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# Crystal structure and magnetic properties of $UFe_5Ga_7$

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ABSTRACT

The new ternary compound $UFe_5Ga_7$ was prepared by an argon arc-melting followed by annealing. This intermetallic compound belongs to the series $UFe_xGa_{12-x}$ and crystallizes in a structure related with the $ThMn_{12}$-type, with $a = 8.6309$ Å and $c = 5.0524$ Å. EDS elemental analysis yielded the phase composition $UFe_{4.9(2)}Ga_{6.8(1)}$, which is very close to the nominal composition. Dc magnetization measurements revealed ferromagnetic type of magnetic ordering in $UFe_5Ga_7$. The Curie temperature of ~439 K was estimated by the temperature dependence of magnetization at a low magnetic field of 0.1 T.



## 1. Introduction

Intermetallic compounds of *f*-elements with the $AFe_xT_{12-x}$ general formula, where A is a lanthanide or actinide element and T stands for Al, Ga, Si, Ge or a transition metal, have been intensively investigated [1–5]. This type of compounds presents a variety of magnetic properties and plays an important role for a better understanding of the iron and *f*-element sublattices contributions to the magnetism of intermetallics.

Several of these compounds crystallize in the tetragonal $ThMn_{12}$-type structure (space group I4/*mmm*), that exists only for $SmFe_{12}$ as a binary intermetallic. Interestingly, the stability of this structure is greatly expanded by the addition of a third element [2]. Materials with this type of structure are usually considered as good candidates for providing new hard magnets due to their high Curie temperature and large magnetocrystalline anisotropy [6].

Aluminium is one of the most studied $ThMn_{12}$ phase stabilizing elements, mainly for a group with low content of transition elements [2,7,8]. The phase equilibria in ternary systems, in which the $ThMn_{12}$-type of structure is observed, were studied for numerous aluminides and the isothermal section at 850 °C for the U–Fe–Al system was reported [9]. For the ternary semi-ordered alloys $UFe_xAl_{12-x}$ it was recently found that the stabilization of the $ThMn_{12}$-type structure requires Al atomic contents higher than 38% and that the magnetic behaviour changes dramatically with small changes in the composition [9]. The $UFe_4Al_8$ compound is known for its complex magnetic structure and uncommon physical properties [10–12]; $UFe_5Al_7$, $UFe_6Al_6$, and $UFe_7Al_5$ are ferromagnetic, but the latter shows two magnetic transitions [1,3,4]. Comparing $UFe_5Al_7$ ($a = 8.6977$ Å, $c = 5.0223$ Å, $T_C = 262$ K) and $UFe_{4.85}Al_{7.15}$ ($a = 8.7065$ Å, $c = 5.0241$ Å, $T_C = 252$ K), during investigations on the $UFe_xAl_{12-x}$ series (with $4.5 \leqslant x \leqslant 5$) [4], it was demonstrated that the magnetic structure of the iron sub lattice changes with the chemical composition because of the occupation of the 8j site by iron atoms.

Gallium is also known as stabilizer of the $ThMn_{12}$-type phases [2]: it stabilizes ternary compounds having the same transition elements as in aluminium compounds, but is not so well studied, especially in actinide systems.

Only five ternary phases belonging to the U–Fe–Ga system have been reported until now: $UFeGa_5$ [13], UFeGa [14], $UFe_6Ga_6$ [15], $U_2FeGa_8$ [16], and $U_4FeGa_{12}$ [17]. Recently the first results on the isothermal section of the U–Fe–Ga ternary phase diagram at 800 °C were presented, with the identification of four new ternary phases and six extended solubility ranges [18]. One of the solubility ranges was $UFe_{12-x}Ga_x$, which crystallizes in the $ThMn_{12}$-type structure and comprises $UFe_5Ga_7$ as the iron lower content composition. In this paper the preliminary results on the structural and magnetic characterization of the new $UFe_5Ga_7$ intermetallic by means of X-ray powder diffraction, SEM/EDS and dc magnetization measurements are presented.

## 2. Experimental details

Samples of $UFe_5Ga_7$ were prepared by arc-melting the appropriate amounts of the elements (purity >99.9% w/w), under a titanium-gettered high purity argon atmosphere in a water-cooled copper earth. The surface of the uranium ingots was cleaned in

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diluted nitric acid prior to the melting. The resulting samples were re-melted at least three times to guarantee homogeneity. Weight losses during this procedure were less than 0.5%. The samples were enveloped in molybdenum foils, placed in a quartz tube, which was subsequently evacuated and flame-sealed. The annealing was carried out during two weeks at 1000 K followed by one week at 1100 K.

X-ray powder diffraction patterns were taken at room temperature using a Philips X'Pert diffractometer (Bragg–Brentano assembly, monochromatized Cu Kα radiation, $10° < 2\theta < 70°$, step width 0.03°, and 50 s of counting time/step). The collected powder data were used for phase identification with the help of the program PowderCell [19].

The samples were polished and etched with *Aqua Regia*, before analyzed by scanning electron microscopy (SEM). A Jeol JSM-7001F field emission microscope, equipped with energy dispersive X-ray spectroscopy (EDS) for chemical analysis through the atomic characteristic X-rays excited by the electron beam operating at 25 kV, was used. At least three EDS points were acquired for each phase. The spatial resolution is 2.5 μm for iron and gallium, and 1 μm for uranium.

The low temperature magnetic characterization was carried out using a SQUID magnetometer (Quantum Design) for temperatures ranging from 4 to 380 K and magnetic fields up to 5.5 T. Measurements of magnetization versus temperature were performed in increasing temperature after zero-field cooling (ZFC) or cooling in the measurement field (field cooling – FC). High temperature magnetization versus temperature was measured using a Quantum Design SQUID MPMS-5S magnetometer. Isofield data were collected at 0.1 and 0.5 T in the 200–750 K temperature range. The data were corrected for the background signal, mainly due to a quartz tube sample holder with a negligible temperature dependent susceptibility of about $-2 \times 10^{-4}$ emu at 5 T.

## 3. Results and discussion

The experimental X-ray powder diffraction patterns of the annealed $UFe_5Ga_7$ samples (Fig. 1) show that the main phase has a structure that is in general compatible with the $ThMn_{12}$-type (space group $I4/mmm$). Uranium dioxide, $UO_2$ (space group $Fm\text{-}3\,m$), is also present in the sample in a small quantity (~5% v/v). However, one foreign peak exists, at $2\theta \sim 31.5°$, and some peaks are doubled, cannot being indexed using this structure type.

The scanning electron microscopy analysis of the $UFe_5Ga_7$ sample shows two zones: a main phase and a minor eutectic region, distributed homogeneously in the first one (Fig. 2). EDS elemental analysis of the primary phase indicates a U:4.9(2)Fe:6.8(1)Ga composition, very close to the nominal one. The minor region is a binary eutectic, localized in small islands, and amounts to ~4% v/v of the sample (obtained by image processing). The small microstructure of the eutectic was not suitable for EDS analysis of the components, but the similarity of contrasts in backscattered mode indicates that one of them is the main phase.

The powder X-ray diffraction and SEM/EDS results show the existence of a $UFe_5Ga_7$ major phase (~95% vol.) and point to the

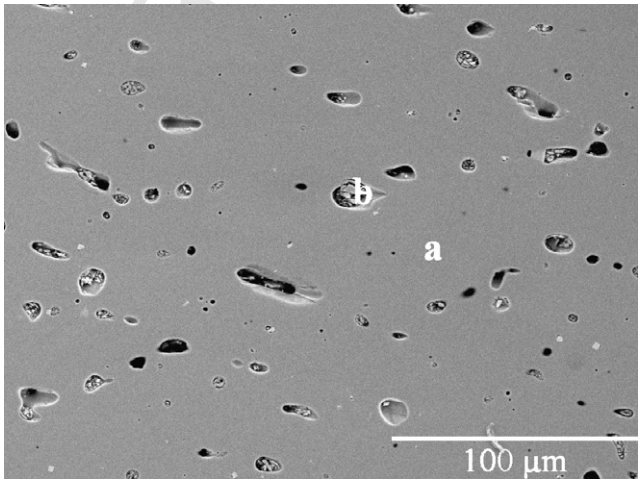


**Fig. 2.** SEM micrograph of the sample $UFe_5Ga_7$: (a) $UFe_7Ga_5$, (b) eutectic phase.

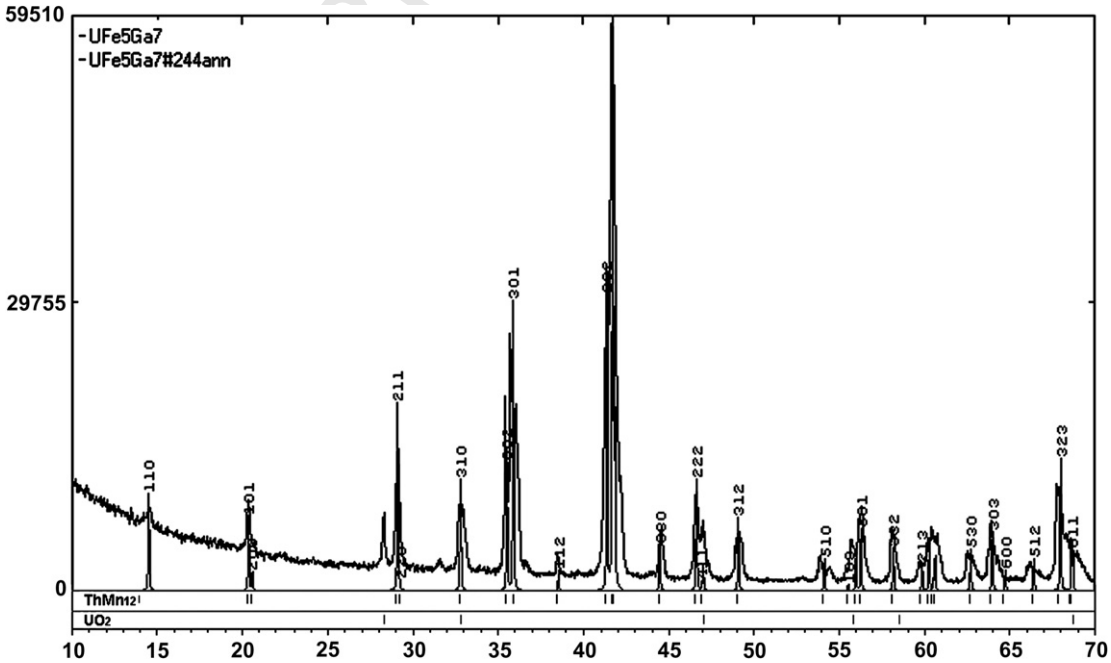


**Fig. 1.** Observed (black) and calculated (grey) X-ray diffraction patterns for the $UFe_5Ga_7$ sample.

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possibility of a superstructure in the lattice of this phase: besides the uranium oxide, there is no evidence of the presence of any other compound in the sample above the detection limit for the X-ray diffraction apparatus (ca. 5% v/v); the minor phase seems to be formed through an eutectic reaction between $UFe_5Ga_7$ and an unidentified phase, the amount of the unknown phase in the sample being <2% v/v. All this means that the minor phase cannot be the cause of the unidentified X-ray peaks, which thus are assumed to originate from the main phase. The tendency to stabilize superstructures was already observed before in this solubility range for the $UFe_6Ga_6$ composition, which does not crystallize in the $ThMn_{12}$-type structure but with the ordered *mmm*-symmetry [20]. The existence of a superstructure does not allow any rietveld refinement of the data, but considering the $ThMn_{12}$-type structure the refinement of the $UFe_5Ga_7$ lattice parameters results in $a = 8.6309$ Å and $c = 5.0524$ Å.

The low temperature dependence of the magnetization for the $UFe_5Ga_7$ sample, $M(T)$, in a field of 5 mT, is shown in Fig. 3. There is no evidence of magnetic transitions from 380 K down to 4 K. However, the ZFC and FC behaviours are typical of a ferromagnet with a Curie temperature above 380 K, showing irreversibility in all the studied temperature range. The high temperature dependence of the magnetization measured in a field of 0.1 T (Fig. 4) shows a ferromagnetic-type behaviour. The Curie temperature can be determined as a minimum of the temperature derivative

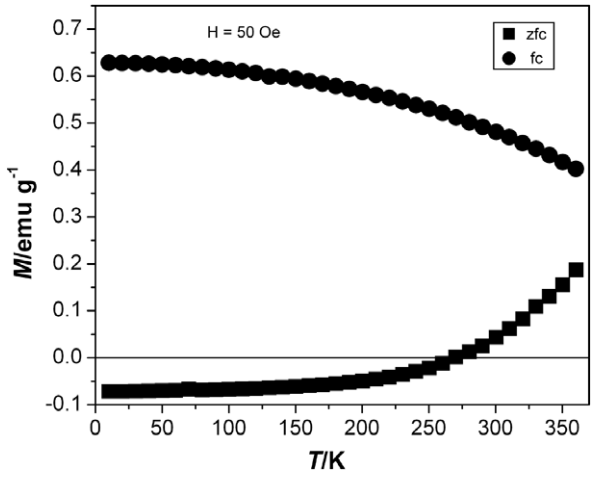


**Fig. 3.** Low temperature dependence of the magnetization for the $UFe_5Ga_7$ compound.

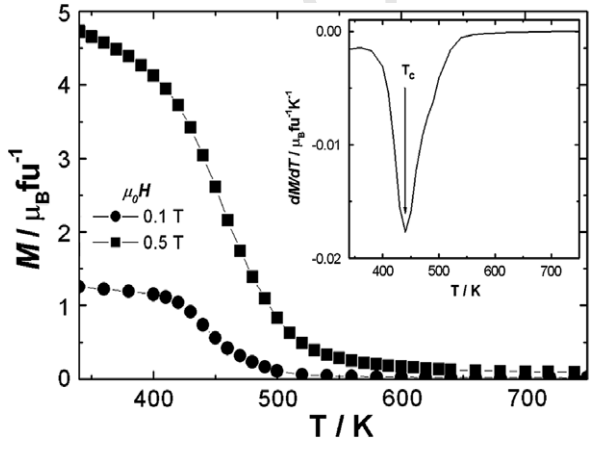


**Fig. 4.** High temperature dependence of the magnetization for the $UFe_5Ga_7$ compound. Inset shows in detail the temperature derivative of the magnetization.

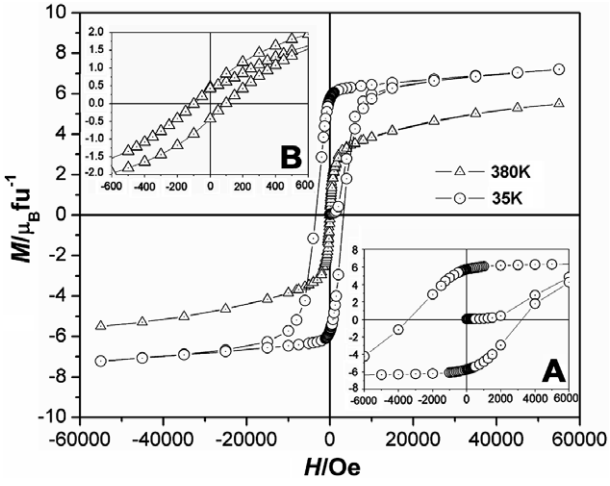


**Fig. 5.** Field dependence of the magnetization and hysteresis loops for the $UFe_5Ga_7$ compound. Insets: Details of the $M(H)$ curves at 35 K (A) and 280 K (B).

of the magnetization. For $UFe_5Ga_7$, the Curie temperature obtained with this procedure amounts to 439(3) K. Similar to other metallic ferromagnets, the inflection point of the magnetization increases with applied field strength, and for instance, attains a value of 450 K in a field of 0.5 T. Clearly, the Curie temperature for $UFe_5Ga_7$ is higher than the ordering temperatures found before for $UFe_5Al_7$, 262(5) K [4] and 268 K [1], and is even higher than that obtained for $UFe_7Al_5$, ferromagnetic below 363 K [3]. However, it is in comparable with that observed for $UFe_6Ga_6$, $T_C = 530(5)$ K [20].

The hysteresis loops obtained at 35 K and 380 K, are shown in Fig. 5. These curves evidence a clear ferromagnetic-type behaviour, in conformity with the $M(T)$ measurements. Note, that there is no saturation for fields up to 5.5 T for all the temperatures studied. At $T = 35$ K, the coercive field $H_c$ is 3.1 T and the remanence is about 5.7 $\mu_B$/f.u., while at 380 K the value obtained for the coercive field is 11 mT and the remanent magnetization 0.4 $\mu_B$/f.u.

## 4. Conclusions

The new uranium ternary gallide, $UFe_5Ga_7$, has been synthesized and characterized by means of X-ray diffraction and magnetic properties. This compound was found to crystallize in a structure related with the $ThMn_{12}$-type and belongs to the family of general formula $UFe_xGa_{12-x}$. However, the $UFe_5Ga_7$ structure is still under investigation due to the presence of unidentified peaks in the powder X-ray diffraction patterns. It is also interesting to notice that the stability of the $UFe_xGa_{12-x}$ family is more limited when the stabilizing element is Ga, compared with the Al case. $UFe_5Ga_7$ is a ferromagnetic-like compound with a Curie temperature of 439(3) K and the coercive field of 0.3 T at 35 K. The transition temperature of $UFe_5Ga_7$ being higher than the one obtained for $UFe_5Al_7$, but it is lower than that of $UFe_6Ga_6$. This observation indicates that although the increase of Ga content decreases the strength of the ferromagnetic interaction as in Al compounds, Ga materials are comparatively more magnetically stable than aluminium ternary compounds with the same stoichiometry. The enhancement in the ordering temperature was found for other compounds with Ga as stabilizing element, compared to compounds where the third element is Al [4].

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## References

[1] H.-S. Li, J.M.D.S. Coey, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, vol. 6, Elsevier Science Publishers B.V., 1991, p. 1.
[2] W. Suski, in: K.A. Gschneider Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 22, North Holland, Elsevier, Amsterdam, 1996.
[3] A.P. Gonçalves, J.C. Waerenborgh, M. Almeida, H. Noël, J. Solid State Chem. 174 (2003) 302.
[4] S. Sério, J.C. Waerenborgh, A.P. Gonçalves, M. Almeida, M. Godinho, J. Magn. Magn. Mater. 302 (2006) 282.
[5] A.P. Gonçalves, J.C. Waerenborgh, G. Bonfait, A. Amaro, M.M. Godinho, M. Almeida, J.C. Spirlet, J. Alloys Compd. 204 (1994) 59.
[6] K.H.J. Buschow, Novel permanent magnetic materials, in: G.J. Long, F. Grandjean (Eds.), Supermagnets, Hard Magnetic Materials, Kluwer, Dordrecht, 1991, p. 49.
[7] F.G. Vagizov, W. Suski, K. Wochowski, H. Drulis, J. Alloys Compd. 219 (1995) 271.
[8] K. Rećko, M. Biernacka, L. Dobrzyński, K. Perzyńskat, D. Satuła, K. Szymański, J. Waliszewski, W. Suski, K. Wochowski, G. André, F. Bourée, J. Phys.: Condens. Matter 9 (1997) 9541.
[9] A.P. Gonçalves, H. Noël, Intermetallics 13 (2005) 580.
[10] J.C. Waerenborgh, A.P. Gonçalves, G. Bonfait, M. Godinho, M. Almeida, Phys. Rev. B 60 (1999) 4074.
[11] G. Bonfait, M. Godinho, P. Estrela, A.P. Gonçalves, M. Almeida, J.C. Spirlet, Phys. Rev. B 53 (1996) R480.
[12] J.A. Paixão, B. Lebech, A.P. Gonçalves, P.J. Brown, G.H. Lander, P. Burlet, A. Delapalme, J.C. Spirlet, Phys. Rev. B 55 (1997) 14370.
[13] Y.N. Grin, P. Rogl, K. Hiebl, J. Less-Comm. Met. 121 (1996) 497.
[14] E. Brück, Hybridization in Cerium and Uranium Intermetallics, PhD Thesis, University of Amsterdam, 1991.
[15] A.P. Gonçalves, M. Almeida, A. Amaro, M. Godinho, J.A. Paixão, J.C. Spirlet, J. Magn. Magn. Mater. 157&158 (1996) 692.
[16] S. Ikeda, T. Okubo, Y. Inada, Y. Tokiwa, K. Kaneco, T.D. Matsuda, E. Yamamoto, Y. Haga, Y. Ōnuki, J. Phys. Condens. Matter 15 (2003) S2015.
[17] R. Jardin, E. Colineau, J.-C. Griveau, P. Boulet, F. Wastin, J. Rebizant, J. Alloys Compd. 432 (2007) 39.
[18] A.P. Gonçalves, H. Noël, O. Tougait, A. Zelinskiy, in: Proceedings of the 38 JdA, Wroclaw, Poland, 2008, P06.
[19] G. Nolze, W. Krauss, PowderCell 2.3 Program, BAM Berlin, 2000
[20] A.P. Gonçalves, J.C. Waerenborgh, S. Sério, J.A. Paixão, M. Godinho, M. Almeida, Intermetallics 14 (2006) 530.



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