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Crystal and Magnetic Structure of New Ternary Uranium Intermetallics: U_3TiX_5 (X = Ge, Sn)

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New compounds with the formula U_3TiX_5 have been synthesized for $X = \mathrm{Ge}$, Sn. The crystal structure of U_3TiGe_5 has been refined from single crystal X-ray diffraction data to $R(F) = 0.032$, $R_w = 0.037$, and was found to crystallize with the hexagonal U_3TiSb_5 structure type, with $a = 8.495(1)$ Å and $c = 5.711(1)$ Å. Isotypism was found from X-ray powder diffraction analysis for the stannide U_3TiSn_5, with $a = 9.200(2)$ Å and $c = 6.128(3)$ Å. Magnetic susceptibility measurements carried out on polycrystalline powder samples reveal ferromagnetic type ordering at $T_C = 76$ and 65 K for U_3TiGe_5 and U_3TiSn_5, respectively. Neutron powder diffraction studies of U_3TiGe_5 show that the uranium magnetic moments have two components: a ferromagnetic component ($M_F = 0.9\ \mu_B$ at 1.4 K) along the c axis and a triangular component ($M_T = 0.4\ \mu_B$ at 1.4 K) in the hexagonal plane antiferromagnetically ordered along the c axis.

Key Words: **uranium compounds, crystal structure, magnetic structure.**

INTRODUCTION

In continuation of our studies on uranium-based compounds showing interesting behavior in the fields of magnetism and superconductivity, we recently reported new results concerning compounds formation and properties in the binary uranium–germanium phase diagram (1–4). The existence of the five binary phases, UGe_3, UGe_2, U_3Ge_5, UGe, and U_5Ge_4, is now well established, and these results are the first step of a systematic study of uranium based ternary germanides. A complete isothermal section of the system U–Ti–Ge has been determined at 1000°C (5), revealing in particular the formation of a new ternary compound U_3TiGe_5. We report here on the crystal and magnetic structure of this new compound and on the magnetic properties of the isostructural ternary stannide U_3TiSn_5.

EXPERIMENTAL

The polycrystalline ingots were obtained by arc melting stoichiometric amounts of the constituent elements under an atmosphere of high-purity argon 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, 5N) and by Strem Chemicals (titanium, 4N). To ensure homogeneity, the arc-melted buttons were turned over and remelted 3 times, with weight losses lower than 0.1%. U_3TiGe_5 melts congruently, and single crystals were directly obtained from arc melting stoichiometric amounts of U, Ti, and Ge. To improve the quality of the crystallites, the arc-melted button was 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 $10°\mathrm{C\,h^{-1}}$, and then cooled down to room temperature in 10 min.

The single-crystal X-ray diffraction data were collected on an 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 (6). Magnetic measurements of an annealed polycrystalline sample were carried out using a Superconducting Quantum Interference Device (SQUID) magnetometer in the temperature range 5–300 K and in the magnetic field range 0–3 Teslas. Neutron diffraction experiments were performed at the Laboratoire Léon Brillouin (Saclay, France) on the powder diffractometer G4.1 at $\lambda = 0.24249$ nm in the range $15° < 2\theta < 95°$. The powdered sample of 6.5 g was inserted in a vanadium cylindrical container. The sample holder was held in a helium cryostat to collect data in the temperature range $1.4 < T < 91$ K. The diffraction patterns were analyzed by a Rietveld-type profile refinement method using the FULLPROF program (7). The neutron scattering lengths were taken from Ref. (8) ($b_U = 0.8417 \times 10^{-12}$ cm, $b_{Ge} = 0.8193 \times 10^{-12}$ cm, $b_{Ti} = -0.33 \times 10^{-12}$ cm) and the uranium (U^{3+}) form factor from Ref. (9) ($\langle j_0 \rangle + c_2 \langle j_2 \rangle$ approximation).

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TABLE 1
X-Ray Crystallographic Data for U_3TiGe_5[a]

Formula	U_3TiGe_5
Space group	$P6_3/mcm$, no. 193
Crystal dimensions (mm)	$0.02 \times 0.02 \times 0.14$
Linear absorption coefficient (cm^{-1})	856.8
Lattice parameters (from CAD4):	
a (Å)	8.4955(4)
c (Å)	5.711(1)
Unit-cell volume ($Å^3$)	357.01(6)
Calculated density	10.46
Formula per unit cell	$Z = 2$
Formula mass	1124.9
Scan range	$1^\circ < \theta < 45^\circ$
hkl range	$-16 < h < 0, 0 < k < 16, 0 < l < 12$
Total observed reflections	2232
Independent reflections with $I > 3\sigma(I)$	506
Secondary extinction coefficient	$g = 2.75\ 10^{-7}$, corr. $= 1/(1 + gI_c)$
Number of variables	14
Residuals	
$R = \sum[\lvert F_o\rvert - \lvert F_c\rvert]/\sum\lvert F_o\rvert$	0.032
$R_w = [\sum_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum_w\lvert F_o^2\rvert]^{1/2}$	0.037
Goodness of fit GOF	1.74

[a] Structure factor tables are available from the authors upon request.

X-RAY STRUCTURE DETERMINATION

The lattice constants determined from least squares analysis of the setting angles of 25 X-ray reflections have the values $a = 8.495(1)$ Å, $c = 5.711(1)$ Å, and $c/a = 0.672$. The X-ray diffraction intensities were corrected for Lorentz and polarization effects and an absorption correction was applied using the program Psiscan. The set of characteristic extinctions observed was ($h0l$) and ($00l$), $l \neq 2n$. This observation is consistent with the following space groups $P6_3cm$ (185), $P\bar{6}c2$ (188), and $P6_3/mcm$ (193). The structure was successfully refined in the centrosymmetric space group $P6_3/mcm$. The positions of one uranium atom in $6g$ and two germanium atoms in $6g$ and $4d$ Wyckoff positions were derived using direct method (program Multan) and the position of the titanium atom in $2b$ was obtained by difference Fourier calculations. Final refinements including anisotropic displacement parameters led to the conventional residuals $R(F) = 0.032$ and $R_w = 0.037$ (for $I > 3\sigma(I)$). The positional parameters, standardized using the program Structure Tidy (10), are listed in Table 2 and the main interatomic distances are in Table 3. A search for parent compounds from a data base of inorganic compounds (11) revealed that U_3TiGe_5 crystallizes with the U_3TiSb_5 structure type (12) suggesting that a similar compound should form also with tin. As expected, the X-ray powder pattern of

TABLE 2
Atomic Parameters (X-Rays) for U_3TiGe_5[a]

Atom	U[b]	Ge(1)	Ge(2)	Ti
Site	$6g$	$6g$	$4d$	$2b$
x	0.61522(5)	0.2631(1)	$\frac{1}{3}$	0
y	0	0	$\frac{2}{3}$	0
z	$\frac{1}{4}$	$\frac{1}{4}$	0	0
B_{11}	0.391(7)	0.44(2)	0.53(2)	0.53(5)
B_{22}	0.52(1)	0.43(3)	B_{11}	B_{11}
B_{33}	0.52(1)	0.72(3)	0.70(4)	0.41(8)
B_{12}	B_{22}	B_{22}	B_{11}	B_{11}
B_{eq} ($Å^2$)	0.463(5)	0.53(2)	0.59(1)	0.49(3)

[a] $B_{13} = B_{23} = 0$.

[b] The form of the anisotropic displacement parameter is

$$\exp[-\tfrac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})],$$

where a^*, b^*, and c^* are reciprocal lattice constants.

TABLE 3
Interatomic Distances (Å) for U_3TiGe_5

U–2Ge(1)	2.894(1)	Ti–6Ge(1)	2.653(1)
1Ge(1)	2.991(1)	2Ti	2.855(1)
4Ge(2)	3.002(1)	6U	3.567(1)
2Ge(1)	3.037(1)		
2U	3.462(1)		
2Ti	3.567(1)		
Ge(1)–2Ti	2.653(1)	Ge(2)–2Ge(2)	2.855(1)
2U	2.894(1)	6U	3.002(1)
1U	2.991(1)	6Ge(1)	3.479(1)
2U	3.037(1)		
4Ge(2)	3.479(1)		
4Ge(1)	3.626(1)		
2Ge(1)	3.872(2)		

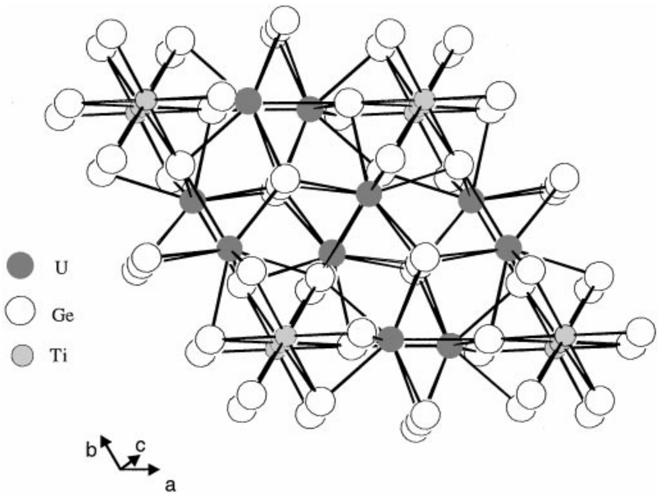

FIG. 1. ORTEP view of the crystal structure of U_3TiGe_5.

U_3TiSn_5 prepared by arc melting the constituent elements and annealing, showed strong similarities with that of U_3TiGe_5. An intensity calculation carried out using the program Lazy-Pulverix with the same positional parameters as those determined for U_3TiGe_5 confirmed the isomorphism of U_3TiSn_5. The lattice parameters of U_3TiSn_5 were calculated by a least-squares refinement of room-temperature X-ray powder diffraction data, using Cu$K\alpha_1$ radiation with an internal standard of silicon, giving the values $a = 9.200(2)$ Å, $c = 6.128(3)$ Å, and $c/a = 0.666$.

A view of the crystal structure of U_3TiGe_5 is displayed in Fig. 1. Uranium is coordinated by nine germanium atoms forming a tricapped trigonal prism, with U–Ge distances ranging from 2.894 to 3.037 Å. The shortest uranium-uranium distance (3.462 Å) is close to the Hill limit (3.4 Å)

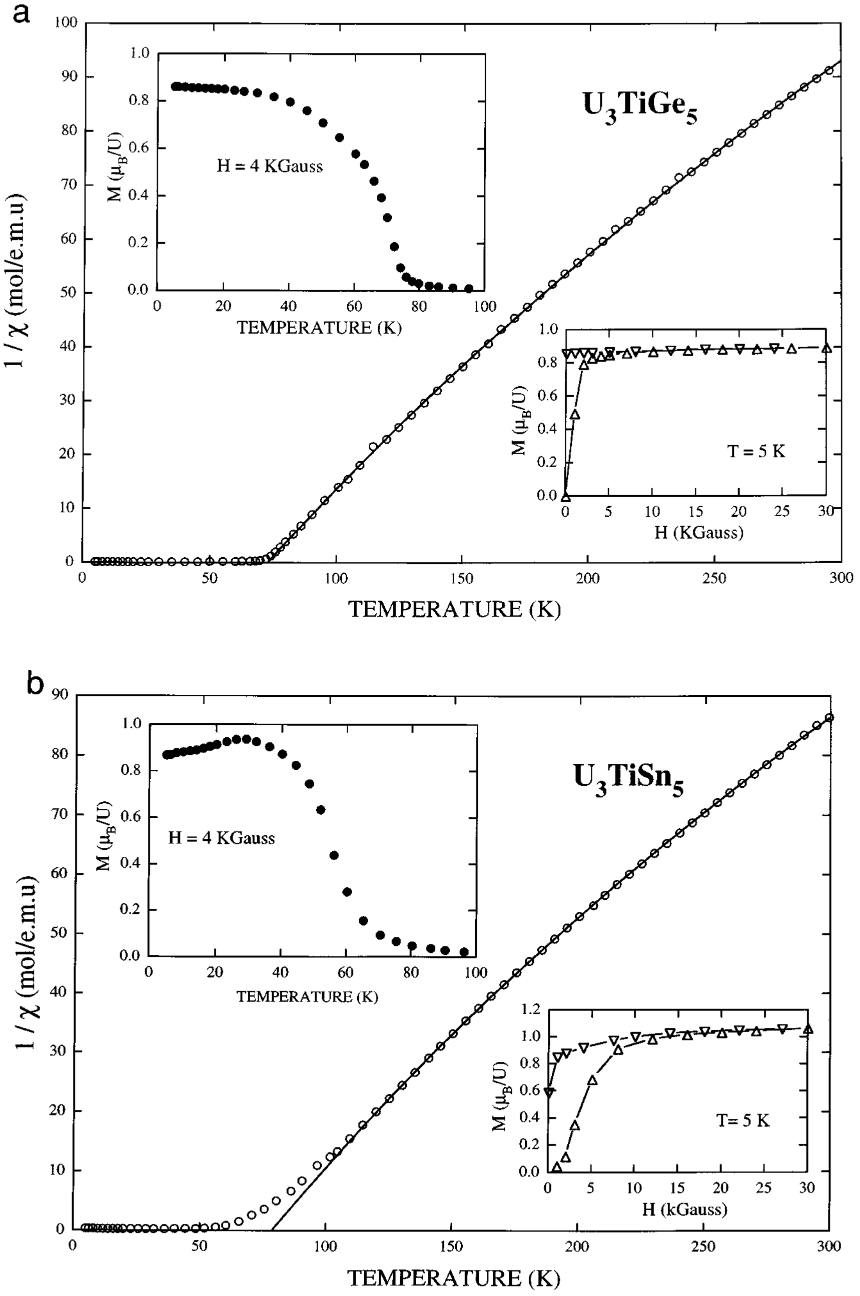

FIG. 2. Temperature dependences of the inverse magnetic susceptibility χ^{-1} of U_3TiGe_5 (a) and of U_3TiSn_5 (b) under 4 kG. The symbols represent the measured values, and the solid line is a fit by the modified Curie–Weiss law. The lower inset shows the first magnetization curve at $T = 5$ K. The upper inset shows the thermal variation of magnetization under 4 kG.

below which some direct 5*f*–5*f* shell overlap is expected to occur. The titanium atoms are coordinated to six germanium atoms forming a triangular antiprism and are aligned in columns along the *c* axis with interatomic distances Ti–Ti $= c/2 = 2.855$ Å.

The U_3TiSb_5 type structure can be considered as an anti Hf_5CuSn_3 (13) type which is an ordered version of the Ti_5Ga_4 structure type. An interesting feature of these series of ternary compounds U_3TiX_5 is that all the corresponding binaries with formula U_5X_4 with X = Ge (3), Sn (14), Sb (15) crystallize in the Ti_5Ga_4 structure type. The titanium sites of Ti_5Ga_4 are occupied either by uranium in the binary U_5X_4 or by the metalloid element in the ternary compound U_3TiX_5.

MAGNETIC BEHAVIOR

Magnetic measurements carried out on an polycrystalline powder sample indicate a ferromagnetic type ordering below $T_C = 76(2)$ K and $T_C = 65(2)$ K for U_3TiGe_5 and

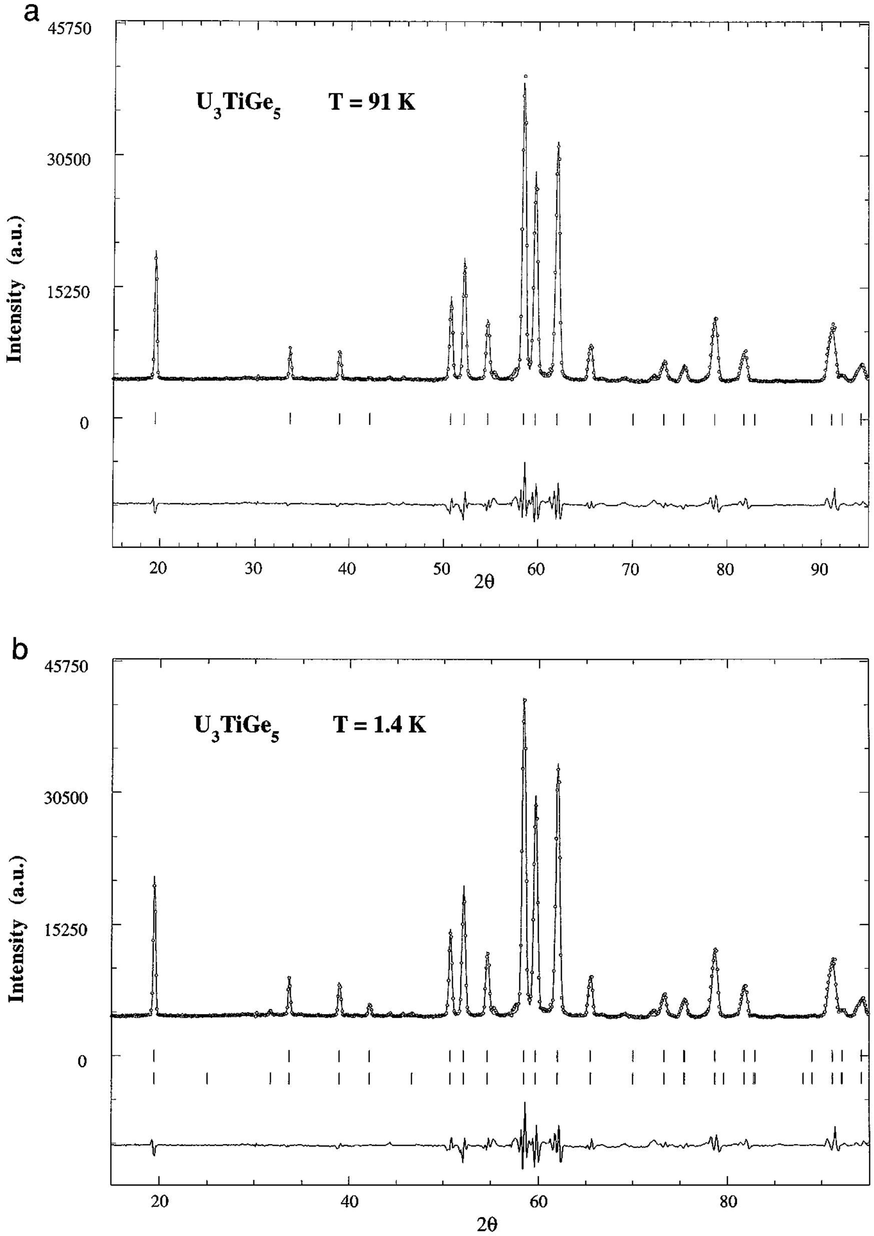

FIG. 3. Neutron powder diffraction pattern of U_3TiGe_5 at 91 K (a) and at 1.4 K (b). The symbols represent the observed points, the solid lines represent the calculated profile and the difference between observed and calculated profiles. The ticks correspond to $2\theta_{hkl}$ Bragg positions either of nuclear (upper ticks) or magnetic (lower ticks) origin.

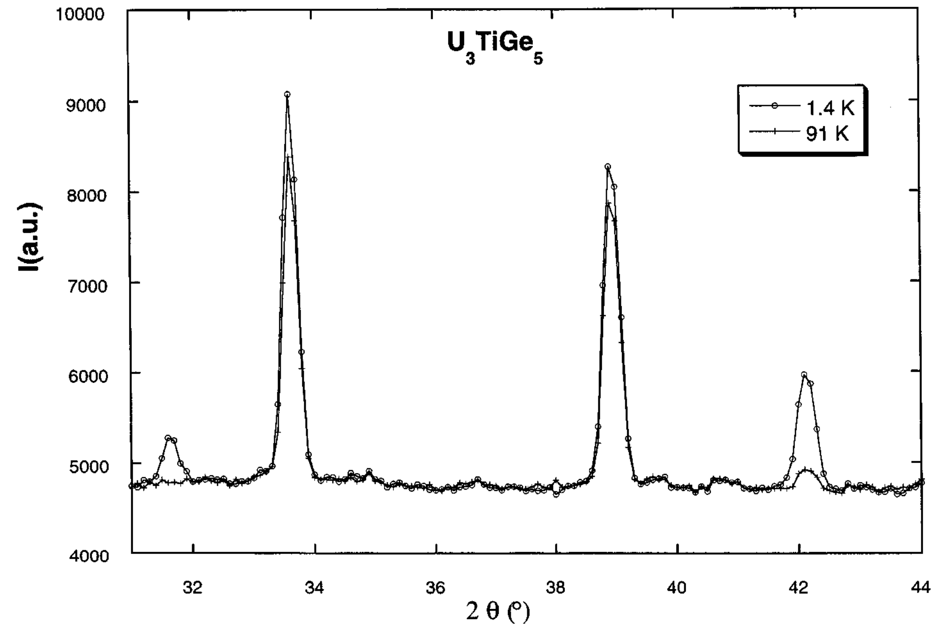

FIG. 4. Evolution of the four main magnetic Bragg peaks (101), (110), (200), and (111).

U_3TiSn_5 respectively. Figure 2 (a, b) displays the thermal variation of the inverse susceptibilities of the two compounds, the lower inset shows the magnetization versus field at 5 K and the upper inset shows the magnetization versus temperature under 4 kG. The measured remanent moment at 5 K is 0.85(1) μ_B/U for the germanide and 0.58(1) μ_B/U for the stannide. The small decrease of the saturated moment below 30 K suggests a slight spin reorientation in this low temperature region for U_3TiSn_5. Above the Curie temperature, the susceptibility of these compounds can be fitted with the modified Curie–Weiss law $\chi = \chi_0 + C/(T - \theta)$, leading to the following values:

	μ_{eff} (μ_B/U)	θ (K)	χ_0 (emu/mol)
U_3TiGe_5	2.24(2)	74(1)	$2.18(2) \times 10^{-3}$
U_3TiSn_5	2.29(2)	78(1)	$2.72(2) \times 10^{-3}$

As usual in such intermetallic systems, the effective paramagnetic moment μ_{eff} is lower than the theoretical free ion values of 3.62 μ_B and 3.58 μ_B for U^{3+} and U^{4+}, due to delocalization and crystal field effects. The constant term χ_0 represents mainly the Pauli-type paramagnetism of the conduction electrons.

NEUTRON DIFFRACTION STUDY OF U_3TiGe_5

Neutron powder diffraction experiments were performed for U_3TiGe_5 above and below T_C, in the temperature range 1.4–91 K. The diffraction patterns show that no crystallographic transition occurs in this temperature range. Rietveld refinement of the nuclear diffraction pattern collected at 91 K (Fig. 3a) confirmed ($R_B = 0.050$) that U_3TiGe_5 crystallizes with the U_3TiSb_5 type structure. The refined values of the only variable positional parameters are $x_U = 0.614(1)$ and $x_{Ge1} = 0.261(1)$.

In comparison to the nuclear pattern at $T = 91$ K, the neutron powder diffraction pattern at $T = 1.4$ K (Figs. 3b and 4) shows additional intensities which are of magnetic origin. These magnetic Bragg peaks are all indexed in the $P6_3/mcm$ space group, i.e., with identical crystallographic and magnetic unit cells. Within this unit cell, six uranium atoms are available with respective magnetic moments M_1 to M_6.

Magnetic representation analysis applied to the $P6_3/mcm$ space group, $k = 0$ propagation vector and (6*g*) crystallographic site, leads to the existence of 12 irreducible representations (τ_1 to τ_{12}, following Kovalev' notation (16)). Among these, only six, namely τ_2, τ_3, τ_4, τ_5, τ_7, and τ_8, which are one-dimensional, are associated to magnetic moments M_1 to M_6 of the same amplitude (Fig. 5).

The best fit to the observed data ($R_B = 0.064$; $R_M = 0.09$) mixes τ_2 and τ_3 "solutions." The uranium magnetic moments in U_3TiGe_5 have two components (Fig. 6): one is ferromagnetic, parallel to the hexagonal *c* axis [τ_3] and equal to $M_F = 0.91(7)$ μ_B at $T = 1.4$ K; the other is antiferromagnetic, perpendicular to *c* [τ_2] and equal to $M_{AF} = 0.42(8)$ μ_B at $T = 1.4$ K. The total ordered uranium magnetic moment amounts then to 1.00(7) μ_B.

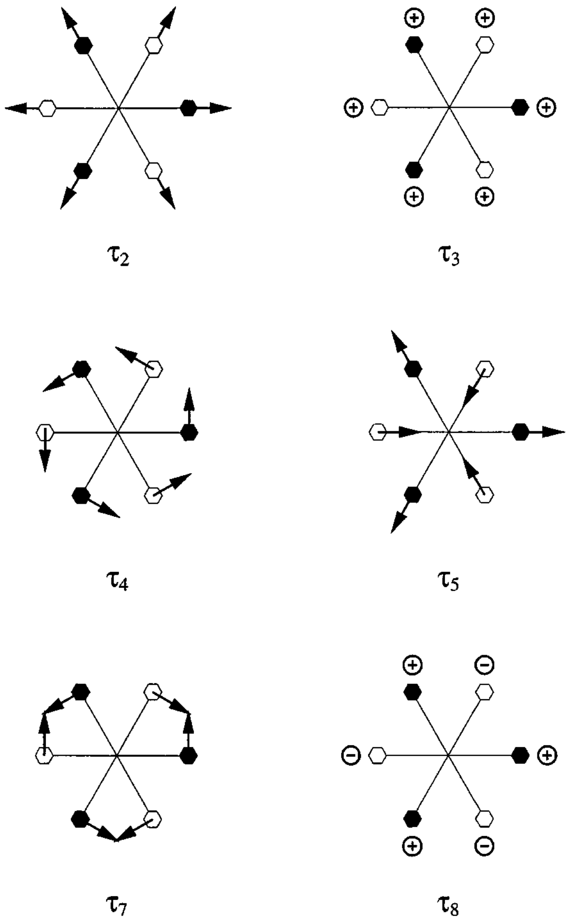

FIG. 5. "$P6_3/mcm$, ($6g$) Wyckoff position, $k = 0$ propagation vector" magnetic structures associated to one-dimensional τ_2, τ_3, τ_4, τ_5, τ_7, and τ_8 irreducible representations. The full (open) symbols are for uranium atoms at $z = \frac{1}{4}$ ($z = \frac{3}{4}$). The magnetic moments are either parallel ((+) or (−)) or perpendicular (arrows) to the hexagonal c axis.

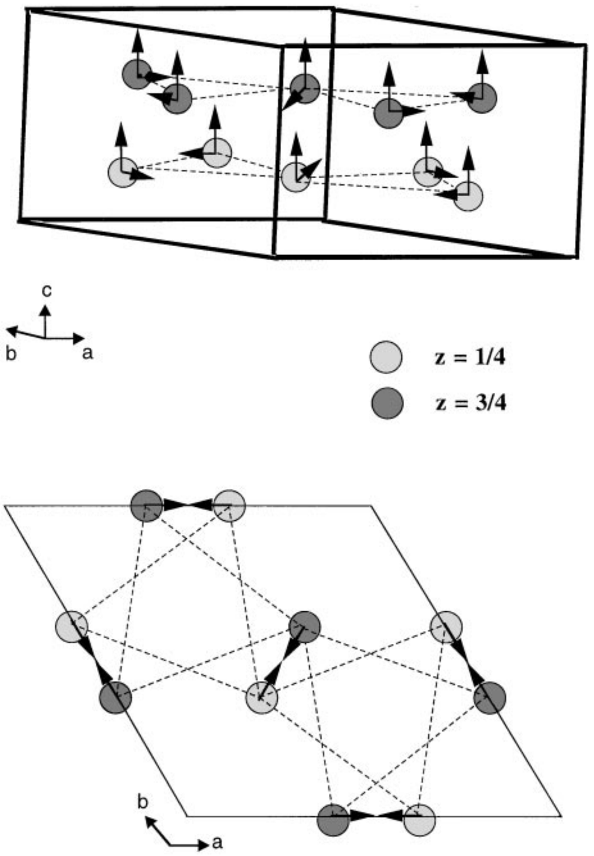

FIG. 6. View of the magnetic components of the magnetic structure of U_3TiGe_5.

In order to determine the magnetic transition temperature in U_3TiGe_5, neutron powder diffraction data have been collected at several temperatures. The thermal variation of the "main" magnetic Bragg peak (111), is shown on Fig. 7, leading to $T_C = 76(2)$ K, in agreement with the magnetic measurements.

CONCLUSION

This paper reports on the characterization of the first ternary compounds isolated in the U–Ti–Ge and U–Ti–Sn systems. U_3TiGe_5 exhibits a rather unusual magnetic structure and it will be interesting to determine that of the isostructural stannide U_3TiSn_5, which orders also ferromagnetically but at lower temperature and with a lower magnetic moment. Moreover this later compound seems to exhibit some spin reorientation around 30 K which could correspond to a transition from a noncollinear to a collinear arrangement of the magnetic moments.

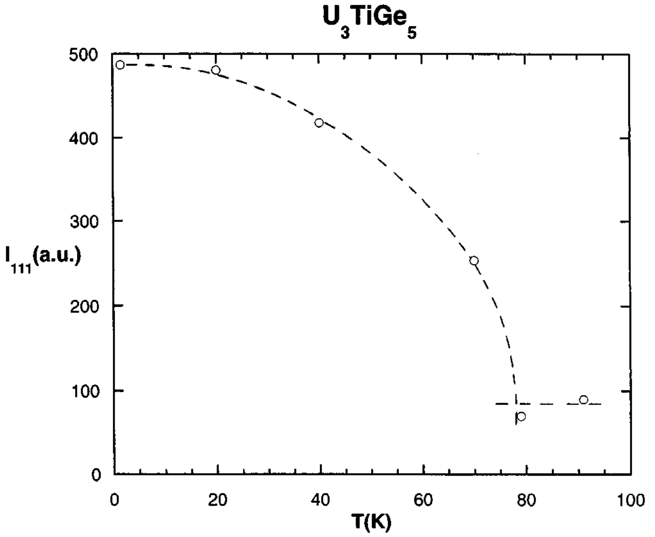

FIG. 7. Thermal variation of the integrated intensity of the (111) Bragg peak, which has a small nuclear component; dashed lines are guides for the eyes.

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