

# Crystal Structure and Magnetism of Novel Compounds $U_3(M', M'')_5$ , $M' = Al, Ga, M'' = Si, Ge$

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Compounds with the formula  $U_3M'_2M''_3$  have been synthesized for  $M' = Al, Ga$  and  $M'' = Si, Ge$ . The crystal structures of  $U_3Al_2Si_3$  and  $U_3Al_2Ge_3$  have been determined from single crystal X-ray counter data and were found to be isopointal with the  $Cr_5B_3$  type. Atom order has been refined for  $U_3Al_2Ge_3$  ( $a = 0.77579(13)$  nm,  $c = 1.10357(28)$  nm), revealing a random occupation for 8Ge + 8Al in the 16l sites and 4Ge in the 4c sites (space group  $I4/mcm-D_{4h}^{18}$ , No. 140,  $Z = 4$ ). For 317 (276) reflections ( $|F_O| > 3\sigma$ ) the obtained residual values,  $R_x = \Sigma|\Delta F|/\Sigma|F_O|$ , were  $R_x = 0.057$  for  $U_3(Al, Si)_5$  and  $R_x = 0.074$  for  $U_3Al_2Ge_3$ , respectively. Isotypism with the crystal structure of  $U_3Al_2Ge_3$  ( $Cr_5B_3$ -type derivative) was confirmed from X-ray powder diffraction analysis for the novel compounds  $U_3Ga_2Si_3$  and  $U_3Ga_2Ge_3$ . Whereas the compounds  $U_3Al_2Ge_3$  and  $U_3Ga_2(Si, Ge)_3$  were obtained at the given stoichiometry, a small homogeneous range was observed for  $U_{3+y}(Al_{1-x}Si_x)_{5-y}$  ranging in as-cast alloys from  $x = 0.64$  to  $x = 0.68$  and  $0 \leq y \leq 0.04$ .  $U_3(Al, Si)_5$  is a high-temperature compound only observed in as-cast alloys and transforms on annealing at temperatures below  $\sim 1000^\circ C$ . For the homologous phases  $U_3Al_2Ge_3$  and  $U_3Ga_2(Si, Ge)_3$  no transformation has been observed in the range from  $600^\circ C$  to the melting. © 1994 Academic Press, Inc.

## 1. INTRODUCTION

In continuation of our research (1) related to proliferation-resistant research reactor fuel materials based on U-Si-Al, this paper focuses on the true crystal structure of ternary compounds near the composition  $U_2AlSi_2$  earlier reported to exist in two modifications with undetermined crystal structure (2, 3) and/or ferromagnetic UAlSi (and isotypic UAlGe), whose powder patterns were tentatively indexed on the basis of a hexagonal unit cell in (4), a tetragonal cell in (5) or an orthorhombic unit cell in (6).

## 2. EXPERIMENTAL DETAILS

The ternary samples, each with a total weight of ca. 1 g, were prepared by argon arc melting proper weightings of the constituent elements on a water-cooled copper

hearth. Nuclear grade uranium was used in the form of U platelets from Merck, Dramstadt, FRG which were surface cleaned in concentrated  $HNO_3$  prior to use. Aluminum was in the form of a 99.999% wire from the Alpha Division Ventron Corp., USA. Gallium was supplied in the form of 99.99% pure ingots from Alcan Electronics, Switzerland, and silicon and germanium were in the form of lumps with 99.999 mass% minimal purity from Alpha Ventron Corp., Karlsruhe, FRG. In order to ensure homogeneity and to minimize weight losses due to vaporization, the samples were remelted several times under the smallest possible electric current. Weight losses generally were less than 0.2%. The reguli were then wrapped in Mo-foil or placed in small  $Al_2O_3$  crucibles, sealed in evacuated quartz tubes, annealed for 72 hr at  $1000^\circ C$ , 100 hr at  $900^\circ C$ , or in some cases for 250 hr at  $600^\circ C$ , respectively, and quenched by submerging the quartz capsules in cold water.

Precise lattice parameters and standard deviations were obtained by a least squares refinement using Guinier Huber  $CuK\alpha_1$  X-ray powder data at room temperature employing an internal standard of 99.9999% pure Ge ( $a_{Ge} = 0.5657906$  nm).

Magnetic properties were studied employing a SHE-SQUID magnetometer in the temperature range from 5 to 300 K and in fields up to 3 Tesla.

Samples used for EMPA analysis have been mounted in epoxy resin and have been ground with progressively finer diamond paste down to  $\frac{1}{4}$   $\mu m$ . After sputtering a thin C-layer to the surface, homogeneous sample areas have been quantitatively analyzed monitoring the  $UM\alpha$ ,  $SiK\alpha$ , and  $AlK\alpha$  radiation at a sample current of 10 nA and an accelerating voltage of 15 kV.

## 3. RESULTS AND DISCUSSION

### 3.1. Structure Determination

Rather small but isodimensional single crystal fragments were selected by mechanical fragmentation of the

TABLE 1  
Crystal Data for  $U_3(Al_{1-x}Si_x)_5$  and  $U_3(Al_{1-x}Ge_x)_5$

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
$U_3Al_{1.76}Si_{3.24}$ , $U_3Al_2Ge_3$ -type, (isopointal with $Cr_5B_3$ -type) <sup>a</sup> Space group $I4/mcm-D_{4h}^{18}$ , No. 140, <i>Z</i> = 4; origin at center $a = 0.76183(8)$ nm, $c = 1.07751(29)$ nm, $V = 0.6254(2)$ nm <sup>3</sup> , $c/a = 1.414$ , $\rho_x = 8.22$ Mgm <sup>-3</sup>										
U1	4 <i>a</i>	0	0	$\frac{1}{4}$	0.0029(3)	0.0029(3)	0.0254(7)	0	0	0
U2	8 <i>h</i>	0.3396(1)	0.8396(1)	0	0.0068(2)	0.0068(2)	0.0006(2)	-0.0030(4)	0	0
Si1	4 <i>c</i>	0	0	0	0.013(3)	0.013(3)	0.031(7)	0	0	0
0.56Si + 0.44Al	16 <i>l</i>	0.6432(6)	0.1432(6)	0.3103(5)	0.006(1)	0.006(1)	0.004(2)	0.001(2)	-0.001(1)	-0.001(1)
$U_3Al_2Ge_3$ , $U_3Al_2Ge_3$ -type, (isopointal with $Cr_5B_3$ -type) <sup>b</sup> Space group $I4/mcm-D_{4h}^{18}$ , No. 140, <i>Z</i> = 4; origin at center $a = 0.77579(13)$ nm, $c = 1.10357(28)$ nm, $V = 0.6642$ nm <sup>3</sup> , $c/a = 1.423$ , $\rho_x = 8.40$ M gm <sup>-3</sup>										
U1	4 <i>a</i>	0	0	$\frac{1}{4}$	0.0093(5)	0.0093(5)	0.031(1)	0	0	0
U2	8 <i>h</i>	0.3404(2)	0.8404(2)	0	0.0106(4)	0.0106(4)	0.0115(5)	-0.0022(7)	0	0
Ge1	4 <i>c</i>	0	0	0	0.011(2)	0.011(2)	0.008(2)	0	0	0
0.50(1) Ge +0.50(1)Al	16 <i>l</i>	0.6460(4)	0.1460(4)	0.3100(3)	0.015(1)	0.015(1)	0.013(1)	0.006(2)	-0.003(1)	-0.003(1)

Note. Anisotropic thermal factors are expressed as  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

<sup>a</sup> Correction for isotropic secondary extinction (Zachariasen) was  $g = 3.7 \times 10^{-7}$ . Residual values:  $R = 0.57$ ,  $R_w = 0.056$ ,  $GOF = 1.8$ .

<sup>b</sup> Correction for isotropic secondary extinction (Zachariasen) was  $g = 6.5 \times 10^{-7}$ . Residual values:  $R = 0.074$ ,  $R_w = 0.088$ ,  $GOF = 2.2$ .

arc melted buttons  $U_{37.5}Al_{25}Si_{37.5}$  and  $U_{37.0}Al_{26.0}Ge_{37.0}$ , respectively. X-ray intensity data were collected on an automatic CAD4-four-circle diffractometer in one octant of the reciprocal space to a limit of  $\sin\Theta/\lambda = 9.0$  nm<sup>-1</sup> for  $U_3(Al,Si)_5$  and  $\sin\Theta/\lambda = 8.0$  nm<sup>-1</sup> for  $U_3(Al,Ge)_5$  using monochromatized MoK $\alpha$  radiation. Sets of 405 and 276 symmetry independent reflections were obtained for  $U_3(Al,Si)_5$  and  $U_3(Al,Ge)_5$ , respectively, by averaging symmetry equivalent reflections out of a total number of 1110 (825) recorded intensities; all observed intensities [ $315$  for  $|F_O| > 2\sigma(F_O)$  for Si and  $276$  for  $|F_O| > 3\sigma(F_O)$  for Ge] were used in the structure refinement. An empirical absorption correction was applied, using  $\Psi$ -psi scans of four independent reflections. The crystallographic data are summarized in Table 1. Analysis of the recorded reflections revealed a body-centered tetragonal pseudo-cubic lattice geometry. The only set of characteristic extinctions observed was  $(0kl)$  for  $k, l = 2n + 1$ ; this observation is essentially consistent with the centrosymmetric types of space group  $I4/mcm$  and/or the noncentrosymmetric types  $I4cm$ ,  $I422$ , or  $I4c2$  with high Laue symmetry.

The prominent peaks of a three-dimensional Patterson map  $P(u, v, w)$  for both crystals were all found to be compatible with U1 in 4*a* and U2 in the 8*h* sites of the centrosymmetric space group  $I4/mcm$ . The positions of the light atoms were clearly resolved from a difference Fourier map  $F_O - F_U$ ; however, due to the practically identical scattering power of Al, Si atoms, further resolu-

TABLE 2  
Interatomic Distances (nm) for  $U_3Al_{1.76}Si_{3.24}$   
and  $U_3Al_2Ge_3$

U1:	2 Si1	0.2694	U1:	2 Ge1	0.2759
	8 Si,Al	0.3000		8 Ge,Al	0.3044
	(8 U2)	0.3930)		(8 U2)	0.4015)
U2:	2 Si1	0.2861	U2:	2 Ge1	0.2917
	2 Si,Al	0.2942		2 Ge,Al	0.2991
	4 Si,Al	0.3089		4 Ge,Al	0.3167
	(2 Si,Al)	0.3349)		(2 Ge,Al)	0.3424)
	1 U2	0.3456		1 U2	0.3502
	(4 U1)	0.3930)		(4 U1)	0.4015)
	(4 U2)	0.4046)		(4 U2)	0.4125)
Si1:	2 U1	0.2694	Ge1:	2 U1	0.2759
	4 U2	0.2861		4 U2	0.2917
	(8 Si,Al)	0.3572)		(8 Ge,Al)	0.3636)
Si,Al:	1 Si,Al	0.2539	Ge,Al:	1 Ge,Al	0.2624
	2 Si,Al	0.2643		2 Ge,Al	0.2638
	1 U2	0.2942		1 U2	0.2991
	2 U1	0.3000		2 U1	0.3044
	(1 Si,Al)	0.3086)		2 U2	0.3167
	2 U2	0.3089		(1 Ge,Al)	0.3204)
	(1 U2)	0.3349)		(1 U2)	0.3424)
	(2 Si1)	0.3572)		(2 Ge1)	0.3636)
	(4 Si,Al)	0.4088)		(4 Ge,Al)	0.4194)
	(1 Si,Al)	0.4142)		(1 Ge,Al)	0.4201)

Note. Distances shown in parentheses are beyond first neighbor interactions.

tion in atom distribution has been attempted for the isotopic U–Al–Ge compound. From Fourier and difference Fourier synthesis, germanium atoms unambiguously could be located in the 4c sites and the remaining germanium in a random distribution with aluminium in the 16l positions.

This refinement of the Al, Si, or Ge atom occupations in both crystal structures confirms those compositions of the compounds where homogeneous samples were obtained (see also Table 3). Atom distribution (Al/Ge) in the 16l sites were refined via the occupancy parameter of 0.703(6) Ge which calculates 0.5 Ge + 0.5 Al assuming full occupation of the site. A corresponding situation was inferred for the homologous and isotopic silicon containing compound yielding 0.56 Si + 0.44 Al for the 16l position in close accordance with the homogeneous sample  $U_3Al_{1.76}Si_{3.24}$  of identical lattice parameters.

With this structure model the intensity data for both single crystals U–Al–Si and U–Al–Ge were refined using the CAD-4 full matrix least-squares program system. Various weighting schemes had no significant influence on the *R*-values obtained nor on the atom parameters de-

rived. The weights used were based upon counting statistics  $\omega_i = 1/\sigma(F_i)^2$ , and intensities were further corrected for isotropic secondary extinction.

The final *R*-values calculated with anisotropic thermal parameters were *R* = 0.057 for  $U_3Al_{1.76}Si_{3.24}$  and *R* = 0.074 for  $U_3Al_2Ge_3$ . The final positional and thermal parameters are given in Table 1; for interatomic distances up to 0.45 nm see Table 2. A listing of  $F_O$  and  $F_C$  data may be obtained on request.

### 3.2. Description of the Crystal Structure of $U_3Al_2Ge_3$

A presentation of the crystal structure of  $U_3Al_2Ge_3$  is shown in Fig. 1. as seen in the three-dimensional view also displaying the rather anisotropic thermal behavior of the U1, U2, Si1 atoms which essentially confirms the strong interactions U1–Si1 (Ge1) and U2–Si1 (Ge1) along rather short interatomic distances when compared to the sum of metal radii (see Table 2). As a characteristic feature, uranium atoms U1 are found in antiprismatic coordination each at the center of an Archimedean antiprism [(Al,Si)<sub>8</sub>]U1 bicapped by two silicon atoms Si1. These

TABLE 3  
Isotopic Compounds  $U_3(M'_{1-x}M''_x)_5$  ( $M' = Al, Ga; M'' = Si, Ge$ ) and Homogeneity Range for  $U_3(Al, Si)_5$

Nominal composition (at.%)	Phase analysis	Structure type	Lattice Parameters (nm)				Microprobe analysis (at.%) U–Al–Si
			<i>a</i>	<i>c</i>	<i>c/a</i>	<i>V</i>	
U–Al–Si							
$U_{37.5}Al_{25.0}Si_{37.5}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76369(7)	1.07656(26)	1.410	0.6279(2)	
	$U(Al, Si)_2$	$MgCu_2$	Traces				
$U_{33.2}Al_{33.6}Si_{33.2}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76184(10)	1.07752(42)	1.414	0.6254(3)	
	$U(Al, Si)_3$	$AuCu_3$	0.42319(4)				0.07579(1)
$U_{45.5}Al_{22.9}Si_{31.6}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76495(16)	1.08221(51)	1.415	0.6333(4)	
	$U(Al, Si)_2$	$MgCu_2$	0.77401(8)				0.4637(1)
	$U_3Si_2$	$U_3Si_2$	Traces				
$U_{44.0}Al_{18.0}Si_{38.0}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76376(19)	1.08183(74)	1.416	0.6308(5)	
	$USi_{1.88}(Al)$	Traces					
$U_{40.0}Al_{20.1}Si_{39.9}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76409(30)	1.08086(41)	1.415	0.6310(5)	
	$U_3Si_2$	$U_3Si_2$	Traces				
$U_{35.0}Al_{25.0}Si_{40.0}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76182(8)	1.07765(33)	1.415	0.6254(2)	
	$U(Al, Si)_3$	$AuCu_3$	Traces				
$U_{37.0}Al_{26.0}Si_{37.0}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76183(8)	1.07751(29)	1.414	0.6245(2)	
	$U(Al, Si)_2$	$MgCu_2$	Traces				
$U_{44.4}Al_{11.5}Si_{44.1}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76291(28)	1.07924(62)	1.415	0.6281(6)	
	$USi$	$FeB, USi$	Traces				
$U_{37.0}Al_{13.0}Si_{50.0}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76202(8)	1.07895(34)	1.416	0.6265(2)	39.6(2)–19.4(2)–41.0(3)
	$U(Al, Si)_{1.88}$	$GdSi_2$					36.2(4)–8.7(7)–55.1(5)
$U_{32.0}Al_{40.0}Si_{28.0}$	$U_3(Al, Si)_5$	$U_3Al_2Ge_3$	0.76184(8)	1.07761(30)	1.414	0.6254(2)	39.5(2)–22.2(2)–38.3(3)
	+ eutectic						
U–M'–M''							
$U_{37.5}Ga_{22.0}Si_{40.5}$	$U_3(Ga, Si)_5$	$U_3Al_2Ge_3$	0.76348(11)	1.08001(27)	1.415	0.6295(2)	
$U_{37.0}Al_{26.0}Ge_{37.0}$	$U_3(Al, Ge)_5$	$U_3Al_2Ge_3$	0.77579(13)	1.10357(28)	1.423	0.6642(3)	
$U_{37.5}Ga_{22.0}Ge_{40.5}$	$U_3(Ga, Ge)_5$	$U_3Al_2Ge_3$	0.77318(12)	1.10033(62)	1.423	0.6578(4)	

TABLE 4  
Evaluation of the Powder Pattern of  $U_2AlSi_2$  Published in Ref. (2)

Ref. (2)			This evaluation											
			$U_3Al_2Si_3$						$UAl_2(Si)$			$U_3Si_2$		
$2\Theta_{obs.}$	$d_{obs.}$	$I_{100}$	$h$	$k$	$l$	$d_{calc.}$	$I_{calc.}$	$h$	$k$	$l$	$h$	$k$	$l$	
16.38	5.407	10	{	0	0	2	5.400	12						
				1	1	0	5.393	6						
19.92	4.453	4							1	1	1			
21.94	4.048	4												
23.27	3.819	49		1	1	2	3.816	64						
27.43	3.249	100		2	1	1	3.253	100				2	1	0
27.96	3.188	14 <sup>a</sup>												
28.62	3.116	53		2	0	2	3.115	60				1	1	1
33.06	2.707	69	{	0	0	4	2.700	40	2	2	0			
				2	2	0	2.697	18						
33.45	2.677	20										2	0	1
34.65	2.587	4 <sup>a</sup>												
35.83	2.504	29										2	1	1
36.21	2.479	61		1	2	3	2.476	91						
37.29	2.409	67	{	1	1	4	2.414	3						
				2	2	2	2.413	3						
				3	1	0	2.412	72						
38.75	2.322	8							3	1	1	3	1	0
39.98	2.253	8 <sup>a</sup>												
44.95	2.015	2										3	2	0
47.60	1.909	8	{	2	2	4	1.908	12						
				4	0	0	1.907	1						
49.94	1.825	22	{	2	1	5	1.825	14						
				3	2	3	1.824	2						
				4	1	1	1.823	15						
50.72	1.798	55	{	0	0	6	1.800	3						
				3	1	4	1.799	46						
				4	0	2	1.798	16						
				3	3	0	1.798	4						
52.93	1.728	6 <sup>a</sup>												
53.71	1.705	35	{	1	1	6	1.707	10						
				3	3	2	1.706	25						
				4	2	0	1.706	12						
55.86	1.645	12		4	1	3	1.645	16						
56.44	1.629	10	{	2	0	6	1.628	11						
				4	2	2	1.626	1						
57.90	1.591	10 <sup>a</sup>												
58.59	1.574	4							4	2	2	3	3	1
59.43	1.554	4										2	2	2
61.61	1.504	4	{	2	2	6	1.497	1				4	2	1
				3	3	4	1.496	2						
				5	1	0	1.496	2						
64.61	1.441	14	{	4	2	4	1.442	12						
				5	1	2	1.442	6						
66.46	1.406	14	{	2	1	7	1.406	12						
				4	1	5	1.405	5						
				5	2	1	1.404	10						
69.70	1.348	4	{	0	0	8	1.350	3				5	1	1
				4	4	0	1.348	5						
71.71	1.315	14		5	2	3	1.318	16				4	1	2
Not observed			{	4	0	6	1.309	10						
				5	1	4	1.309	2						
				5	3	0	1.308	4						
74.55	1.272	12	{	3	3	6	1.272	14						
				6	0	0	1.271	8						

TABLE 4—Continued

Ref. (2)			This evaluation											
$2\Theta_{\text{obs.}}$	$d_{\text{obs.}}$	$I_{100}$	$U_3Al_2Si_3$			$UAl_2(Si)$			$U_3Si_2$					
			$h$	$k$	$l$	$d_{\text{calc.}}$	$I_{\text{calc.}}$	$h$	$k$	$l$	$h$	$k$	$l$	
79.37	1.206	4	2	2	8	1.207	2							
			4	4	4	1.206	5							
Not observed			4	1	7	1.185	5							
			5	2	5	1.184	4							
			6	1	3	1.184	1							
			5	4	1	1.184	5							
81.56	1.179	10	3	1	8	1.178	8							
			5	3	4	1.177	6							
			6	2	2	1.177	6							
84.15	1.150	6	5	1	6	1.150	3							
			6	0	4	1.150	10							
85.67	1.133	4	2	1	9	1.132	6							
			5	4	3	1.131	6							
90.55	1.084	2	4	3	7	1.085	1							
93.38	1.059	4	1	1	10	1.059	2							
			4	2	8	1.059	4							
			7	1	2	1.058	4							
95.40	1.041	6	5	2	7	1.043	7							
			5	4	5	1.043	3							
			7	2	1	1.043	3							
Not observed			2	0	10	1.039	3							
Not observed			6	0	6	1.038	2							
			6	4	2	1.038	6							
100.44	1.002	3	5	1	8	1.002	1							
			6	2	6	1.002	5							
			7	3	0	1.002	7							

Note.  $U_3Al_2Ge_3$ -type:  $a = 0.7632(3)$  nm,  $c = 1.0796(9)$  nm;  $MgCu_2$ -type:  $a = 0.7687(17)$  nm;  $U_3Si_2$ -type:  $a = 0.7295(12)$  nm,  $c = 0.3898(6)$  nm.

<sup>a</sup> Reflections not identified.

silicon atoms Si1 occupy the centers of the uranium octahedra  $[U_1_2U_2_4]Si1$  forming chains of octahedra alternating with Archimedean antiprisms along [001]. The successive arrangement of the  $3^2 \cdot 4 \cdot 3 \cdot 4$  and  $\frac{1}{2} \cdot 4^4$  nets of atoms closely resembles the  $Cr_5B_3$ -type structure which in fact is isopointal with the crystal structure of  $U_3Al_2Ge_3$ ; the rather divergent  $c/a$ -ratios, however, suggest different bond formation.

The only metal aluminosilicides found among the numerous representatives of  $Cr_5B_3$ -type compounds (see, e.g., Ref. (7)) are the  $T_5(Si_{1-x}Al_x)_3$  - solution phases of the transition metals T, i.e.,  $Ta_5(Si_{1-x}Al_x)_3$  ( $0 \leq x \leq 0.4$  at  $1400^\circ C$  (8)) where Si and Al-atoms were said to randomly share the boron sites of  $Cr_5B_3$ . Besides borides, silicides, and phosphides there is also an intermetallic branch of the  $Cr_5B_3$ -type phases comprising compounds such as  $Ba_5Pb_3$ ,  $Ca_5Ag_3$ ,  $Yb_5(Ag, Au, Sn)_3$ ,  $Tl_5Te_3$ , etc. Site occupation in  $U_3(Al, Ge)_5$ , however, contrasts that of  $Cr_5B_3$ , suggesting anti-type behavior:  $Cr1Cr_2_4B1B_2_2 \equiv Ba1Ba_2_4Pb1Pb_2_2 \equiv Ge1(Ge_2, Al)_4U1U_2_2$ .

### 3.3. Isotypic Compounds and Homogeneous Range of $U_3(Al, Si)_5$

The variation of the unit cell dimensions as obtained from ternary multiphase cast alloys U–Al–Si revealed a significant homogeneous range not only with respect to Al/Si substitution but obviously also with respect to the small but significant U/Al exchange (see Table 3).

X-ray powder data of samples with nominal composition close to  $U_3Ga_2Si_3$  and  $U_3Ga_2Ge_3$  revealed powder patterns resembling that of  $U_3Al_2Ge_3$ . Besides small amounts of  $U_2Ga_3$  and  $UGa_2$  (in case of  $U_3Ga_2Si_3$ ), the powder patterns were completely indexed on the basis of an  $U_3Al_2Ge_3$ -type unit cell (see Table 3). By use of the atom parameters as determined for  $U_3Al_2Ge_3$  (Table 1), excellent agreement is obtained between observed and calculated X-ray powder intensities in all cases, thus confirming isotypism with the crystal structure of  $U_3Al_2Ge_3$ . It has to be mentioned, however, that  $U_3(Al, Si)_5$  is a high-temperature phase only observed in arc melted alloys,

which decomposes after annealing the samples at 900°C for 100 hr. The transformation reaction, however, becomes slow at lower temperatures, i.e., as cast samples annealed at 800°C for 150 hr still revealed the  $U_3(Al, Si)_5$  high-temperature phase in major amounts. A significantly increased range of stability has been observed for the isotypic and homologous compounds  $U_3(Al, Ge)_5$ ,  $U_3(Ga, Si)_5$ , and  $U_3(Ga, Ge)_5$ , where no phase transition behavior could be observed in the temperature range from 650°C

TABLE 5  
Evaluation of the Powder Pattern of  $UAlGe$  Published in Ref. (4)

Ref. (4)			This evaluation								
$\Theta_{obs.}$	$d_{obs.}$	$I_{obs.}$	$U_3Al_2Ge_3$			$U(Al, Ge)_3$					
			$h$	$k$	$l$	$d_{calc.}$	$I_{calc.}$	$h$	$k$	$l$	
8.034	5.511	12	{	0	0	2	5.529	7			
				1	1	0	5.491	5			
10.429	4.255	25							1	0	0
11.387	3.901	20		1	1	2	3.896	30			
13.434	3.316	34		2	1	1	3.313	67			
14.020	3.180	20		2	0	2	3.178	33			
14.908	2.994	28							1	1	0
16.198	2.761	14		0	0	4	2.764	38			
16.290	2.746	12		2	2	0	2.746	20			
17.750	2.527	65		2	1	3	2.528	100			
18.308	2.452	88	{	1	1	4	2.469	5	1	1	1
				2	2	2	2.459	1			
				3	1	0	2.456	81			
21.245	2.126	18							2	0	0
23.276	1.949	61		2	2	4	1.948	13			
Not observed				4	0	0	1.941	2			
23.951	1.897	20							2	1	0
24.362	1.867	10		2	1	5	1.865	6			
Not observed				3	2	3	1.860	3			
Not observed				4	1	1	1.857	11			
Not observed				0	0	6	1.843	4			
24.800	1.836	12		3	1	4	1.836	45			
24.818	1.835	30	{	4	0	2	1.832	7			
				3	3	0	1.830	4			
26.166	1.747	4		1	1	6	1.747	7			
26.317	1.737	23	{	3	3	2	1.738	14	2	1	1
				4	2	0	1.737	14			
27.336	1.677	18		4	1	3	1.677	16			
27.568	1.664	8		2	0	6	1.665	8			
30.369	1.524	4	{	3	3	4	1.526	1			
				5	1	0	1.523	2			
30.809	1.504	10							2	2	0
31.588	1.471	11	{	3	1	6	1.474	2			
				4	2	4	1.470	12			
				5	1	2	1.468	4			
32.385	1.438	8	{	2	1	7	1.438	12			
				4	1	5	1.434	3			
32.575	1.431	7		5	2	1	1.430	7			

Note.  $U_3Al_2Ge_3$ -type:  $a = 0.7766(4)$  nm,  $c = 1.1057(6)$  nm;  $AuCu_2$ -type:  $a = 0.4251(3)$  nm.

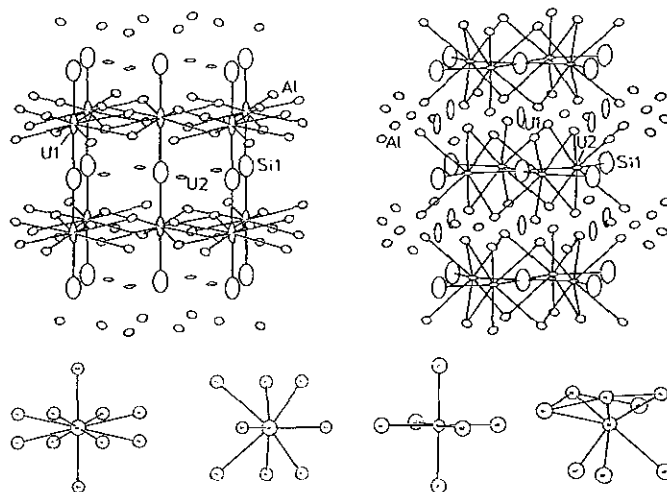


FIG. 1. Representation of the crystal structure of  $U_3(Al, Si)_5$  ( $U_3Si_2Al_3(U_3Ge_2Al_3T, anti-Cr_3B_3)$ ) in three-dimensional view (ORTEP-Graphs displaying the coordination grid around U1 and U2 atoms). The nearest neighbor coordination of each of the independent crystallographic sites is shown (from left to right: central atoms are U1, U2, Si1, and Al).

up to the melting. As these phases are easily obtained via arc melting, a congruent melting behavior is suggested.

Our results essentially confirm earlier observations on cast alloys of a high-temperature compound labeled as  $U_2AlSi_2$  (2) or  $UAlSi$  (5) with crystal structure then unknown. With respect to the new results obtained from our crystal structure determination, a detailed evaluation of the X-ray powder data reported in (2) for the as-cast alloys ( $2\Theta$ ,  $d$ ,  $I$ ) became possible (see Table 4). Except for a very few undefined reflections a least-squares refinement revealed a three-phase structure of the alloy  $U_2AlSi_2$  with  $U_3(Al, Si)_5$  as the major phase together with smaller amounts of  $U_3Si_2$  and  $U(Al, Si)_2$ . The multiphase character of the sample of  $U_2AlSi_2$  confirms the slight changes in composition toward homogeneous  $U_3(Al, Si)_5$ . It has to be emphasized, however, that we did not succeed in completely indexing the powder pattern on a hexagonal base cell as published in (4) for  $UAlSi$  or isotypic  $UAlGe$ . In a more recent paper (6)  $UAlSi$  and  $UAlGe$  have been reported with a tentative orthorhombic cell without any further details given. A least-squares refinement of the

TABLE 6  
Magnetic Data for the Compounds  $U_3(M'_{1-x}M''_x)_5$

Phase	Ord. Temp. [K]	$\mu_{ord.}$ $\mu_B/U$	$\mu_{eff.}$ $\mu_B/U$	$\Theta_p$ [K]	$\chi_0 \times 10^6$ [emu/mole]
$U_3Al_2Si_3$	36	0.45	1.99	11	3024
$U_3Al_2Ge_3$	70	1.10	2.66	71	404
$U_3Ga_2Si_3$	65	0.65	1.92	57	3440
$U_3Ga_2Ge_3$	90	1.16	2.74	88	—

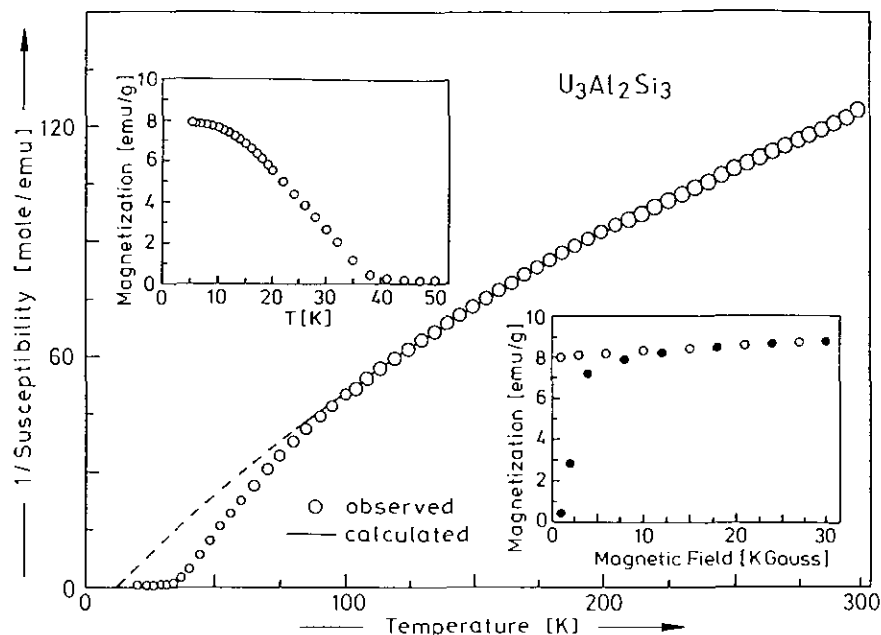


FIG. 2. Reciprocal susceptibility for  $U_3Al_2Si_3$ . Upper inset: magnetization versus temperature; lower inset: magnetization versus field.

X-ray powder data published (4) for  $UAlGe$  ( $hkl$ ,  $I$ ,  $\Theta$ ) unambiguously proved the two-phase structure of their alloy actually being a heterogeneous mixture of  $U_3Al_2Ge_3$  with smaller amounts of  $U(Al,Ge)_3$ . Details of our evaluation of the data of (4) are presented in Table 5.

Attempts to prepare homologous compounds substituting Al with In (Ga), or with Sn, Pb, in combination with Al or Ga proved to be unsuccessful for the as-cast alloys

as well as for specimens annealed at 650 or 900°C, respectively. Similarly no rare earth combination checked for Y, Gd, or Er has been found.

### 3.4. Magnetism of $U_3M_2M_3$ Compounds

The magnetic behavior of these phases is summarized in Table 6 and in Figs. 2–5. The paramagnetic parameters

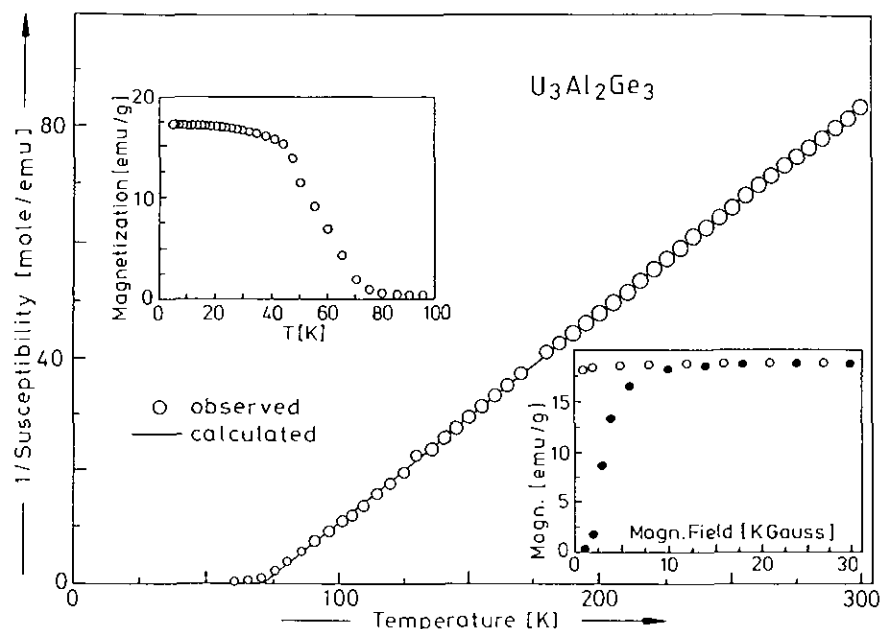


FIG. 3. Reciprocal susceptibility for  $U_3Al_2Ge_3$ . Upper inset: magnetization versus temperature; lower inset: magnetization versus field.

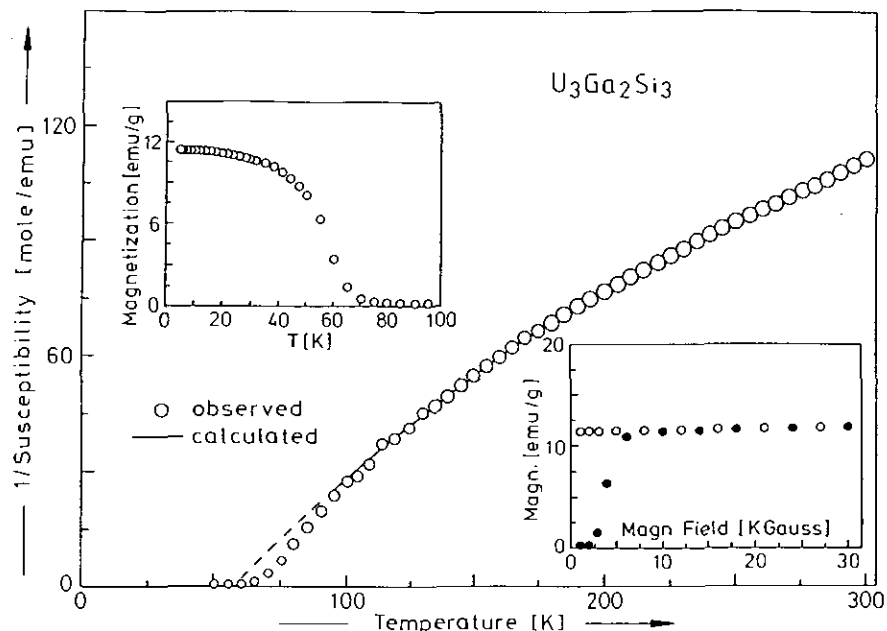


FIG. 4. Reciprocal susceptibility for  $U_3Ga_2Si_3$ . Upper inset: magnetization versus temperature; lower inset: magnetization versus field.

have been evaluated from a least-squares fit to a modified Curie-Weiss law  $\chi = \chi_0 + C/T - \Theta_p$ , where  $C$  is the Curie constant,  $\Theta_p$  is the paramagnetic Curie-Weiss temperature, and  $\chi_0$  is the temperature-independent Pauli term. All compounds exhibit ferromagnetic ordering, with higher Curie temperatures and magnetic moments for germanides than for silicides. The U-U distances are a little

larger in the former than in the latter materials (0.3502 and 0.3456 nm for  $U_3Al_2Ge_3$  and  $U_3Al_2Si_3$ , respectively) but in both cases the  $5f$ -delocalization via direct  $5f-5f$  overlap can be neglected. Furthermore magnetic interactions are much stronger in the binary uranium germanides, where some are ferromagnets (9), than in the binary silicides, none of them being ordered (10). Therefore, such

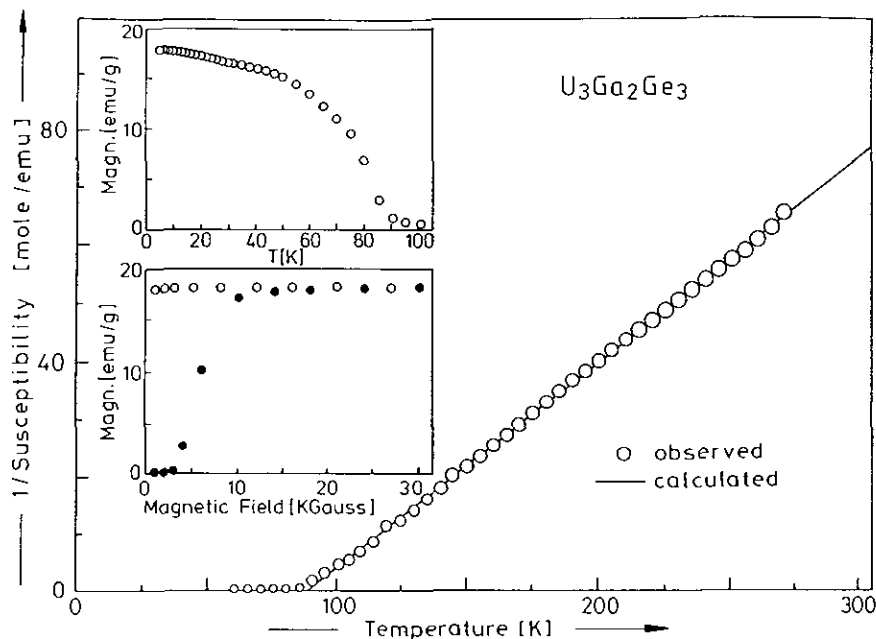


FIG. 5. Reciprocal susceptibility for  $U_3Ga_2Ge_3$ . Upper inset: magnetization versus temperature; lower inset: magnetization versus field.



an increase of the magnetic interactions from silicides to germanides has to be related to uranium-ligand hybridization effects.

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