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Crystal structure and magnetic properties of the uranium germanide U_5Ge_4

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Abstract

The crystal structure of the uranium germanide U_5Ge_4 was determined and refined from single crystal X-ray diffraction data to R = 0.043, Rw = 0.054. U_5Ge_4 crystallizes in the hexagonal Ti_5Ga_4 ($P6_3/mcm$) structure type (filled up Mn_5Si_3 type) with the following lattice parameters: $a = 8.744(4)$ Å and $c = 5.863(2)$ Å. Investigation of neighbouring compositions, using X-ray powder diffraction refinements and microprobe analysis, revealed that the binary compound U_5Ge_4 is in equilibrium with the other binary UGe (ThIn type) and U metal dissolving 3% of germanium, whatever the annealing temperature in the range of 1000–1300°C. These results rule out the existence of the binary compositions U_5Ge_3 and U_7Ge, which were previously reported. Magnetic measurements on an annealed polycrystalline powder sample of U_5Ge_4 indicate nearly temperature independent paramagnetic behaviour down to 2 K. © 1997 Elsevier Science S.A.

Keywords: Uranium germanides; Crystal structure; Magnetic properties

1. Introduction

We have recently clarified the most germanium rich part of the binary U–Ge phase diagram by single crystal X-ray diffraction showing [1] that UGe_2 crystallizes in the orthorhombic $ZrGa_2$ structure type instead of the $ZrSi_2$ type as was previously claimed [2]. The alloy with nominal composition U_3Ge_4 [2] was also shown to be a two phase mixture, i.e. UGe (ThIn type) [3] and U_3Ge_5 (AlB_2 type) [4]. In the other part of this phase diagram two binary compounds were reported: U_5Ge_3 [2] which was claimed to crystallize with the Mn_5Si_3 structure type and U_7Ge [5] without any X-ray characterisation for the latter, and recently, a superconductive transition has been observed for these two compounds [6] at $T_c = 0.99$ K and 1.40 K, respectively. We report here our investigations by X-ray and microprobe analysis of the region of the binary U–Ge phase diagram with 51–100% U content.

2. Experimental

The polycrystalline ingots were obtained by arc melting stoichiometric amounts of the constituent elements under a high purity argon atmosphere on a water-cooled copper hearth, using a Ti–Zr alloy as an oxygen getter. The materials were used in the form of ingots as supplied by Merck AG. (uranium, 99.8% pure, germanium, 99.999% pure). In order to ensure homogeneity, the arc melted buttons were turned over and remelted three times, with weight losses lower than 0.1%. To improve the quality of the crys-

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tallites, the arc melted buttons were wrapped in tantalum foils and annealed in the temperature range of 1300–1000°C in a high frequency furnace for several hours.

X-ray powder patterns were collected on an INEL CPS 120 curve multidetector diffractometer, after mixing the samples with pure silicon as standard.

Electronic metallographic examination was performed on some samples, using a scanning electron microscope and a semiquantitative microanalysis of the phases was carried out by an energy-dispersive X-ray microanalyzer.

The single crystal X-ray diffraction data were collected on an Enraf-Nonius CAD-4 four circle diffractometer with the experimental conditions listed in Table 1. The data processing was carried out on a VAX 3100 computer using the MOLEN package [7].

3. X-ray structural determination

Single crystals suitable for crystal structure determination were found in the annealed sample with 63% of U content. The hexagonal lattice constants, determined from least squares analysis of the setting angle of 25 X-ray reflections have the values: a = 8.744(4) Å, c = 5.863(2) Å. They differ significantly from those previously reported [2] for U_5Ge_3 (a = 8.58 Å, c = 5.79 Å), although the c/a ratio remains unchanged (0.670). The X-ray diffraction intensities were corrected for Lorentz and polarisation effects and an absorption correction was applied using the program *psiscan*. The structure was successfully refined in the centrosymmetric space group $P6_3/mcm$. The positions of two independent uranium atoms in 6g and 4d Wyckoff positions were derived using direct methods (*program multan*) and the positions of two independent germanium atoms in 6g and 2b were obtained from subsequent difference Fourier calculations. The composition of the investigated crystal is thus U_5Ge_4 and no deviations from full occupancies of the atomic sites could be observed. Final refinement, including anisotropic parameters, leads to the conventional factors R(F) = 0.043 and Rw = 0.054. This result reveals that U_5Ge_4 crystallizes in the Ti_5Ga_4 structure type (filled structure of the Mn_5Si_3 type) as was also reported for the stannide U_5Sn_4 [8] and for the antimonide U_5Sb_4 [9]. A view of the structure of U_5Ge_4 is displayed in Fig. 1, the positional parameters standardized using the program *Structure Tidy* [10] are listed in Table 2 and the interatomic distance are in Table 3. Each uranium atom U(1) is coordinated by 6 Ge(1) atoms and two other U(1) atoms with a rather short distance of 2.93 Å. Such a short distance close to that found in U metal (2.75 Å in αU and 3.03 Å in βU) was also observed in the other binary UGe [3] (ThIn structure type). These structures are characterized by straight –U–U– chains along the shortest axis, here the c axis of the hexagonal cell. In fact, both the Ti_5Ga_4 and ThIn structure types were also observed in the binary U–Sn system [8].

Table 1
Crystallographic data for U_5Ge_4

Formulae	U_5Ge_4
Space group	$P6_3/mcm$, n°193
Crystal dimensions (mm)	0.06 × 0.06 × 0.12
Linear absorption coefficient (cm^{-1})	1134.7
Lattice parameters (from CAD4):	
a (Å)	8.744(4)
c (Å)	5.863(2)
Unit-cell volume ($Å^3$)	388.2(2)
Calculated density ($g\ cm^{-3}$)	12.67
Formula per unit cell	Z = 2
Formula weight (g)	1480.5
Scan range	$1° < \theta < 40°$
hkl range	$0 < h < 15$
	$0 < k < 15$
	$0 < l < 10$
Total observed reflections	975
Independent reflections with $I > 3\sigma$	561
Secondary extinction coefficient	$1.97\ 10^{-8}$, corr. = $1/(1 + gI_c)$
Number of variables	14
Reliability factors:	
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.043
$R_w = [\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma_w\lvert F_o\rvert^2]^{1/2}$	0.054
Goodness of fit GOF	1.15

Two samples with the previously reported compositions U_5Ge_3 and U_7Ge were analysed by SEM either directly after the arc melting process, or after annealing at 1300 and 1000°C, respectively. The Figs. 2 and 3 show representative microstructures of these compositions, revealing nothing but U_5Ge_4 and U metal which solubilise 3% of germanium. The X-ray powder analyses of these samples by least squares refinement of the lattice parameters are listed in Table 4. These refinements reveal a small but significant homogeneity range corresponding to an increase of the lattice parameters with the uranium content. This is in agreement with our microprobe analyses indicating a maximum variation of 2% of the uranium content, i.e. 57.5% instead of 55.5% of uranium for pure U_5Ge_4. The formation of U_5Ge_3 (63% of uranium) was not observed using SEM or X-ray methods. Thus the compositions U_5Ge_3 and U_7Ge should be considered as two-phase-regions.

On account of these results, the question as to why there is such a large difference between the lattice parameters determined for U_5Ge_4 and those previously reported for the composition U_5Ge_3 [2] is still open. It should be pointed out that the c/a ratio is quite different for the two structure types. For in-

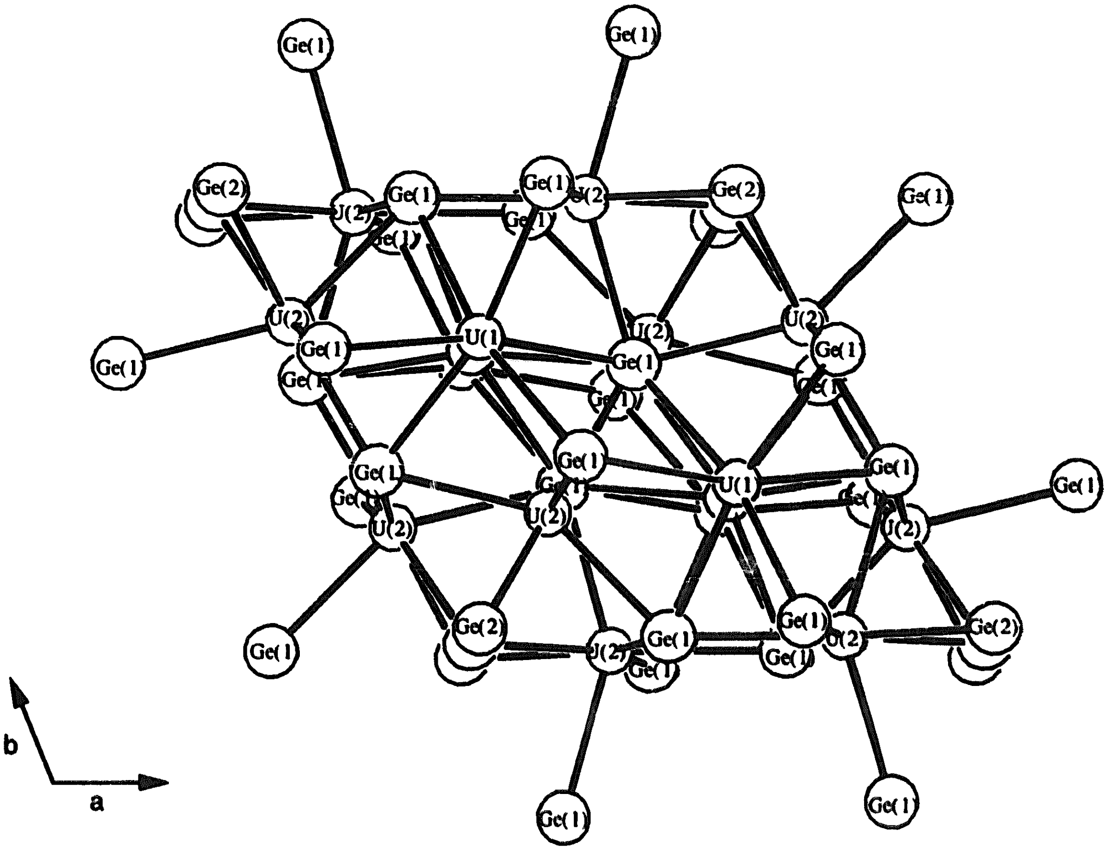

Fig. 1. Ortep view of the structure U_5Ge_4.

Table 2
Atomic parameters for U_5Ge_4

Atom	U(1)	U(2)	Ge(1)	Ge(2)
Site	4d	6g	6g	2b
x	1/3	0.2823(1)	0.6217(4)	0.0
y	2/3	0.0	0.0	0.0
z	0.0	1/4	1/4	0.0
B_{11}	0.37(2)	0.44(2)	0.59(6)	0.32(7)
B_{22}	B_{11}	0.43(3)	0.76(9)	B_{11}
B_{33}	0.96(3)	0.85(2)	1.05(7)	0.5(1)
B_{12}	B_{11}	B_{22}	B_{22}	B_{11}
B_{eq}(Å^2)	0.57(1)	0.57(1)	0.78(5)	0.37(4)

$B_{13} = B_{23} = 0.0$.
The form of the anisotropic displacement parameter is exp $[-1/4(h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3))]$ where a^*, b^* and c^* are reciprocal lattice constants.

Table 3
Inter-atomic distances (Å) for U_5Ge_4

U(1)	2U(1)	2.931(0)	U(2)	2Ge(2)	2.870(1)
	6Ge(1)	3.107(1)		1Ge(1)	2.968(3)
	6U(2)	3.484(1)		2Ge(1)	2.978(2)
				2Ge(1)	3.049(1)
				4U(1)	3.484(1)
				4U(2)	3.832(1)
Ge(1)	1U(2)	2.968(3)	Ge(2)	6U(2)	2.870(1)
	2U(2)	2.978(2)		2Ge(2)	2.931(0)
	2U(2)	3.049(1)		6Ge(1)	3.618(3)
	4U(1)	3.107(1)			
	2Ge(2)	3.618(3)			
	2Ge(1)	3.622(4)			

stance, as shown in the Table 5, the c/a ratio is always equal to 0.67 for the filled structure (Ti_5Ga_4 type), and 0.69 for the empty structure (Mn_5Si_3 type). We found the ratio 0.67 for our samples which is exactly the same as for U_5Ge_3. We can postulate that either the reported lattice parameters were measured with a very large uncertainty almost forty years ago, or the change in lattice parameters is due to the presence of impurities. It is worth mentioning here that we have recently discovered a new ternary germanide U_3TiGe_5 [13] which crystallizes with the anti-Ti_5Ga_4 structure type (U_3TiSb_5 type [14]) and has quite similar lattice parameters ($a = 8.495(1)$ Å and $c = 5.711(1)$ Å) to those reported for U_5Ge_3.

4. Magnetic behaviour

Magnetic measurements on an annealed polycrystalline sample were performed using a superconducting quantum interference device (SQUID) magne-

Table 4
X-ray powder analyses of different U–Ge compositions

Composition		Phase analysis	Lattice parameters (Å)					Heat treatment
%U	%Ge		a	b	c	c/a	V	
50	50	UGe(ThIn type)	9.826(5)	8.941(2)	5.849(2)			1300°C
52	48	UGe(ThIn type) U_5Ge_4(Ti_5Ga_4 type)	9.831(6) 8.739(5)	8.943(5)	5.846(1) 5.859(2)	 0.670	 387.5	1300°C
55	44	U_5Ge_4(Ti_5Ga_4 type)	8.744(1)		5.863(2)	0.670	388.0	1300°C
63	37	U_5Ge_4(Ti_5Ga_4 type)	8.748(7)		5.917(6)	0.676	392.1	Arc melted
63	37	U_5Ge_4(Ti_5Ga_4 type)	8.770(5)		5.926(6)	0.675	394.7	1300°C
88	12	U_5Ge_4(Ti_5Ga_4 type)	8.775(4)		5.927(3)	0.675	395.2	1000°C

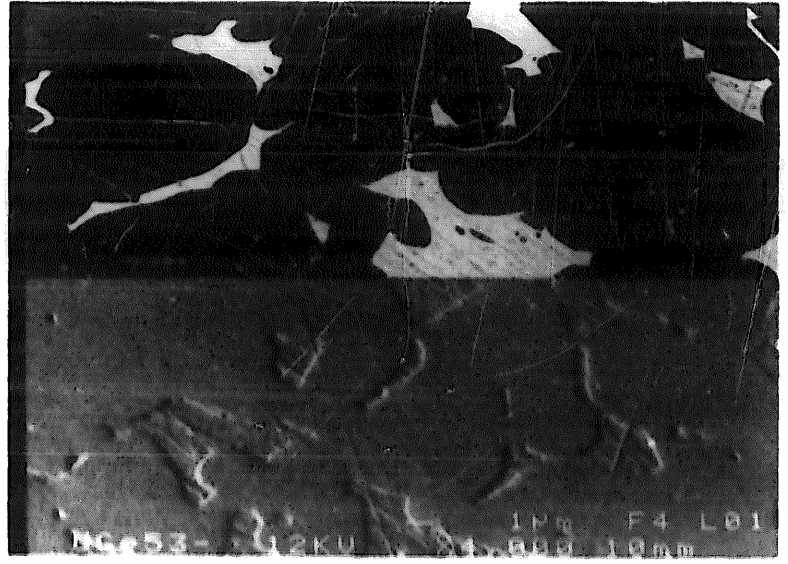

Fig. 2. Microstructure of the composition U_5Ge_3 annealed at 1300°C. The top view shows Uranium (white) dissolving 3% of Ge and U_5Ge_4 (black). The lower view shows the difference in hardness of these two phases, as revealed from polishing.

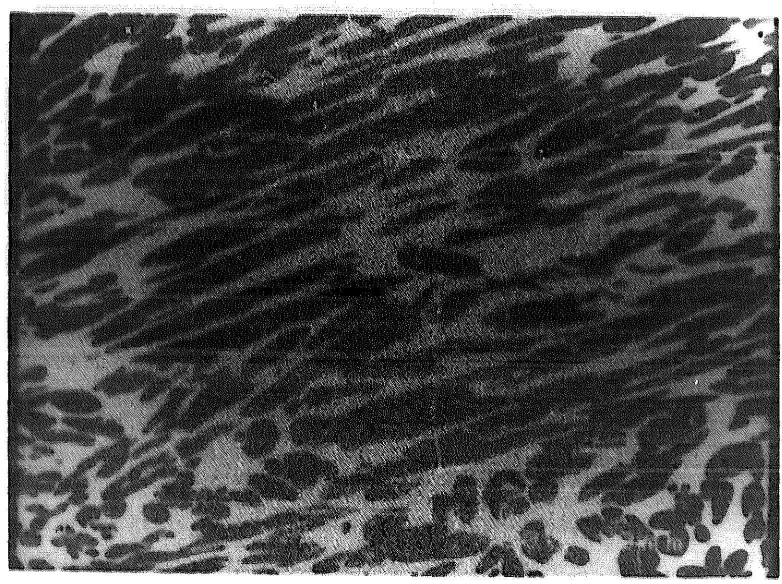

Fig. 3. Microstructure of the composition U_7Ge annealed at 1000°C. U_5Ge_4 (black) with 57.5% of uranium and U metal (white) with 3% of Germanium.

Table 5
Comparison of the c / a ratio in the Ti_5Ga_4 and Mn_5Si_3 structure type

Structure type	Compound	Lattice parameters (Å)			References
		a	c	c/a	
Ti_5Ga_4	U_5Ge_4	8.744	5.863	0.670	This work
	U_5Sn_4	9.327	6.230	0.668	[8]
	U_5Sb_4	9.237	6.211	0.672	[9]
	Th_5Sn_4	9.643	6.445	0.668	[11]
	Th_5Pb_4	9.741	6.585	0.676	[12]
Mn_5Si_3	'U_5Ge_3'	8.58	5.75	0.670	[2]
	Th_5Sn_3	9.332	6.477	0.694	[11]
	Th_5Pb_3	9.411	6.521	0.693	[12]

tometer in the temperature range 2–300 K and in an applied magnetic field of 4 kG.

As shown in Fig. 4, U_5Ge_4 exhibits nearly temperature-independent-paramagnetic behaviour down to 2 K. This feature could be explained by direct overlap between the 5f shells of uranium U(1) along the c axis, according to the short distance between each uranium U(1) atom, and delocalisation of the U(2) 5f electrons, probably occurring via hybridization effects with the s-p shells of the surrounding germanium atoms. However, magnetic ordering with nearly the same magnetic moment for both U(1) and U(2) sublattices was observed in the isostructural antimonide U_5Sb_4 [9] by neutron diffraction, and we have shown recently [15] that U_5Sn_4 also exhibits ferromagnetic ordering. The U(1)–U(1) distance is shorter in the germanide (2.93 Å) than in the antimonide (3.10 Å) or in the stannide (3.11 Å), but all of them are significantly lower than the Hill limit of 3.4 Å below which cooperative magnetic ordering is very rarely encountered due to the delocalization effect.

The onset of superconductivity at lower temperatures as observed [5] for the composition U_5Ge_3 at $T = 0.99$ K, should be checked in U_5Ge_4 in order to ascertain the intrinsic nature of the transition, as U metal is itself a superconductor.

5. Conclusions

The previously reported binary uranium germanides U_5Ge_3 and U_7Ge were not observed in the course of this study either by X-ray powder and crystal analyses or by microprobe experiments. The corresponding samples are mixtures of the binary U_5Ge_4 and U metal dissolving 3% of germanium, whatever the annealing temperature. U_5Ge_4 was shown from single crystal data to crystallize with the Ti_5Ga_4 structure type. It exhibits nearly Temperature-Independent-Paramagnetic behaviour down to 2 K.

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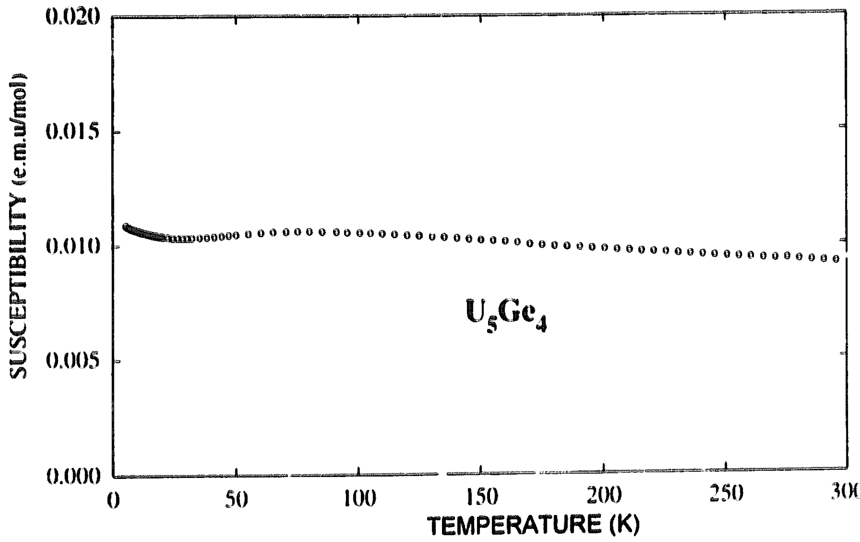

Fig. 4. Inverse susceptiblity vs. temperature of an annealed polycrystalline sample of U_5Ge_4.

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