The binary system Pu–Si: crystallochemistry and magnetic properties

P Boulet, F Wastin, E Colineau, J C Griveau and J Rebizant

European Commission, Joint Research Centre, Institute for Transuranium Elements,
Postfach 2340, 76125 Karlsruhe, Germany

E-mail: boulet@itu.fzk.de

Abstract
The crystallochemistry of the plutonium–silicon binary system is being
investigated. We report on the observation of five binary phases: $PuSi_2$ ($ThSi_2$
and AlB_2 type), PuSi (FeB type), Pu_3Si_2 (U_3Si_2 type) and Pu_5Si_3 (W_5Si_3 type).
Preliminary characterizations of the electronic properties of $PuSi_2$ ($ThSi_2$ type)
and PuSi (FeB type) were undertaken by SQUID magnetometry and electrical
resistivity measurements. $PuSi_2$ does not order magnetically down to 2 K,
whereas PuSi undergoes a ferromagnetic transition at $T_C \sim 72$ K.

1. Introduction

A systematic re-investigation of the phase relations in the actinide binary systems was
undertaken. Works on uranium [1–3] and neptunium [4, 5] systems have reported that few
systems have been extensively studied and even the uranium binary systems are not fully
known. For the transuranium systems almost nothing is known, although, due to its general
interest in nuclear technology, the plutonium binary system was found to be better described in
the literature than the corresponding uranium or neptunium systems. However, their magnetic
properties were poorly resolved or unknown. We have therefore revisited the plutonium system
and report here the first results obtained on the Pu–Si binary system.

2. Crystallochemistry

X-ray powder analyses of Pu–Si samples from the complete range of the binary phase diagram
were conducted. No new compounds in addition to those previously reported in the literature [6]
were obtained and the phase diagram reported is confirmed. As shown in table 1, our x-ray
powder and single-crystal analyses revealed the existence of five intermediate phases. Unlike
the case for other actinide–silicon systems such as U–Si and Np–Si, for plutonium the $AuCu_3$
type does not exist whereas the two defect $AnSi_{2-x}$ compounds of $ThSi_2$ and AlB_2 types
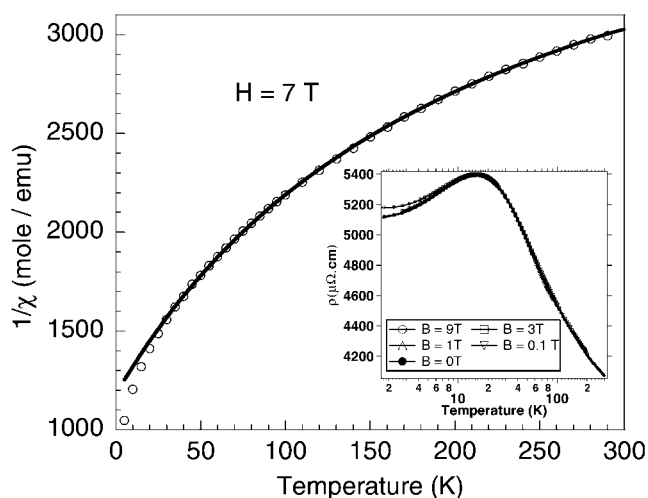
Figure 1. The temperature dependence of the inverse magnetic susceptibility of $PuSi_2$ ($ThSi_2$ type). The inset shows the temperature dependence (on a logarithmic scale) of the electrical resistivity under different fields.

Table 1. X-ray powder diffraction results on the Pu–Si binary system.

Compound	Structure	Space group	a (Å)	b (Å)	c (Å)	References
$PuSi_2$	$ThSi_2$	$I4_1/amd$	3.9707(3)		13.6809(5)	This work
			3.967(1)		13.72(3)	[7]
			3.98(1)		13.58(5)	[8]
$PuSi_2$	AlB_2	$P6/mmm$	3.8793(6)		4.0860(8)	This work
			3.875(4)		4.102(7)	[6]
PuSi	FeB	$Pnma$	7.9360(1)	3.8510(1)	5.7336(1)	This work
			7.933(3)	3.847(1)	5.727(5)	[6]
Pu_3Si_2	U_3Si_2	$P4/mbm$	7.5061(3)		4.0642(3)	This work
			7.483(2)		4.048(2)	[6]
Pu_5Si_3	W_5Si_3	$I4/mcm$	11.4035(8)		5.448(3)	This work
			11.407(5)		5.444(3)	[6]

are observed. The equiatomic compound is found to crystallize with the FeB-type form, as observed for the Np and U systems. The part with the richest plutonium concentration shows two phases, Pu_3Si_2 (U_3Si_2 type) and Pu_5Si_3 (W_5Si_3 type). It is interesting to note that except for the latter, all these phases have homologues in the uranium and neptunium systems.

3. Magnetization and transport property measurements

Magnetic susceptibility and electrical resistivity measurements were performed on bulk samples of $PuSi_2$ ($ThSi_2$ type) and PuSi (FeB type), using a Quantum Design SQUID magnetometer MPMS-7 and a PPMS-9 in the temperature range 2–300 K and in magnetic fields up to 7 and 9 T respectively.

The results of the physical property characterization of $PuSi_2$ ($ThSi_2$ type) are displayed in figure 1. Some magnetization measurements for $PuSi_2$ were already mentioned by Olsen [9] and no evidence for any magnetic transitions reported. Our measurements are in agreement with this assessment. The reciprocal of the susceptibility displayed in figure 1
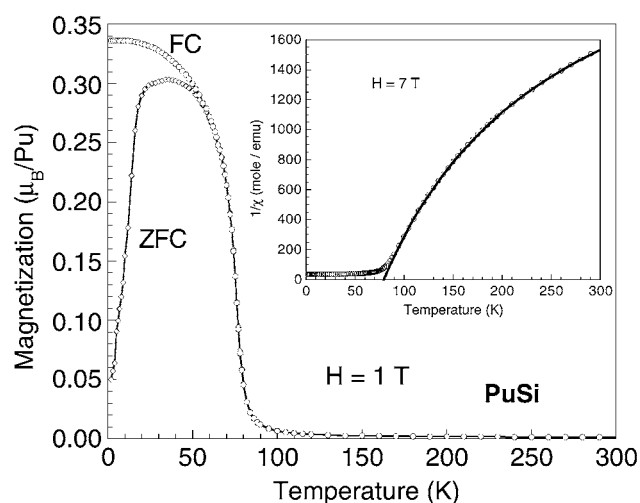
Figure 2. The thermal variation of the magnetization under 1 T of PuSi (FC and ZFC). The inset shows the fit by a Curie–Weiss law of the inverse magnetic susceptibility.

indicates a paramagnetic behaviour down to 2 K. In the higher-temperature range, the susceptibility obeys a modified Curie–Weiss law with $\mu_{eff} \sim 0.54\ \mu_B$, $\theta_p \sim -58$ K and $\chi_0 \sim 230 \times 10^{-6}$ emu mol^{-1}. The electrical resistivity curves are displayed in the inset of figure 1. The resistivity increases with decreasing temperature, goes through a broad maximum around 18 K and then decreases, although no evidence of magnetic ordering is seen in the magnetic susceptibility curves. This would suggest spin fluctuation behaviour and requires further study at low temperature. The resistivities measured in fields up to 9 T show little change. A slight increase of the resistivity value and an upturn at low temperature may be observed which could also suggest that the compound undergoes magnetic ordering at lower temperatures.

In the case of PuSi, no previous magnetic measurements were reported. Our magnetization curves are displayed in figure 2. The magnetization (field cooled (FC) and zero-field cooled (ZFC)) versus temperature under an applied magnetic field of 1 T indicate the onset of ferromagnetic-like order below $T_C = 72$ K. The inset shows the temperature dependence of the inverse magnetic susceptibility χ^{-1} under 7 T. At high temperature, the curve follows a modified Curie–Weiss law with $\mu_{eff} \sim 0.72\ \mu_B$, $\theta_p \sim 79$ K and $\chi_0 \sim 357 \times 10^{-6}$ emu mol^{-1}. The θ_p-value determined is close to T_C which indicates the absence of crystal field effects in PuSi. The general feature of the resistivity curve, displayed in figure 3, is a metal-like behaviour. At the magnetic transition temperature the resistivity sharply decreases with decreasing temperature. The change of the slope $(\mathrm{d}\rho/\mathrm{d}T)$ shows maxima which corroborate the Curie temperature derived from the magnetization data. In the ordered regime, the resistivity follows a T^2-law consistent with ferromagnetic ordering.

4. Conclusions

The Pu–Si binary phase diagram was re-investigated. The five phases, two defect phases, PuSi$_2$ (ThSi$_2$ and AlB$_2$ type), and three other phase types, PuSi (FeB type), Pu$_3$Si$_2$ (U$_3$Si$_2$ type) and Pu$_5$Si$_3$ (W$_5$Si$_3$ type), previously reported in the literature, were confirmed and no new phases observed. The first magnetic and transport property measurements for PuSi$_2$ (ThSi$_2$ type) and
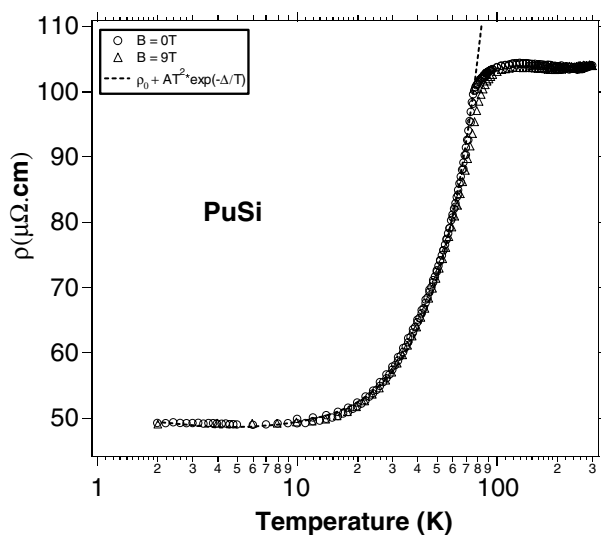
Figure 3. The temperature dependence (on a logarithmic scale) of the electrical resistivity under 1 and 9 T for PuSi. The line displays the fit by a T^2-law.

PuSi are reported. PuSi is found to order ferromagnetically around 72 K whereas $PuSi_2$ does not show magnetic ordering, but the resistivity suggests spin fluctuation behaviour. The values of the effective moments of $PuSi_2$ and PuSi are consistent with a $5f^5$ electronic configuration, i.e. a Pu^{3+} charge state. It is interesting to note that for the USi_2 and $NpSi_2$ homologues, the values of the effective moments indicated respectively $5f^3$ and $5f^4$ configurations, i.e. U^{3+} and Np^{3+}.

Acknowledgments

References

[1] Remschnig K, Le Bihan T, Noël H and Rogl P 1992 *J. Solid State Chem.* **97** 391
[2] Troc R, Noël H and Boulet P 2002 *Phil. Mag.* B **82** 805
[3] Boulet P and Noël H 1998 *Solid State Commun.* **107** 135
[4] Boulet P, Bouëxière D, Rebizant J and Wastin F 2001 *J. Solid State Chem.* **156** 313
[5] Boulet P, Bouëxière D, Rebizant J and Wastin F 2003 *J. Alloys Compounds* **349** 172
[6] Land C C, Johnson K A and Ellinger F H 1965 *J. Nucl. Mater.* **15** 23
[7] Ellinger F H 1961 *Metal Plutonium* ed A S Coffinberry and W N Miner (Chicago, IL: The University of Chicago Press) ch 25, pp 240–54
[8] Zachariasen W H 1949 *Acta Crystallogr.* **2** 94
[9] Olsen C E 1960 *J. Appl. Phys.* **31** 340