

# Crystal Structure and Magnetic Behavior of the Uranium Monogermanide UGe

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The crystallographic structure of the uranium monogermanide UGe has been determined from single crystal X-ray diffraction data. UGe crystallizes with the orthorhombic ThIn type (*Pbcm*),  $a = 9.827(2)$  Å,  $b = 8.932(7)$  Å,  $c = 5.841(2)$  Å,  $Z = 12$ . Anisotropic refinements gave  $R = 0.044$  and  $R_w = 0.048$  for 986 reflections and 37 variables. Uranium and germanium atoms each occupy three crystallographic positions. The uranium U(3) form endless metallic chains running along the  $c$  axis, with a U–U interatomic distance of 2.92 Å. Magnetic measurements on an annealed polycrystalline powder indicate a Curie–Weiss-type behavior down to 2 K and an average effective magnetic moment of  $2.47 \mu_B/\text{U}$ . © 1997 Academic Press

## EXPERIMENTAL

Polycrystalline ingots of both compositions  $\text{U}_3\text{Ge}_4$  and UGe were obtained by arc melting 3:4 and 1:1 molar ratios of the constituent elements under partial pressure of high purity argon on a water-cooled copper hearth, using a Ti–Zr alloy as an oxygen absorber. The elements were used in the form of ingots as supplied by Merck AG. In order to ensure homogeneity, the samples were turned over and remelted three times, with weight losses lower than 0.1%. The arc molten buttons were wrapped in tantalum foil, heated in a high frequency furnace for 12 h at 1200°C under vacuum, slowly cooled down to 900°C at a rate of 10°C/h, and then down to room temperature in 10 min.

The X-ray powder diffraction pattern of the sample with composition  $\text{U}_3\text{Ge}_4$  showed some additional peaks which could not be indexed with the reported lattice parameters (3) but which could be attributed to the next binary  $\text{U}_3\text{Ge}_5$  (8). In fact, all the lines indexed with the above set of parameters were found to correspond to the powder pattern of the sample with composition UGe.

## X-RAY STRUCTURE DETERMINATION

Single crystals suitable for crystal structure determination were found in the annealed samples. The X-ray diffraction data were collected on an *Enraf-Nonius CAD-4* four-circle diffractometer under the experimental conditions listed in Table 1. The data processing was carried out on a *vax 3100* computer using the *Molen* package (9).

The lattice constants, determined from least squares analysis of the setting angle of 25 X-ray reflections have the values  $a = 9.827(2)$  Å,  $b = 8.932(7)$  Å, and  $c = 5.841(3)$  Å. The X-ray diffraction intensities were corrected for Lorentz and polarization effects and an absorption correction was applied using the program *psiscan*. The inspection of the systematic extinctions revealed that the  $0kl$ ,  $k \neq 2n$  and  $h0l$ ,  $l \neq 2n$  were not present, which is consistent with the space group *Pbcm* (No. 57). The positions of three independent uranium atoms U(1) in (4d), U(2) in (4d) and U(3) in (4c) were

## INTRODUCTION

The binary uranium–germanium phase diagram which is most currently used as a reference in the literature (1, 2) was established from earlier works by Makarov and Bykov (3) who reported some crystallographic data on the compounds  $\text{UGe}_3$ ,  $\text{UGe}_2$ ,  $\text{U}_3\text{Ge}_4$  and  $\text{U}_5\text{Ge}_3$  and by Alcock and Grievson (4) who indicated the existence of two other binaries UGe and  $\text{U}_3\text{Ge}_5$ . We have recently shown (5) that  $\text{UGe}_2$  crystallizes with the  $\text{ZrGa}_2$ -type structure instead of the  $\text{ZrSi}_2$ -type structure as previously claimed (3). Up to now no crystallographic data have been available in the literature for the monogermanide UGe. On the other hand,  $\text{U}_3\text{Ge}_4$  was reported (3) to crystallize with an orthorhombic unit cell with the lattice parameters  $a = 5.87$  Å,  $b = 9.88$  Å, and  $c = 8.98$  Å, but the crystal structure was not determined.  $\text{U}_3\text{Ge}_4$  was also reported (6, 7) to exhibit ferromagnetic ordering below 94 K which we have shown to be the Curie temperature of the next binary  $\text{U}_3\text{Ge}_5$  (8). We report here new results which clarify part of this region of the binary system U–Ge.

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**TABLE 1**  
**Crystallographic Data for UGe<sup>a</sup>**

Formula	UGe
Space group	<i>Pbcm</i> , No. 57
Crystal dimensions (mm)	0.04 × 0.08 × 0.1
Linear absorption coefficient (cm <sup>-1</sup> )	1065
Lattice parameters (from CAD4):	
<i>a</i> (Å)	9.827(2)
<i>b</i> (Å)	8.932(7)
<i>c</i> (Å)	5.841(2)
Unit cell volume (Å <sup>3</sup> )	512.7(5)
Calculated density	12.07
Formula per unit cell	<i>Z</i> = 12
Formula weight (g)	310.6
Scan range	1° < $\theta$ < 40°
<i>hkl</i> range	0 < <i>h</i> < 17 0 < <i>k</i> < 16 0 < <i>l</i> < 10
Total observed reflections	1850
Independent reflections with <i>I</i> > 2 $\sigma$	986
Secondary extinction coefficient	<i>g</i> = 7.97 10 <sup>-8</sup> , corr. = 1/(1 + <i>gI</i> <sub>c</sub> )
Number of variables	37
Reliability factors	
$R = \sum [ F_o  -  F_c ] / \sum  F_o $	0.044
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	0.048
Goodness of fit GOF	1.36

<sup>a</sup> Structure factor tables are available from the authors upon request.

derived using direct methods (program *multan*) and the positions of three independent germanium atoms Ge(1) in (4*d*), Ge(2) in (4*d*), and Ge(3) in (4*c*) were obtained from a subsequent Fourier difference calculation. A series of refinements of the positional and isotropic thermal parameters converged to the the agreement factors *R* = 0.062 and

*R*<sub>w</sub> = 0.071. Refinement cycles carried out including anisotropic thermal parameters lead to *R* = 0.048 and *R*<sub>w</sub> = 0.054, revealing slightly larger anisotropic thermal vibrations in the (*b*, *c*) plane. The final refinements including occupation factors for all atoms showed a slight deficiency for the U(3) crystallographic site, with an occupation factor of 0.92, and led to *R* = 0.044 and *R*<sub>w</sub> = 0.048. Further difference Fourier calculations did not reveal any significant residual electron density peaks. The composition of the investigated crystal is thus U<sub>2.92</sub>Ge<sub>3</sub>, i.e., U<sub>0.97</sub>Ge, but a nonstoichiometric domain could not be significantly proved from our synthesis experiments.

The positional parameters standardized using the program *Structure Tidy* (10) are listed in Table 2 and the interatomic distances in Table 3. A view of the structure of UGe is displayed in Fig. 1. A search for parent compounds from a data base of inorganic compounds (11) revealed that UGe crystallizes with the ThIn-type structure (12), which is also adopted by the uranium monostannide USn (13), but not by the uranium monosilicide USi which crystallizes with a large tetragonal unit cell (14). As a result of the standardization of the positional parameters, the origin of the crystallographic cell is shifted by *c*/2 with respect to that of ThIn. The ThIn-type structure and its relation to other structure types have previously been described (11). The three independent uranium atoms U(1), U(2), and U(3) are coordinated by 9, 7, and 6 germanium atoms, respectively, with interatomic U–Ge bonding distances ranging from 2.829(3) Å to 3.152(4) Å (Fig. 1, Table 3). An interesting crystallographic property is the very short interatomic distance U(3)–U(3) of 2.92 Å, corresponding to *c*/2, which is close to that in uranium metal (2.75 Å in  $\alpha$ U and 3.03 Å in  $\beta$ U). So, we can consider that the U(3) uranium atoms form endless metallic chains

**TABLE 2**  
**Atomic Parameters for UGe**

Atom	U(1)	U(2)	U(3)	Ge(1)	Ge(2)	Ge(3)
Site	4 <i>d</i>	4 <i>d</i>	4 <i>c</i>	4 <i>d</i>	4 <i>d</i>	4 <i>c</i>
Occupation	1	1	0.92(2)	1	1	1
<i>x</i>	0.11064(8)	0.31838(8)	0.61006(8)	0.1524(2)	0.4047(2)	0.0839(2)
<i>y</i>	0.53849(9)	0.12570(9)	1/4	0.8672(3)	0.4476(3)	1/4
<i>z</i>	1/4	1/4	0.0	1/4	1/4	0.0
<i>B</i> <sub>11</sub>	0.13(2)	0.36(2)	0.07(2)	0.26(6)	0.19(7)	0.30(6)
<i>B</i> <sub>22</sub>	0.60(2)	0.52(2)	0.71(2)	0.71(7)	0.80(7)	0.52(6)
<i>B</i> <sub>33</sub>	0.27(2)	0.37(2)	0.39(2)	0.52(6)	0.61(6)	0.57(6)
<i>B</i> <sub>12</sub>	0.01(2)	−0.01(2)	0	0.08(6)	−0.04(6)	0
<i>B</i> <sub>13</sub>	0	0	0	0	0	0
<i>B</i> <sub>23</sub>	0	0	−0.02(2)	0	0	−0.04(6)
<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )	0.33(1)	0.42(1)	0.39(1)	0.50(3)	0.53(3)	0.46(3)

*Note.* 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*<sup>\*</sup>, *b*<sup>\*</sup>, and *c*<sup>\*</sup> are reciprocal lattice constants.

**TABLE 3**  
Interatomic Distances (Å) for UGe

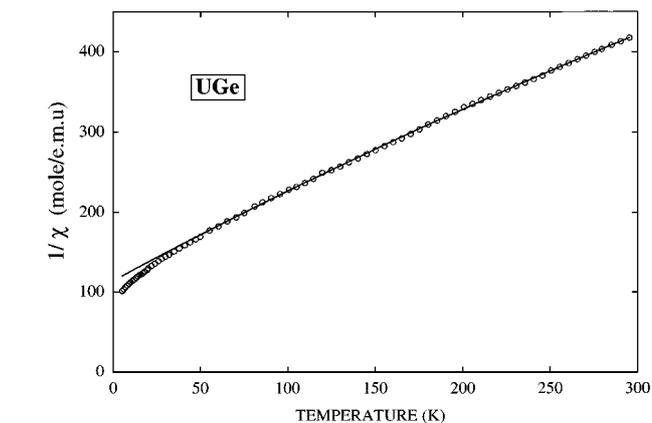
U(1)–1Ge(1)	2.963(3)	U(2)–1Ge(1)	2.829(3)
2Ge(3)	2.973(1)	2Ge(3)	2.944(3)
1Ge(2)	3.001(4)	1Ge(2)	2.998(3)
1Ge(1)	3.004(3)	2Ge(2)	3.111(1)
2Ge(3)	3.060(2)	1Ge(2)	3.152(4)
2Ge(1)	3.067(1)	2U(3)	3.403(1)
2U(3)	3.637(1)	2U(2)	3.668(1)
2U(1)	3.706(1)	2U(1)	3.853(1)
2U(2)	3.853(1)		
U(3)–2U(3)	2.920(2)	Ge(1)–U(2)	2.829(3)
2Ge(1)	2.945(3)	2Ge(3)	2.936(4)
2Ge(2)	3.053(3)	2U(3)	2.945(3)
2Ge(2)	3.073(3)	1U(1)	2.963(3)
2U(2)	3.403(1)	1U(1)	3.001(4)
2U(1)	3.637(1)	2U(1)	3.067(1)
Ge(2)–U(2)	2.998(3)	Ge(3)–2Ge(3)	2.920(2)
1U(1)	3.001(4)	2Ge(1)	2.936(4)
2U(3)	3.053(3)	2U(2)	2.944(3)
2U(3)	3.073(3)	2U(1)	2.973(1)
2U(2)	3.111(1)	2U(1)	3.060(2)
1U(2)	3.152(4)		

running along the  $c$  axis, with some defects along the chains.

### MAGNETIC BEHAVIOR

Magnetic measurements of an annealed polycrystalline sample were performed using a SQUID magnetometer in the temperature range 2–300 K in an applied magnetic field of 4 kGauss.

Figure 2 displays the thermal variation of the inverse susceptibility. A fit of the experimental points in the temperature range 40–300 K using the modified Curie–Weiss law



**FIG. 2.** Thermal variation of the inverse susceptibility of UGe. The line corresponds to the fit of the experimental data according to the modified Curie–Weiss law.

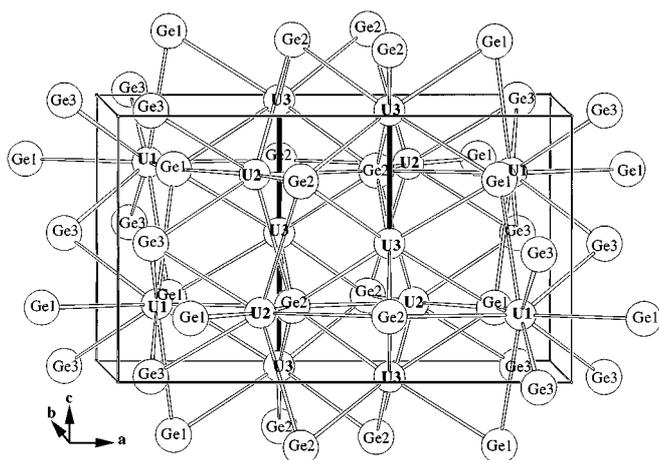
$\chi = \chi_0 + C/T - \theta$  gives the temperature independent susceptibility term  $\chi_0 = 422 \times 10^{-6}$  emu/mol, the paramagnetic Curie temperature  $\theta = -92$  K, and an averaged effective paramagnetic moment  $\mu_{\text{eff}} = \sqrt{8c} = 2.47 \mu_B/\text{U}$ . In spite of the large negative value of  $\theta$ , any antiferromagnetic transition was detected down to 2 K. The value of the effective magnetic moment is low compared to the free ion values of  $3.58 \mu_B$  for  $\text{U}^{4+}$  ( $^3H_4$  ground term) and  $3.62 \mu_B$  for  $\text{U}^{3+}$  ( $^4I_{9/2}$  ground term). Values in the range 2.8–3.4  $\mu_B$  are usually found for uranium compounds and are generally attributed to crystal field effects. In UGe, the short U(3)–U(3) distance indicates a strong overlap of the corresponding  $5f$  orbitals with the formation of U–U metal bonds, so that the U(3) atoms with delocalized  $5f$  electrons should not bear any local magnetic moment. Calculations considering only U(1) and U(2) yield an effective moment of 3.03  $\mu_B/\text{U}$  which lies in the range of the usual values.

### CONCLUSION

The previously reported binary uranium germanide  $\text{U}_3\text{Ge}_4$  does not exist and the corresponding samples are mixtures of the two neighboring binaries UGe and  $\text{U}_3\text{Ge}_5$ , whatever the annealing temperature. The orthorhombic lattice parameters reported for the composition  $\text{U}_3\text{Ge}_4$  correspond in fact to those of the monogermanide UGe, which we have shown to crystallize with the ThIn structure type. The ferromagnetic properties reported for  $\text{U}_3\text{Ge}_4$  (6, 7) are characteristic of the next germanium richer binary  $\text{U}_3\text{Ge}_5$ .

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**FIG. 1.** View of the structure of UGe. The U(3)–U(3) bonds and the uranium–germanium bonding distances and coordination are shown.

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