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TITLE: THERMAL CONDUCTIVITY AND LORENZ NUMBER OF PLUTONIUM AND PLUTONIUM–GALLIUM ALLOYS

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THERMAL CONDUCTIVITY AND LORENZ NUMBER OF PLUTONIUM AND PLUTONIUM-GALLIUM ALLOYS

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The thermal diffusivities of Pu, Pu-2.7 at.% Ga, Pu-3.5 at.% Ga, and Pu-6.6 at.% Ga were measured from 25°C to around 500°C using a laser flash technique and electronic data acquisition. Although the Lorenz number, L, of pure Pu is well below the Sommerfeld value, L_0, except for the α-phase, L exceeds L_0 for the alloys at all temperatures and has a pronounced minimum around 200°C. At the lower temperatures we attribute the excess to lattice conduction and at temperatures above 200°C the excess is attributed to an electronic component. The negative deviation of L from L_0 for pure Pu is ascribed to a reduction of the electron mobilities in those energy ranges where the 5f bands overlap the conduction bands.

INTRODUCTION

This paper presents the results of thermal diffusivity measurements on a series of Pu-Ga alloys as a continuation of the diffusivity study begun by Lewis, et al., who reported results on 1 wt% Ga (3.3 at.% Ga).[1] Our study included high-purity unalloyed Pu and three stabilized delta phase Pu-Ga alloys (2.7, 3.5, and

6.6 at.% Ga) in the temperature range 20-580°C. A number of elements, such as Al, Am, Ga, and Ce form solid solutions with Pu, resulting in an fcc delta-phase alloy that is stable to below room temperature. The measurements on the Pu + 3.5 at.% Ga alloy reported here are within 10% of the values reported previously by Kruger and Robbins,[2] and along with the previous work by Andrew[3,4] give a comprehensive picture of the thermal conductivity of Pu and Pu-Ga alloys.

EXPERIMENTAL METHOD

The experimental method used in this study was similar to the flash diffusivity measurement technique described by Parker et al.[5] The front surface of a disk-shaped specimen was heated instantaneously by infrared radiation from a Nd-glass laser and the temperature rise on the back surface was measured by "Platinel 2" thermocouple wires contacting the Pu sample. The rear surface temperature was monitored on an oscilloscope operating in single-sweep, memory mode and stored in an electronic data acquisition system. An enlarged trace of the rear surface temperature-time history was used to obtain the rise-time data for the diffusivity calculation. The following equation, from Cowan,[6] was used to calculate the thermal diffusivity:

$$\frac{T}{T_{max}} = 1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-n^2\pi^2\alpha t/z^2} \qquad (1)$$

where T is rear surface temperature at time t, α is the thermal diffusivity, and z is the thickness of the specimen disk. The solutions of this equation for a series of T/T_{max} are given in Table I. The heat loss corrections were included by calculating

Table I. Solutions to the Diffusivity Equations

T/T_{max}	α = constant $z^2/t(x)$
0.1	0.0661 $z^2/t(0.1)$
0.2	0.0843 $z^2/t(0.2)$
0.3	0.1013 $z^2/t(0.3)$
0.4	0.1190 $z^2/t(0.4)$
0.5	0.1388 $z^2/t(0.5)$
0.6	0.1622 $z^2/t(0.6)$
0.7	0.1919 $z^2/t(0.7)$
0.8	0.2331 $z^2/t(0.8)$

the diffusivities at the T/T_{max} values given in Table I and extrapolating to zero time. This method of making the heat loss correction gives approximately the same results as the Cowan technique.[6]

The diffusivity apparatus and associated inert atmosphere glovebox were previously described by Lewis et al.[1] Laser alignment and specimen temperature were checked by measuring the diffusivity of a sample of round-robin Armco Fe. Measured values of α were within 5% of the results of Cody, Abeles, and Beers.[7]

Our Pu specimens were 10 mm in diameter and about 1.3 mm thick. The unalloyed Pu specimen was 99.99 wt% Pu. The Pu-Ga alloys were prepared from Pu stock with a purity greater than 99.98 wt% Pu. The impurities were mainly Fe, Si, C, W, Ta, Al, and Ni; the overall concentration was, in all cases, less than 500 wt ppm. The Pu-Ga alloys were annealed at 440°C for 200 h to insure delta-phase stability and homogeneity.

Thermal conductivity values, λ, were calculated from the thermal diffusivities ($\lambda = \alpha$ D Cp) using measured density values, D, specspecific heat, Cp from Kay and Loasby[8] for Pu and from Rose et al.[9] for the Pu-Ga alloys. The accuracy of the thermal conductivity values are probably within 10% since the specific heat data was taken from the literature and corrected for the Ga content.

RESULTS

The thermal diffusivity values are given in Table II for the Pu-Ga alloys and these alloys along with the unalloyed Pu are shown on Fig. 1. The diffusivity data were fitted to straight lines using a linear regression technique. These equations are given in Table III. Diffusivity values obtained from the equations in Table III, along with values of specific heat and electrical resistivity used to calculate the thermal conductivities and Lorenz numbers, are presented in Table IV for all Pu specimens.

DISCUSSION

The thermal diffusivity, shown in Fig. 1 as a function of temperature, can be adequately represented by straight lines for all phases of Pu. A small amount of Ga increases the thermal diffusivity, but further additions of Ga cause it to decrease. The same behavior as a function of Ga content is shown by the thermal conductivity in Fig. 2. The data below 25°C are extrapolated from previous results at -198°C.[3,4] The Lorenz number of pure Pu is well below the Sommerfeld value, L_0 (2.45×10^{-8} V^2/K^2) in the β, γ, δ', and ε phases (see Table IV). However, the alloys have Lorenz numbers generally above L_0 (see Table IV).

Table II. Measured Diffusivity Data for the Pu-Ga Alloys

2.7 at.% Ga		3.5 at.% Ga		6.6 at.% Ga	
T °C	α x10^{6}m^2/s	T °C	α x10^{6}m^2/s	T °C	α x10^{6}m^2/s
22	3.97	22	3.72	22	3.33
100	4.45	102	4.37	101	3.82
205	5.32	202	4.98	205	4.70
305	5.99	225	5.17	305	5.40
402	6.55	354	6.08	400	6.09
503	7.39	430	6.58	500	6.60
		503	7.10	550	6.88
				580	7.22

Table III. Straight Line Approximation Equations for Thermal Diffusivity Data, where T is in °C and α is in m^2/s

Unalloyed Pu

monoclinic: α-phase	$\alpha = 1.69 \times 10^{-6} + 3.7 \times 10^{-9} T$
b.c. monoclinic: β-phase	$\alpha = 2.03 \times 10^{-6} + 6.5 \times 10^{-9} T$
f.c. orthorhombic: γ-phase	$\alpha = 1.95 \times 10^{-6} + 7.2 \times 10^{-9} T$
f.c. cubic: δ-phase	$\alpha = 2.75 \times 10^{-6} + 5.0 \times 10^{-9} T$
b.c. cubic: ε-phase	$\alpha = 3.02 \times 10^{-6} + 4.1 \times 10^{-9} T$

f.c. cubic δ-phase Pu-Ga alloys

Pu + 2.7 at.% Ga:	$\alpha = 3.80 \times 10^{-6} + 7.1 \times 10^{-9} T$
Pu + 3.5 at.% Ga:	$\alpha = 3.60 \times 10^{-6} + 7.0 \times 10^{-9} T$
Pu + 6.6 at.% Ga:	$\alpha = 3.22 \times 10^{-6} + 6.9 \times 10^{-9} T$

From $k-k_0$ we can calculate an excess thermal conductivity, Δk, by means of

$$\Delta k/k \quad (k-k_0)/k \qquad (3)$$

Values of Δk are shown in Fig. 3. At low temperatures, Δk has the general behavior of a lattice thermal conductivity; it decreases with increasing temperature and also decreases with increasing solute content. Above 200°C, however, Δk increases with temperature, an unlikely behavior for lattice thermal conductivity. For comparison, we have included a curve of the lattice thermal conductivity of pure

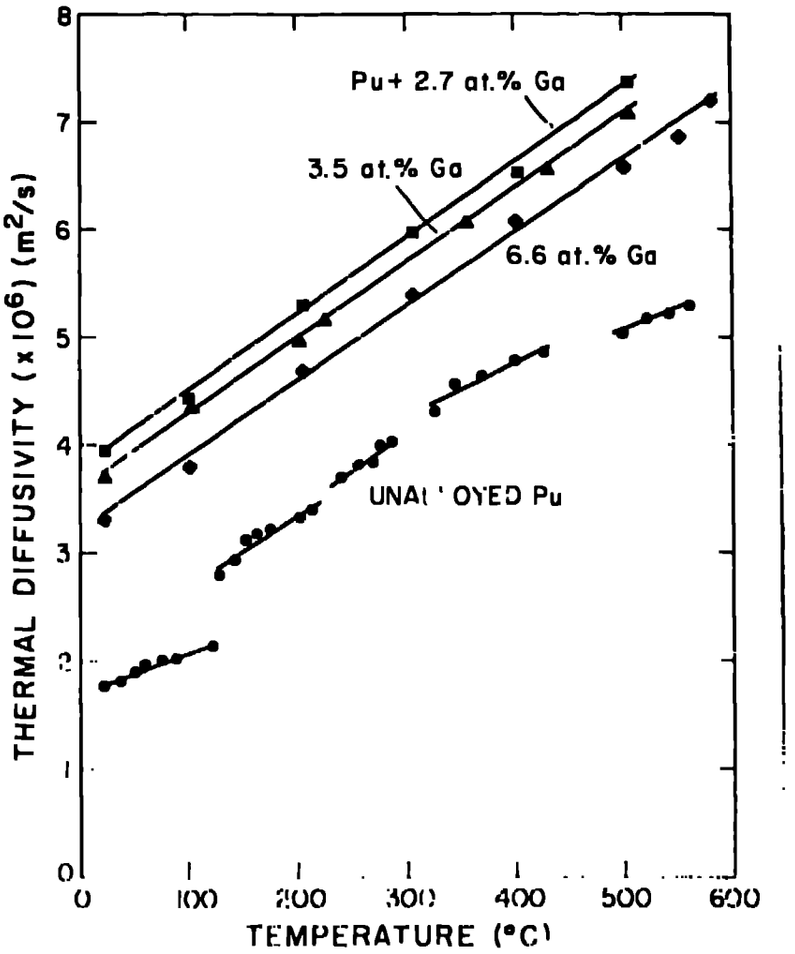

Fig. 1. Thermal diffusivity of the four plutonium specimens as a function of temperature.

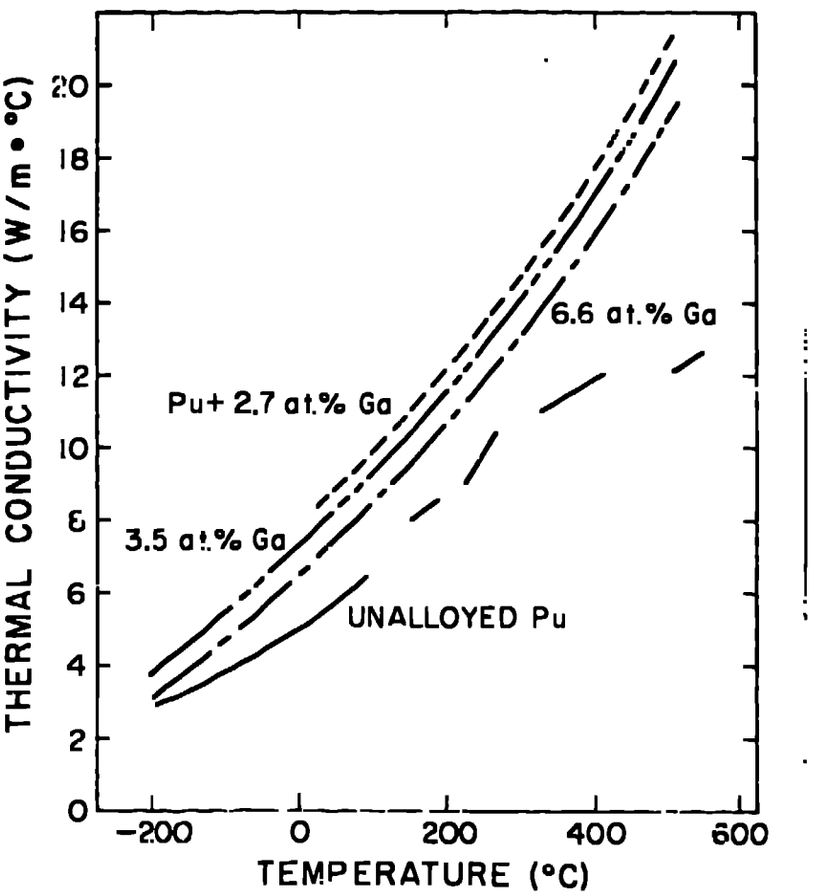

Fig. 2. Thermal conductivity of the four plutonium specimens in Fig. 1 as a function of temperature.

Table IV. Calculated Values for Thermal Conductivity and Lorenz Numbers for High-Purity Unalloyed Pu

Pu Type $Dx10^{-3}kg/m^3$	T °C	α $x10^6m^2/s$	Cp J/g°C	λ W/m°C	ρ $x10^8\Omega m$	L $x10^8V^2/K^2$
Unalloyed Pu						
α-phase	25	1.78	0.1481	5.20	142	2.48
19.71	100	2.10	0.1598	6.62	140	2.48
β-phase	150	3.10	0.1448	7.87	108	1.99
17.58	200	3.31	0.1490	8.67	108	1.98
γ-phase	225	3.53	0.1494	8.97	107	1.93
17.02	275	3.96	0.1552	10.46	107	2.04
δ-phase	325	4.40	0.1552	10.97	100	1.83
15.81	425	4.85	0.1577	12.10	100	1.73
ε-phase	500	5.04	0.1464	12.10	114	1.78
16.39	550	5.26	0.1464	12.62	114	1.75
Pu-Ga Alloys						
2.7 at.% Ga	25	3.98	0.1364	8.53	109	3.12
15.738	100	4.51	0.1389	9.85	108	2.85
	200	5.22	0.1439	11.81	107	2.67
	300	5.92	0.1540	14.33	107	2.68
	400	6.63	0.1669	17.40	107	2.77
	500	7.33	0.1845	21.26	108	2.97
3.5 at.% Ga	25	3.78	0.1372	8.18	110	3.02
15.713	100	4.30	0.1397	9.42	108	2.73
	200	4.99	0.1448	11.39	108	2.60
	300	5.69	0.1548	13.89	108	2.62
	400	6.38	0.1682	16.92	108	2.72
	500	7.08	0.1845	20.74	108	2.90
6.6 at.% Ga						
15.657	25	3.39	0.1406	7.46	113	2.83
15.610	100	3.91	0.1423	8.68	112	2.61
15.579	200	4.59	0.1481	10.50	110	2.46
15.533	300	5.28	0.1582	12.97	110	2.44
15.487	400	5.97	0.1724	15.94	110	2.61
15.471	500	6.66	0.1900	19.57	110	2.78
15.441	580	7.21	0.2050	22.82	110	2.94

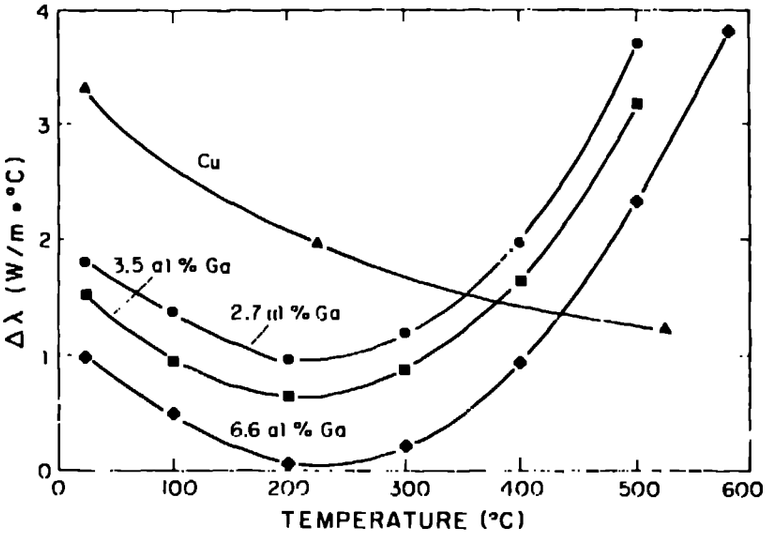

Fig. 3. The excess thermal conductivity of the three Pu-Ga alloys and the lattice conductivity of Cu as a function of temperature.

Table V. Calculated Lattice Conductivities for Pu-Ga Alloys from Scaling λ_g with $(cT)^{-1}$. ($\Delta\lambda$ and λ_g units are W/m°C)

	2.7 at.% Ga		3.5 at.% Ga		6.6 at.% Ga	
T, °C	$\Delta\lambda$	λ_g	$\Delta\lambda$	λ_g	$\Delta\lambda$	λ_g
25	1.83	1.81	1.54	1.54	1.00	1.11
100	1.39	1.62	0.96	1.38	0.52	0.99
200	0.98	1.44	0.66	1.22	0.06	0.89
300	1.21	1.31	0.89	1.12	0.21	0.80
400	1.99	1.30	1.65	1.03	0.95	0.74
500	3.72	1.12	3.20	0.96	2.35	0.69

Cu,[10] obtained from the lattice thermal conductivities of dilute Cu alloys and extrapolated to higher temperatures as 1/T. At low temperatures, $\Delta\lambda$ lies below the lattice thermal conductivity, λ_g, of Cu as one would expect for alloys. At high temperatures, however, $\Delta\lambda$ values for the alloys lie well above λ_g of Cu, this supports the belief that the excess thermal conductivity, $\Delta\lambda$, at higher temperatures is not due to lattice waves.

The lattice thermal conductivity, λ_g, should vary inversely as the square root of cT, where c is the solute concentration and T the absolute temperature.[11] At 25°C (298 K), values of $\Delta\lambda$ do indeed vary roughly as $c^{-\frac{1}{2}}$. If we identify $\Delta\lambda$ of the 3.5 at.% alloy at 25°C with λ_g, we can estimate λ_g at other temperatures and other concentrations: these estimates are given in Table V. The remaining discrepancy $\Delta\lambda_e = \Delta\lambda - \lambda$ is attributed to an electronic effect. We see that $\Delta\lambda_e$ is negative at 100 and 200°C, though this conclusion is somewhat uncertain in view of the uncertainty of estimating λ_g. However, at high temperatures $\Delta\lambda_e$ becomes clearly positive, and increases with temperature, and it seems to be relatively insensitive to composition at the highest temperatures.

Positive values of $\Delta\lambda_e$ are found in many transition metals; negative values of $\Delta\lambda_e$, or negative deviations of L from L_o at high temperatures seem to be a peculiarity of Pu. Negative deviations can be explained if the product of the density of states and the electron mobility has a maximum at the Fermi energy. In Pu the Fermi energy falls near a minimum between 5f electron subbands.[12] These electrons, however, do not necessarily contribute significantly to the electronic conductivity. The high density of states of the 5f electrons reduces the mobility of the electrons in the other bands (s, p, and d), so that the product of their density of states and mobility has a minimum at the energies where the density of states of the 5f electrons has a maximum, and a maximum near the Fermi surface, where the 5f electron density has a minimum. This could explain the low value of the Lorenz number in pure Pu. In the delta-phase alloys, the Lorenz number exceeds L_o at high temperatures; this is qualitatively similar to the behavior of the Lorenz number of many transition metals and indicates that the 5f electrons act quite differently in the alloys than in pure Pu. A complete description of the electronic transport properties must await a better understanding of the electronic structure.

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