalum wires fused together with americium metal were employed. A weight was hung on one of the Ta wires and the assembly heated. The melting point was taken as the temperature when the wires parted and the weight fell. This could have been due to a f.c.c.-b.c.c. transition in the americium since it involves a major rearrangement of atoms. A sample transforming in this manner has little strength and could easily part under such a test. The d.h.c.p.-f.c.c. transition involves a smaller rearrangement of atoms and the metal might not weaken as much as in the case of the f.c.c.-b.c.c. Thus, the sample possible could remain intact during a d.h.c.p.-f.c.c. transition and part during the f.c.c.-b.c.c. rearrangement.

We therefore believe that we missed the d.h.c.p.-f.c.c. transition, due to its presumably small latent heat, and observed a f.c.c.-b.c.c. transition at 1072°C, followed by melting at 1173°C. Such an assignment is, of course, very tentative. The recent work of Wade and Wolf[3] offers very strong supporting evidence for our interpretation. They report a solid–solid transition at 1079° and a melting point of 1176°C for americium. These numbers are in very good agreement with our values of 1072° and 1173°C. Wade and Wolf used a thermal arrest method employing a resistance heater. Their determinations were made *in vacuo*.

Wade and Wolf also determined the latent heats to be 1·40 kcal/mole for the solid-solid transition and 3·44 kcal/mole for fusion. Using these values and our experimentally determined transition slopes, one can estimate the volume changes of the transition from the Clapeyron equation

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}.$$

The predicted volume changes are for

f.c.c. → b.c.c.? $\Delta V = 0{\cdot}192$ cm³/mole

b.c.c.? → liquid $\Delta V = 0{\cdot}398$ cm³/mole.

The percentage volume changes based on the density at room temperature are then 1·1 per cent for the solid–solid transition and 2·26 per cent for fusion.

It is of interest to test Kraut and Kennedy's [12, 13] melting point relation in the case of americium. The relation is

$$\frac{T}{T_0} = 1 + C\frac{\Delta V}{V_0} \tag{1}$$

where

$C$ = a constant,

$T_0$ = melting temperature at 1 atm, °K

$$-\frac{\Delta V}{V_0} = \frac{V_0 - V}{V_0}.$$

Gilvarry[14] and Vaidya and Raja Gopal [15] have derived a similar expression by differentiating the Lindemann melting temperature with respect to volume and assuming that the Grüneisen parameter is constant, to obtain the volume dependence of the Debye temperature.

The pertinent equations are

$$\text{Lindemann } T_m = CM\theta^2 V^{2/3} \tag{2}$$

$$\text{Grüneisen } \quad V = \frac{\mathrm{d}\ln\theta}{\mathrm{d}\ln V}. \tag{3}$$

The resultant expression is

$$\frac{T}{T_0} = \left(\frac{V}{V_0}\right)^{(2/3-2\gamma)}. \tag{4}$$

This equation is then expanded about $V = V_0$ and only the linear terms are kept

$$\frac{T}{T_0} = 1 + (2\gamma - 2/3)\frac{\Delta V}{V_0} + \cdots. \tag{5}$$

Thus $C$ in the Kraut and Kennedy relations corresponds to

$$C = 2\gamma - 2/3. \tag{6}$$

Kraut and Kennedy[13], however, object to the expansion of equation (4) since their linear law apparently holds for compression of 0·3 to 0·5, for NaCl and the alkali metals. At $\Delta V/V_0 = 0{\cdot}5$, the higher terms in equation (5) are not negligible.

Figure 5 shows that the melting point of americium is expressed well by the linear law.

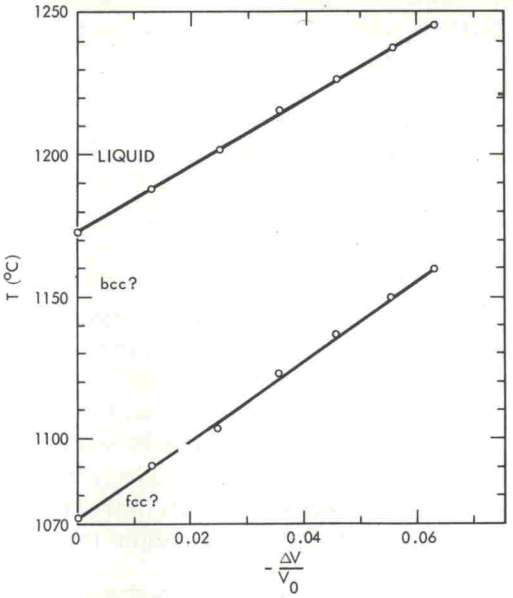



Fig. 5. Transition temperatures vs. compression for americium.

In addition, the solid–solid transition also shows a straight line on such a plot. Fischer [16] has shown that some solid–solid transitions in uranium and plutonium also obey the linear law.

The constant $C$ in equation (1) is 0·816 which, from equation (6), predicts a Grüneisen parameter of 0·74 for americium. This number seems to be too high, for, using the density and thermal expansion data of McWhan *et al.* [1, 2] and the 1 atm compressibility data in this report, and estimating the specific heat to be 5·90 cal/mole/°K, the Grüneisen parameter

$$\gamma = \frac{V\alpha}{\beta C_V}$$

is calculated to be 0·55. Thus the Grüneisen parameter as estimated from the melting curve appears to be too high.

The method used to estimate $C_V$ was as follows: First the Debye temperature was estimated from the Lindemann model (Reference [9], p. 378). Then the lattice contribution to $C_V$ was estimated from the Debye model (Lewis *et al.*[17]). Since we are relating $\gamma$ to the Lindemann model, where only lattice contributions are considered, only the lattice contribution to $C_V$ was used.

It also seemed of interest to test the Kraut and Kennedy linear law with other actinides; results are shown for neptunium and americium in Fig. 6. The law expresses the data for plutonium fairly well, although the slope is negative. The melting curve is that of Stephens[18] and the compressibility data are from Bridgman[19]. The expression does not hold well for either the melting curve or solid–solid transformation of neptunium[11]; however, the compressibility data are accurate to only +10 per cent which is within the deviation of the data in Fig. 6 from a straight line. The Grüneisen parameters for neptunium can be estimated from equation (5); it is $\gamma = 1{\cdot}72$. The Grüneisen parameter calculated from thermal properties[20, 21] is 2·24.

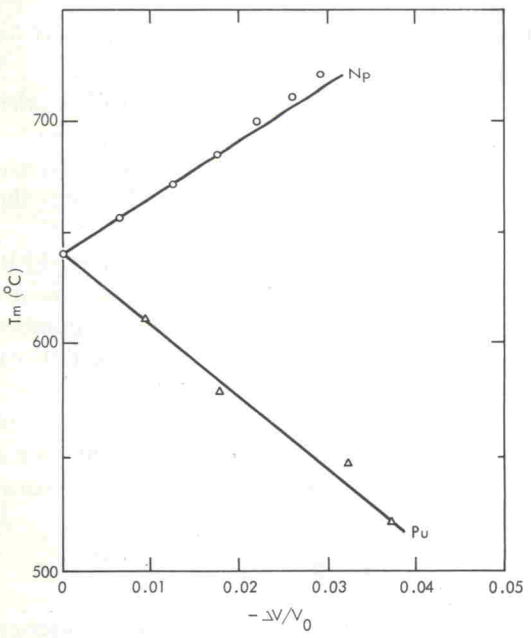



Fig. 6. Melting curves vs. compression for neptunium and plutonium.

Elements with large negative melting slopes such as plutonium show the danger of using equation (5) too literally; use of equation (5) predicts a negative Grüneisen parameter.

In conclusion, the melting curves of neptunium, plutonium, and americium are reasonably well-expressed by the Kraut and Kennedy melting law. However, the Gilvarry and Vaidya and Raja Gopal expression did not seem to yield correct Grüneisen parameters for these three actinides.

### 3.4. *Resistance*

The pressure effect on resistance of americium at room temperature was small. Unfortunately, we were unable to anneal our samples which were cut from cold-worked material. Therefore, the curve is of qualitative value only. Note the rise in resistance at 90 kbar. The data shown are based on calibrations assuming the high-pressure bismuth transformation occurs at 80 kbar. The 'transition' was repeatedly observed in a girdle anvil device, indicating that the effect was reversible. Resistance drift with time at high pressure also indicates a first-order transition. However, when we attempted to follow the temperature dependence of the transition by heating the sample in a girdle anvil die, the effect disappeared. At 50°C, there was no rapid resistance rise. This indicated that the effect was due to residual strain in the sample which was annealed out by moderate heat. These two sets of information are contradictory; X-rays under pressure will be necessary to determine whether there is a first-order phase transition.

If the effect is due to a phase transition, one can estimate that it is from d.h.c.p. to f.c.c. Piermarini and Weir[22] have reported that La, Pr, and Nd all transform from d.h.c.p. to f.c.c. with increasing pressure and, in fact, Jayaraman[23] has proposed the following sequences of phases with pressure for trivalent rare-earth elements:

h.c.p. → Sm structure → d.h.c.p. → f.c.c.

Since americium is similar to the trivalent rare earths, it is not unreasonable to expect a d.h.c.p. → f.c.c. transition. If this is the case, it is presumably the same d.h.c.p. → f.c.c. transition observed by McWhan *et al.*[1, 2] at 600–700°C.

*Acknowledgements*—The authors gratefully acknowledge the help of the following: E. M. Cramer and P. C. Wallace for X-ray analysis and metallographic examination; J. R. Humphrey and W. Z. Wade for americium purification and reduction; A. L. Langhorst for spectrographic analyses; and R. Link for welding the tantalum capsules. We also wish to thank W. J. Ramsey and A. E. Abey for reading the manuscript.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

## REFERENCES

1. McWHAN D. B., CUNNINGHAM B. B. and WALLMAN J. C., *J. inorg. nucl. Chem.* **24**, 1025 (1962).
2. McWHAN D. B., Thesis. University of California, Berkeley (1961).
3. WADE W. Z. and WOLF T., *J. inorg. nucl. Chem.*, **29**, 2577 (1967).
4. STEPHENS D. R., *J. Phys. Chem. Solids* **25**, 423 (1964).
5. KENNEDY G. C. and NEWTON R. C., *Solids Under Pressure* (Edited by W. Paul and D. M. Warschauer), p. 163. McGraw–Hill, New York (1963).
6. STEPHENS D. R., *J. Phys. Chem. Solids* **26**, 943 (1965).
7. HANNEMAN R. E. and STRONG H. M., ASME Paper 64-WA/PT-21, ASME Winter Meeting (1964).
8. STROMBERG H. D. and STEPHENS D. R., ASME Paper 64-WA/PT-13, ASME Winter Meeting (1964).
9. GSCHNEIDNER K. A. Jr., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 16, p. 276. Academic Press, New York (1964).
10. GESCHNEIDER K. A. Jr., *Rare Earth Alloys*. Van Nostrand, New York (1961).
11. STEPHENS D. R., *J. Phys. Chem. Solids* **27**, 1201 (1966).
12. KRAUT E. A. and KENNEDY G. C., *Phys. Rev. Lett.* **16**, 608 (1966).
13. KRAUT E. A. and KENNEDY G. C., *Phys. Rev.* **151**, 668 (1966).
14. GILVARRY J. J., *Phys. Rev. Lett.* **16**, 1089 (1966).
15. VAIDYA S. N. and RAJA GOPAL E. S., *Phys. Rev. Lett.* **17**, 635 (1966).
16. FISCHER R. B., *J. nucl. Mater.* **21**, 355 (1967).
17. LEWIS G. N., RANDALL M., PITZER K. N. and BREWER L., *Thermodynamics*, 2*nd* Edn., p. 660. McGraw–Hill, New York (1961).
18. STEPHENS D. R., *J. Phys. Chem. Solids* **24**, 1197 (1963).
19. BRIDGMAN P. W., *J. appl. Phys.* **30**, 214 (1959).
20. ZACHARIASEN W. H., *Acta Crystallogr.* **5**, 664 (1952).
21. ELDRED D. W. and CURTIS G. C., *Nature* **179**, 910 (1957).
22. PIERMARINI G. J. and WEIR C. E., *Science* **144**, 69 (1964).
23. JAYARAMAN A., *Phys. Rev.* **139**, A690 (1965).