

# Synthesis and characterization of novel ternary uranium germanides with niobium and tantalum

T. Le Bihan<sup>a</sup>, H. Noël<sup>a</sup> and P. Rogl<sup>b</sup>

<sup>a</sup>Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS 1495, Université de Rennes I, avenue du Général Leclerc, 35042 Rennes (France)

<sup>b</sup>Institut für Physikalische Chemie der Universität Wien, Währingerstrasse 42, A-1090 Wien (Austria)

## Abstract

Novel compounds,  $U_2Nb_3Ge_4$  and  $U_2Ta_3Ge_4$ , have been synthesized by argon arc melting the elemental combinations. The crystal structure of  $U_2Nb_3Ge_4$  ( $a = 7.0178(6)$  Å,  $b = 13.473(2)$  Å,  $c = 7.1500(7)$  Å; space group, *Pnma*;  $Z = 4$ ) has been determined from single-crystal X-ray counter data to be isotypic with the ordered  $Sm_5Ge_4$  type.  $U_2Ta_3Ge_4$  ( $a = 7.015(2)$  Å,  $b = 13.454(3)$  Å,  $c = 7.139(2)$  Å) from X-ray powder intensity data was found to crystallize with the same atom order as  $U_2Nb_3Ge_4$ .  $U_2Nb_3Ge_4$  and  $U_2Ta_3Ge_4$  are ferromagnets below  $T_c = 130$  K and 105 K respectively.

## 1. Introduction

Intensive studies have been devoted to the physics of strong electron correlations in metallic systems involving 5f electron metals. With respect to the observed possibility for cooperative magnetism to arise from a heavy Fermi liquid phase and to suppress or coexist with heavy fermion superconductivity [1], the search for novel materials, which might develop some of these features, has focused our interest on a systematic study of the ternary 5f and the early 4d (5d) element silicides and germanides. In the present paper we describe the preparation, the structural chemistry and the magnetic behaviour of the novel compounds  $U_2Nb_3Ge_4$  and  $U_2Ta_3Ge_4$ .

## 2. Experimental details

The compounds  $U_2Nb_3Ge_4$  and  $U_2Ta_3Ge_4$  have been synthesized by argon arc melting ingots of the elements. To ensure homogeneity, the alloy buttons were flipped over and remelted several times. For annealing, the buttons were wrapped in protective Ta foil and heated under vacuum in an induction furnace for two days at 1400 °C. Attempts to synthesize " $U_2Ta_3Si_4$ " were unsuccessful.  $U_2Nb_3Si_4$  was found [2] to adopt a different crystal structure with the  $Sc_2Re_3Si_4$ -type and will be the subject of a forthcoming paper.

Small single crystals of  $U_2Nb_3Ge_4$  were obtained by heating the arc-melted button at a temperature of about

1550 °C for 3 h followed by slow cooling. The same technique applied to  $U_2Ta_3Ge_4$  did not reveal any significant growth of the microcrystals preformed in the arc-melting process.

## 3. Structural chemistry

### 3.1. The crystal structure of $U_2Nb_3Ge_4$

Single-crystal X-ray diffraction of  $U_2Nb_3Ge_4$  was performed on an automatic Enraf-Nonius CAD-4 four-circle diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.710$  69 Å). The lattice parameters were obtained by least-squares refinement of the setting angles of 25 reflections. Details of the intensity data collection and crystallographic data are summarized in Table 1.

The structure of  $U_2Nb_3Ge_4$  was solved in the space group *Pnma* (number 62). Intensities, corrected for Lorentz and polarization effects, were corrected for absorption in the final stage of refinement by means of the DIFABS program [3]. All calculations were carried out on a micro VAX 3100 computer with the use of the SDP crystallographic software [4]. The positions of all atoms were assigned by analogy with the structure of  $Ce_2Sc_3Si_4$  [5], which is a fully ordered representative of the  $Sm_5Ge_4$  type. Refinement was performed by a full-matrix least-squares calculation that included a site population analysis. There were no indications of significant deviation from full occupancies. The final residual value  $R_F$  was 0.047. The final positional and thermal parameters are listed in Table 2 and selected

TABLE 1. Crystallographic data for  $U_2Nb_3Ge_4$  (ordered  $Sm_5Ge_4$  type)

Space group	$Pnma$ , number 62, origin at centre
Lattice parameters (from CAD-4) (Å)	$a = 7.018(1)$ ; $b = 13.473(2)$ ; $c = 7.150(1)$
Cell volume (Å <sup>3</sup> )	$V = 676.01(1)$
Formula units per cell	$Z = 4$
Formula weight	$M = 1045.1$
Calculated density (Mg m <sup>-3</sup> )	$\rho_x = 10.27$
Crystal size (mm <sup>3</sup> )	$0.10 \times 0.02 \times 0.02$
Scan range ( $\theta$ )	$1^\circ \leq \theta \leq 35^\circ$
Range in $hkl$	$+11$ ; $+21$ ; $+11$
Linear absorption coefficient (Mo $K\alpha_1$ ) (mm <sup>-1</sup> )	$\mu = 67.12$
Total number of reflections	1736
Reflections with $I > 2\sigma(I)$	847
Secondary extinction coefficient	$g = 1.43 \times 10^{-7}$ , corr. = $1/(1 + gI_c)$
Number of variables	47
Goodness of fit	1.156
Conventional residual ( $F$ )	$R_F = 0.047$
Weighted residual, $w = 1/\sigma^2(F)$	$R_w = 0.056$

TABLE 2. Atom parameters

Atom	Position	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
U	8d	0.5064(1)	0.09325(5)	0.67130(9)	0.378(8)	0.00186(8)	0.00058(2)	0.00170(7)	0.0000(1)	0.0000(2)	0.0000(1)
Nb(1)	8d	0.3400(2)	0.1252(1)	0.1683(2)	0.41(2)	0.0025(2)	0.00047(6)	0.0019(2)	-0.0001(3)	0.0011(5)	-0.0003(3)
Nb(2)	4c	0.1677(4)	1/4	0.4948(3)	0.35(3)	0.0022(4)	0.00047(9)	0.0013(3)	0	0.0004(6)	0
Ge(1)	8d	0.6729(3)	0.0426(2)	0.0429(3)	0.40(3)	0.0023(3)	0.00053(8)	0.0017(3)	-0.0001(3)	0.0001(5)	-0.0003(3)
Ge(2)	4c	0.0398(4)	1/4	0.1257(4)	0.39(4)	0.0019(5)	0.0006(1)	0.0016(4)	0	0.0008(7)	0
Ge(3)	4c	0.8071(4)	1/4	0.6365(4)	0.41(4)	0.0020(4)	0.0006(1)	0.0017(4)	0	0.0002(8)	0

$$B = (4/3) \sum_{i,j} \beta_{i,j} a_i \cdot a_j$$

The coefficients for anisotropic thermal measurements are expressed as  $\exp(-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$ . Standard deviations in the least-significant digits are given in parentheses.

TABLE 3. Interatomic distances (ångströms) for  $U_2Nb_3Ge_4$ 

U-1Ge(1)	2.879(2)	Nb(1)-1Ge(1)	2.623(3)	Ge(1)-1Nb(1)	2.623(3)
U-1Ge(3)	2.882(2)	Nb(1)-1Ge(2)	2.639(3)	Ge(1)-1Nb(1)	2.720(3)
U-1Ge(1)	2.981(2)	Nb(1)-1Ge(2)	2.713(3)	Ge(1)-1Nb(1)	2.739(3)
U-1Ge(3)	2.996(2)	Nb(1)-1Ge(1)	2.720(3)	Ge(1)-1Ge(1)	2.754(4)
U-1Ge(2)	3.004(2)	Nb(1)-1Ge(1)	2.739(3)	Ge(1)-1Nb(2)	2.807(2)
U-1Ge(1)	3.018(2)	Nb(1)-1Ge(3)	2.762(3)	Ge(1)-1U	2.879(2)
U-1Ge(1)	3.043(2)	Nb(1)-1Nb(2)	3.078(3)	Ge(1)-1U	2.981(2)
U-1Nb(1)	3.337(2)	Nb(1)-1U	3.337(2)	Ge(1)-1U	3.018(2)
U-1Nb(2)	3.382(2)	Nb(1)-1Nb(1)	3.363(3)	Ge(1)-1U	3.043(2)
U-1U	3.510(1)			Ge(2)-2Nb(1)	2.639(3)
				Ge(2)-1Ge(3)	2.652(4)
		Nb(2)-1Ge(3)	2.725(4)	Ge(2)-2Nb(1)	2.713(3)
		Nb(2)-1Ge(2)	2.750(4)	Ge(2)-1Nb(2)	2.750(4)
		Nb(2)-1Ge(2)	2.788(4)	Ge(2)-1Nb(2)	2.788(4)
		Nb(2)-2Ge(1)	2.807(2)	Ge(2)-2U	3.004(2)
		Nb(2)-1Ge(3)	2.812(4)		
		Nb(2)-2Nb(1)	3.078(3)	Ge(3)-1Ge(2)	2.652(4)
		Nb(2)-2U	3.382(2)	Ge(3)-1Nb(2)	2.725(4)
				Ge(3)-2Nb(1)	2.762(3)
				Ge(3)-1Nb(2)	2.812(4)
				Ge(3)-2U	2.882(2)
				Ge(3)-2U	2.996(2)

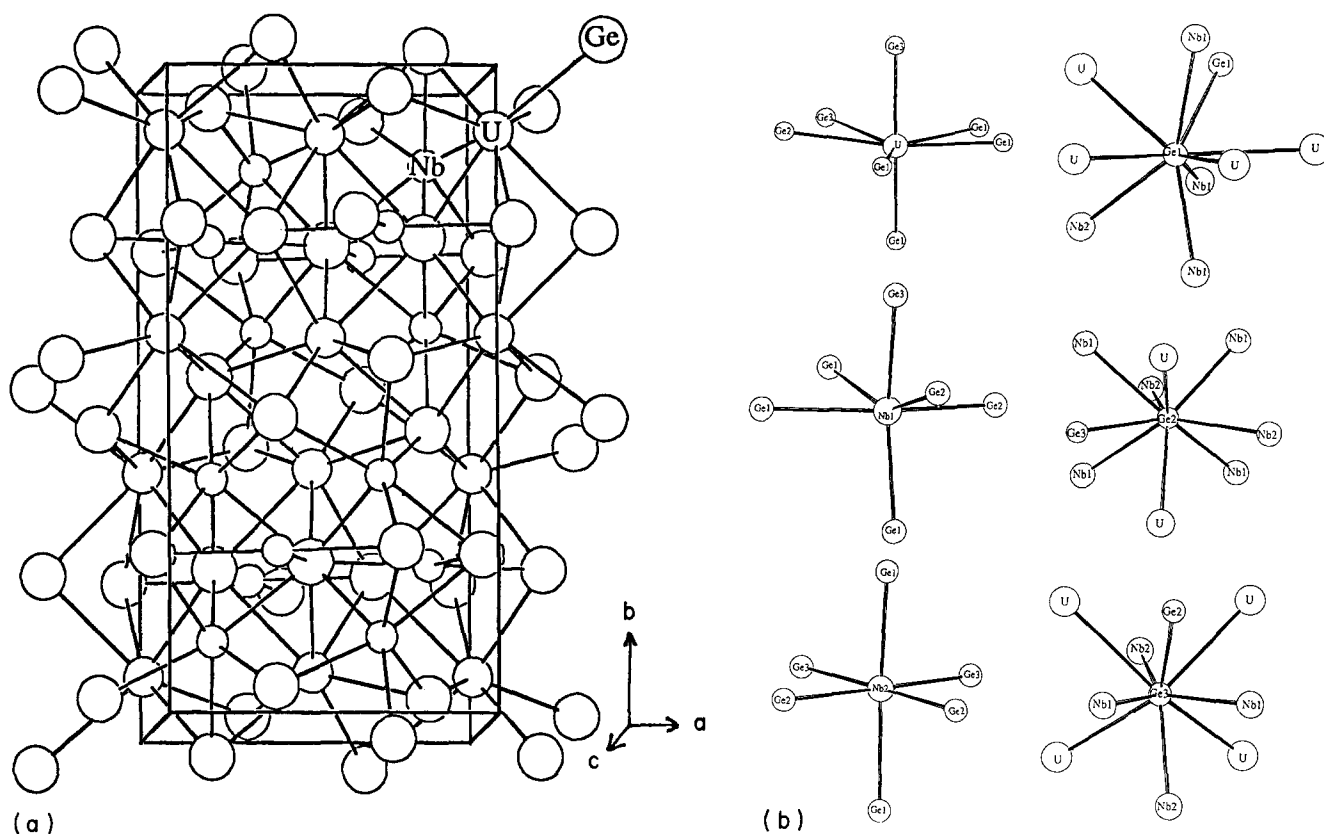


Fig. 1. Representation of the crystal structure of  $U_2Nb_3Ge_4$  (ordered  $Sm_5Ge_4$  type) in three-dimensional view (ORTEP graph displaying the coordination grid). The nearest-neighbour coordination of each of the independent crystallographic sites is shown.

TABLE 4. Magnetic data for  $U_2Nb_3Ge_4$  and  $U_2Ta_3Ge_4$

Compound	Ferromagnetic ordering temperature (K)	$\mu_{\text{eff}}$ ( $\mu_B$ (U atom) $^{-1}$ )	$\Theta_P$ (K)	$\chi_0$ ( $\times 10^{-3}$ cm $^3$ mol $^{-1}$ )
$U_2Nb_3Ge_4$	130	2.27	119	2.65
$U_2Ta_3Ge_4$	105	2.42	95	1.60

interatomic distances are gathered in Table 3. A listing of the structure factors is available from the authors.

The crystal structure of  $U_2Nb_3Ge_4$  is shown in Fig. 1. Uranium atoms are surrounded by seven germanium atoms which form a pentagonal bipyramid. Four niobium atoms are situated at a distance between 3.33 and 3.42 Å and a further uranium atom is located at a distance of 3.51 Å, slightly exceeding the Hill limit [6]. The two niobium atoms, Nb(1) and Nb(2), have six neighbouring germanium atoms in octahedral coordination. Nb(1)–Nb(2) distances (3.08 Å) can be compared with metallic bonds ( $r_{\text{Nb}} = 1.473$  Å). The three germanium atoms are in tetrakaidecahedral coordination polyhedra which in the case of Ge(2) and Ge(3) represent trigonal tricapped prisms, but are rather distorted for Ge(1) atoms.

The hitherto known ternary representatives of the  $Sm_5Ge_4$  type form a rather small group of silicides and

germanides in combination with metals such as Nb, Mo, W and one of the electropositive elements such as Sc, Ce and Zr [7]. Except for small homogeneous ranges observed in  $(Sc_{1-x}Mo_x)_5Ge_4$  and  $(Sc_{1-x}W_x)_5Ge_4$  complete ordering among the metal atoms has been reported with the largest atom naturally occupying the site with the highest coordination number. Nevertheless, Seropegin *et al.* [8] announced a different occupation of the metallic sites for  $Zr_2Nb_3Ge_4$  with the zirconium atoms in the 8d position of scandium in  $Ce_2Sc_3Si_4$ , with the following distribution: Nb $_8$  (8d) Zr $_8$  (8d) Nb $_4$  (4c) Ge $_{16}$  (4c,4c,8d) in correspondence to Ce $_8$  (8d) Sc $_8$  (8d) Sc $_4$  (4c) Si $_{16}$  (4c,4c,8d). In view of the atom site distribution we obtained for  $U_2Nb_3Ge_4$ , the results announced by Seropegin *et al.* seem to be wrong, *i.e.* the zirconium atoms should rather be in the same position as uranium in  $U_2Nb_3Ge_4$  and/or cerium in isotopic  $Ce_2Sc_3Si_4$ .

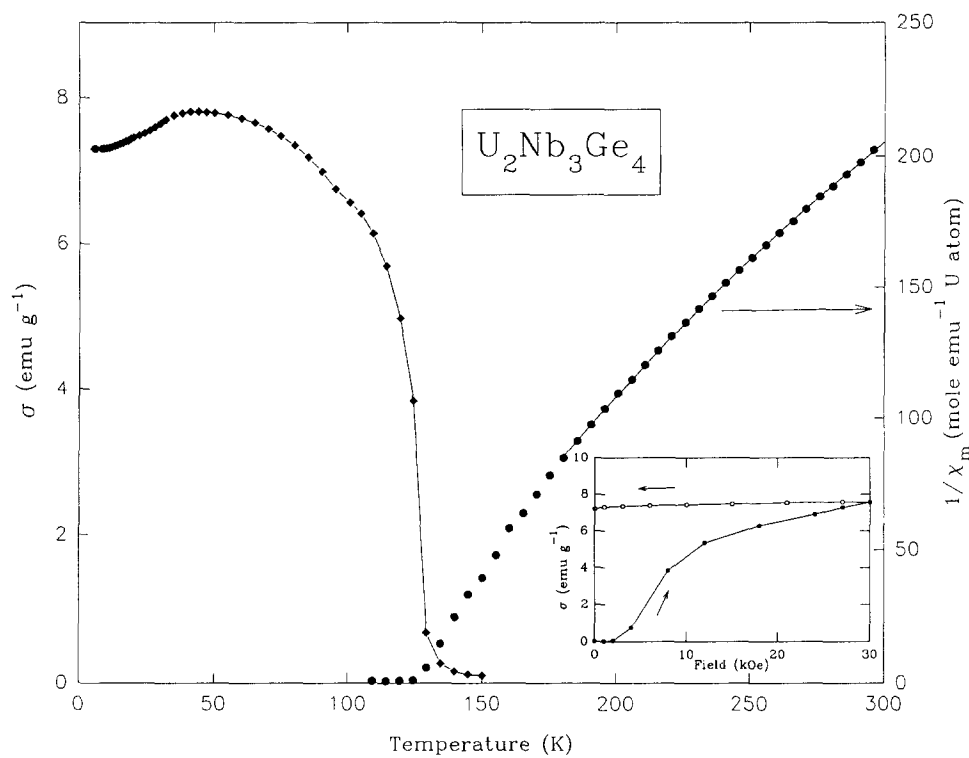


Fig. 2. Magnetization (left-hand scale) and reciprocal susceptibility per uranium atom (right-hand scale) vs. temperature for  $U_2Nb_3Ge_4$ . Magnetization vs. field is also shown.

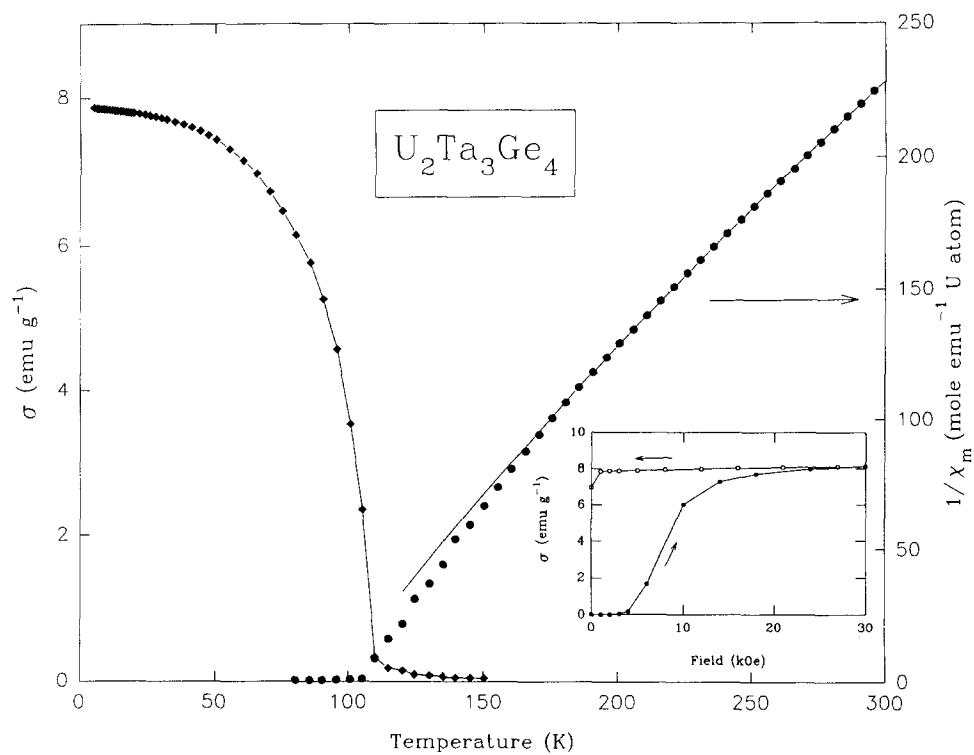


Fig. 3. Magnetization (left-hand scale) and reciprocal susceptibility per uranium atom (right-hand scale) vs. temperature for  $U_2Ta_3Ge_4$ . Magnetization vs. field is also shown.

### 3.2. Isotypic $U_2Ta_3Ge_4$

The X-ray powder pattern of  $U_2Ta_3Ge_4$  was completely indexed on the basis of a primitive tetragonal unit cell:  $a = 7.015(2) \text{ \AA}$ ,  $b = 13.454(3) \text{ \AA}$  and  $c = 7.139(2) \text{ \AA}$ . By use of the atom parameters as determined for  $U_2Nb_3Ge_4$  (Table 2), excellent agreement is obtained between observed and calculated X-ray powder intensities, confirming isotypism among these compounds.

## 4. Magnetism

The magnetic properties have been studied using a superconducting quantum interference device magnetometer, and are summarized in Table 4 and in Figs. 2 and 3. Paramagnetic susceptibilities have been fitted according to the modified Curie–Weiss law:  $\chi_M = \chi_0 + C/(T - \Theta)$ .

### 4.1. $U_2Nb_3Ge_4$

Figure 2 shows the ferromagnetic behaviour of this compound. The saturated magnetization is not approached below 3 T where the value of the ordered uranium moment reaches about  $0.7 \mu_B$ . As can be seen from the thermal variation of the magnetization,  $U_2Nb_3Ge_4$  is ferromagnetic below  $T_c = 130 \text{ K}$ .

### 4.2. $U_2Ta_3Ge_4$

As can be seen in Fig. 3,  $U_2Ta_3Ge_4$  also exhibits a ferromagnetic behaviour at low temperature ( $T_c = 105 \text{ K}$ ). In contrast to  $U_2Nb_3Ge_4$ , magnetization appears

to be saturated below 3 T with a magnetization equal to  $0.95 \mu_B (\text{U atom})^{-1}$ .

## Acknowledgments

This research was sponsored by the CEC as a Human Capital and Mobility Network ERBCHRXCT930284. P.R. wishes to thank the Austrian National Science Foundation FFWF for support under Grant P8218. T.L. is grateful to the Austrian–French Programme for Technical–Scientific Exchange for a research stipend in Vienna (Project A11). H.N. is indebted to Region Bretagne for financial support.

## References

- 1 N. Grewe and F. Steglich, in K.A. Gschneidner, Jr., and L.R. Eyring (eds.), *Handbook on the Physics and the Chemistry of the Rare Earths*, Vol. 14, North-Holland, Amsterdam, 1991.
- 2 T. Le Bihan, *Ph.D. Thesis*, Université de Rennes I, April 1993.
- 3 N. Walker and D. Stuart, *Acta Crystallogr. A*, 39 (1983) 158.
- 4 B.A. Frenz, Enraf-Nonius CAD-4-SDP. In H. Schenk, R. Olthof-Hazekamp, H. Von Konigsveld and G.C. Bassy (eds.), *Computing in Crystallography*, Delft University Press, Delft, 1978, p. 64.
- 5 I.R. Mokraya, O.I. Bodak and E.I. Gladyshevskii, *Sov. Phys. Crystallogr.*, 24 (6) (1979) 729.
- 6 H.H. Hill, in W.N. Miner (ed.), *Plutonium 1970 and Other Actinides*, AIME, New York, 1970, p. 2.
- 7 P. Villars and D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM International, Metals Park, OH, 2nd edn., 1991.
- 8 Yu.O. Seropegin, V.V. Tabachenko and M.G. Mys'kiv, *Sov. Phys. Crystallogr.*, 29 (1984) 95.