Magnetic Properties of the $U_2Fe_{17-x}M_xC_y$ Intermetallic Compounds with M = Al, Si, and Ge

B. Chevalier, P. Rogl,[1] and J. Etourneau

Laboratoire de Chimie du Solide du CNRS, Université Bordeaux I, 351 Cours de la Libération, F-33405 Talence, France

"U_2Fe_{17}" does not exist in thermodynamic equilibrium; however, alloying uranium with electron donor elements such as Al, Si, or Ge yields compound formation with crystal structures isotypic with the Th_2Ni_{17}-type or derivative structures such as $U_2Fe_{12.8}Si_{4.2}$. The octahedral voids can be partially filled with carbon atoms without exceeding one carbon atom per formula unit. Powder X-ray diffraction of the carbon-containing compounds in all cases revealed the Th_2Ni_{17}-type of structure with a small increase in volume by ~0.0075 nm³ per interstitial carbon atom per formula unit. There is only a small influence of the carbon-induced volume increase on the ferromagnetic ordering temperature of the alloys. © 1995 Academic Press, Inc.

I. INTRODUCTION

Although R_2Fe_{17}-compounds are among the most prominent binary rare earth iron phases, no equilibrium phase "U_2Fe_{17}" has been mentioned in the accepted version of the U–Fe binary phase diagram (1).

Previous investigations demonstrated the stabilizing influence of Si or Ge additions on the formation of thermodynamically stable phases $U_2Fe_{17-x}M_x$ with M = Si and Ge which are ordered ferromagnetically (2–5). The homogeneity range of these compounds depends strongly on the experimental conditions of preparation. After melting and quenching, the silicides $U_2Fe_{17-x}Si_x$ exist for $3.3 \leq x \leq 4.5$ but they decompose partially after annealing at 850–900°C (3). In contrast, the germanides $U_2Fe_{17-x}Ge_x$ are obtained as single phase for $2 \leq x \leq 3$ only after annealing at 850°C (5). The crystal structures, in which novel phases have been observed to crystallize (Th_2Ni_{17}-type or derivative types; see Refs. 3, 5, 6), contain octahedral voids [$U_2Fe,M)_4$], suitable for the incorporation of small interstitials such as carbon or nitrogen atoms. Carbon and nitrogen solubility in R_2Fe_{17} rare earth–iron compounds crystallizing in the rhombohedral Th_2Zn_{17}-type or in the hexagonal Th_2Ni_{17}-type has proven to efficiently increase the ferromagnetic ordering temperatures as well as to increase or even induce uniaxial magnetocrystalline anisotropy (7–10).

We have extended our investigations both on the uranium–iron–aluminum system and on the formation of $U_2Fe_{17-x}M_xC_y$ compounds with M = Al, Si, and Ge. The present paper is devoted to the magnetochemical influence of carbon on the ferromagnetic behavior of these novel materials.

II. EXPERIMENTAL

The samples, each of a weight of ca. 1 g, were prepared from the elements by levitation melting in a water-cooled Hukin crucible under purified argon. Starting materials were depleted nuclear grade uranium platelets which, prior to use, were surface cleaned in dilute nitric acid. Iron and aluminum of 99.95 mass % minimum purity were obtained from Alfa Ventron, Karlsruhe, Germany. Silicon and germanium with a purity of 99.99% from Pechiney, France and Alfa-Ventron, Germany, respectively, were used in the form of solid pieces. Carbon with a purity of 99.99% from Carbonne Lorraine, France, was added to the premelted master alloys in the form of small flakes. To ensure homogeneity all samples were remelted several times. Due to the controlled melting conditions, weight losses in all cases were practically negligible (<5‰). The alloys were then wrapped in protective molybdenum foil, sealed in evacuated silica tubes, annealed for 180 hr, and quenched by submerging the quartz capsules in water.

All samples were characterized through their Guinier powder patterns, which were recorded with $CuK\alpha_1$ radiation using 5N silicon (a = 0.54307 nm) as an internal standard. The lattice constants were obtained by least-squares fits of the powder data.

Magnetization measurements were carried out between 4.2 and 900 K using a pendulum susceptometer. Magnetic thermal scans above room temperature were performed on samples sealed in very small quartz tubes with almost no free volume, so that oxygen contamination was minimal.

[1] On leave from the Institut für Physikalische Chemie der Universität Wien, Währingerstrasse 42, A-1090 Vienna, Austria.

TABLE 1
Crystallographic and Magnetic Data of Compounds $U_2Fe_{17-x}M_xC_y$ (M = Al, Si, Ge)

Phase	Structure type and space group	a (nm)	c (nm)	c/a	V (nm³)	T_c (K)	Refs.
$U_2Fe_{12}Al_5$	Th₂Ni₁₇ P6₃/mmc	0.8574(2)	0.8440(3)	0.984	0.5373(3)	298	a
$U_2Fe_{12}Al_5C_{0.75}$	Th₂Ni₁₇ P6₃/mmc	0.8588(2)	0.8440(3)	0.983	0.5391(3)	315	a
$U_2Fe_{13.5}Si_{3.5}$	Th₂Ni₁₇ P6₃/mmc	0.8343(2) 0.8334	0.8243(6) 0.8234	0.988 0.988	0.4969(4) 0.4953	510 512	a (3, 4)
$U_2Fe_{13.5}Si_{3.5}C_{0.5}$	Th₂Ni₁₇ P6₃/mmc	0.8368(2)	0.8235(6)	0.984	0.4993(4)	522	a
$U_2Fe_{13.5}Si_{3.5}C_{0.73}$	Th₂Ni₁₇ P6₃/mmc	0.8389(1)	0.8236(3)	.0.982	0.5019(2)	522	a
$U_2Fe_{13.5}Si_{3.5}C_1^b$	Th₂Ni₁₇ P6₃/mmc	0.8399(4)	0.8228(4)	0.980	0.5026(5)	—	a
$U_2Fe_{12.75}Si_{4.25}$	U₂Fe₁₂.₈Si₄.₂ P6/mmm	0.8373^c 0.4836(3)	0.8157^c 0.4075(4)	0.974 0.843	0.4952 0.0825(4)	458 458	a ^{a}(3)
$U_2Fe_{12.75}Si_{4.25}C_{0.63}$	Th₂Ni₁₇ P6₃/mmc	0.8389(4)	0.8211(4)	0.979	0.5004(5)	484	a
$U_2Fe_{12.75}Si_{4.25}C_1^b$	Th₂Ni₁₇ P6₃/mmc	0.8384(3)	0.8220(3)	0.980	0.5003(3)	—	a
$U_2Fe_{14.5}Ge_{2.5}$	Th₂Ni₁₇ P6₃/mmc	0.8433(3) 0.8424	0.8374(6) 0.8360	0.993 0.992	0.5157(4) 0.5138	544 545	a ^{a}(5)
$U_2Fe_{14.5}Ge_{2.5}C_{0.5}$	Th₂Ni₁₇ P6₃/mmc	0.8481(6)	0.8367(9)	0.987	0.5212(8)	547	a

^{a} This work.

^{b} Sample was multiphase.

^{c} Lattice parameters of the corresponding cell with the geometry of Th₂Ni₁₇-type, $a = a_0\sqrt{3}$, $c = 2c_0$.

III. RESULTS AND DISCUSSION

A. Compound Formation and Carbon Solubility

The alloy series $U_2Fe_{17-x}M_xC_y$ (M = Si, Ge). Analyses of the X-ray powder Guinier data for the intermetallic combinations as well as for the samples with carbon (see Table 1) confirm the crystal symmetry of the Th₂Ni₁₇-type structure in all cases. The only exception is the alloy at the silicon-rich end of the homogeneous region, namely $U_2Fe_{12.75}Si_{4.25}$. In a recent and detailed study this compound was found to crystallize with a small hexagonal subcell corresponding to the Gd₂Fe₁₇- or U₂Fe₁₂.₈Si₄.₂-type structure (3). It must be mentioned, however, that small but significant deviations from the ideal Th₂Ni₁₇-type have been observed in the $U_2Fe_{17-x}Si_x$ system. These deviations essentially refer to the partial replacement of a pair of iron atoms by one larger uranium atom. Assuming long-range order for the substitution, the ideal Th₂Ni₁₇-type is easily derived from its CaCu₅ base type, $6UT_5 - 2U + 2(2T) = 2U_2T_{17}$, where T is a mixture of Fe and Si. Devia-

tions from these long-range order substitutions have been observed in the region $U_2Fe_{17-x}Si_x$, $3.3 \leq x < 4.5$, and have been refined from single crystal and powder X-ray data (3, 6). In contrast, the ternary germanides $U_2Fe_{17-x}Ge_x$ with $2 \leq x \leq 3$ adopt the ideal Th₂Ni₁₇-type (5).

Small additions of carbon, however, tend rather to stabilize the Th₂Ni₁₇-type of structure, as generally found throughout this investigation. It is assumed that the incorporation of carbon will not alter the partially ordered Fe/Si or Fe/Ge atom distribution, as observed in the carbon free alloys. Carbon solubility was never observed to exceed one carbon atom per formula unit, and in most cases was at a maximum at about 0.75 carbon per formula unit (see Table 1). This behavior is quite similar to that encountered among the rare earth intermetallics containing carbon, $R_2Fe_{17-x}M_xC_y$, where R = Ce, Pr, Nd, Sm and M = Al, Ga, and $0 \leq y \leq 1$, which crystallize with the Th₂Zn₁₇-type of structure (7). The ideal crystal structures of Th₂Ni₁₇ and Th₂Zn₁₇ are closely related since they are both based on the CaCu₅-type with different

FIG. 1. Temperature dependence of the magnetization of "UFe_8Al_4" at a field of 0.29 T.
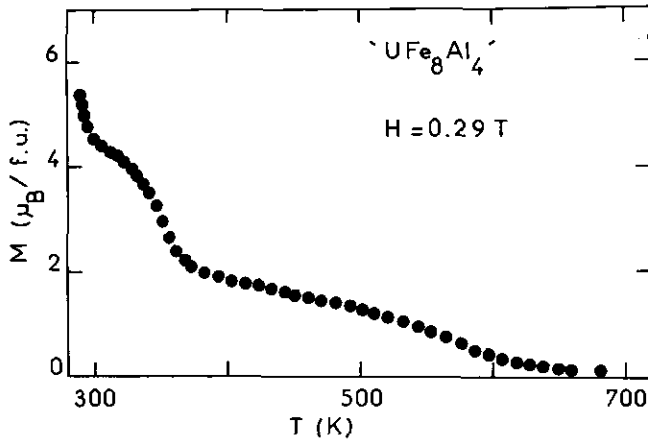

FIG. 2. Temperature dependence of the magnetization of $U_2Fe_{12}Al_5$ at a field of 0.59 T.

modes of stacking. With stacking sequences of two and three units respectively, the c-axes of the two structure types are in a simple relation: $c(Th_2Ni_{17})/c(Th_2Zn_{17}) = \frac{2}{3}$. Referring to one octahedron [Th_2M_4] per stacking unit suitable for nonmetal (carbon) incorporation, the maximum number of carbon atoms per unit cell is thus two for the Th_2Ni_{17}-type and three for the ideal Th_2Zn_{17}-type. In both cases, $R_2Fe_{17-x}M_xC_y$ and $U_2Fe_{17-x}M_xC_y$, only about 30% of the available octahedral voids are occupied by carbon atoms. In case of the uranium-containing phases, the volume increase resulting from carbon solubility is about 0.0075 nm^3 per carbon atom and formula unit (see Table 1) in close agreement with earlier results on $Sm_2Fe_{17-x}M_xC_y$ (11).

The Alloy System $U_2Fe_{12}Al_5C_y$. Recently, Zeleny *et al.* (12) have reported on the formation of a UFe_8Al_4 compound which crystallizes in the tetragonal $ThMn_{12}$-type. The thermomagnetic curve for this material obtained by melting of the elements then annealing at 1200 K reveals at least two magnetic transitions, one at 356 K and the other at the relatively large temperature near 480 K. These authors have attributed these two magnetic transitions to UFe_6Al_6 and UFe_8Al_4, respectively.

We have prepared the "UFe_8Al_4" alloy. The temperature dependence of its magnetization, given in Fig. 1, exhibits three peculiarities: two sharp decreases observed respectively near 300 and 360 K and a very broad decrease in the temperature range from 500 to 600 K. Microprobe analysis indicates that the alloy "UFe_8Al_4" is a heterogeneous mixture containing $UFe_{7.5}Al_{4.5}$, $U_2Fe_{12}Al_5$, and $\alpha Fe(Al)$. In view of this result, the new compound $U_2Fe_{12}Al_5$ has been synthesized and obtained in phase pure form. After annealing at 800°C, it crystallizes in the hexagonal Th_2Ni_{17}-type structure (Table 1). Whereas rather small amounts of silicon or germanium are sufficient to stabilize the $U_2Fe_{17-x}M_x$ phase, aluminum is less
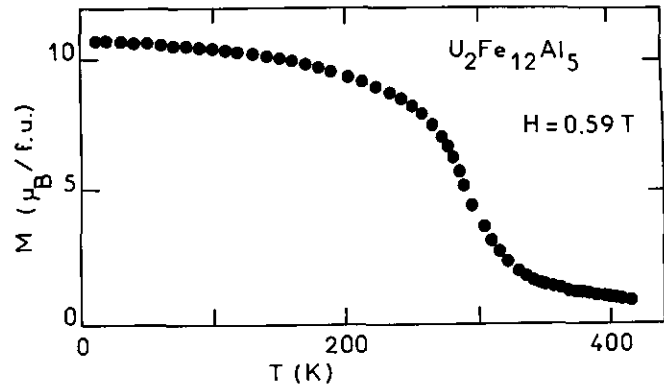
efficient, i.e., replacement of at least 30% of the iron atoms is necessary to form the $U_2Fe_{12}Al_5$ phase.

An X-ray powder diffraction study reveals that the corresponding carbon-containing alloys $U_2Fe_{12}Al_5C_y$ are single phase when $0 \le y \le 0.75$ (Table 1).

B. Ferromagnetic Properties

The temperature dependence of the magnetization of $U_2Fe_{12}Al_5$ is characteristic of ferromagnetic behavior (Fig. 2). The Curie temperature T_c determined from the infection point of the magnetization curve is equal to 298(5) K. This temperature corresponds to that where the first magnetic anomaly is observed for the "UFe_8Al_4" sample (Fig. 1). Any peak attributed to the occurrence of a spin reorientation transition appears in the magnetization curve of $U_2Fe_{12}Al_5$ (Fig.2).

Figure 3 and 4 present some examples of the magnetization curves versus temperature for the $U_2Fe_{17-x}M_xC_y$
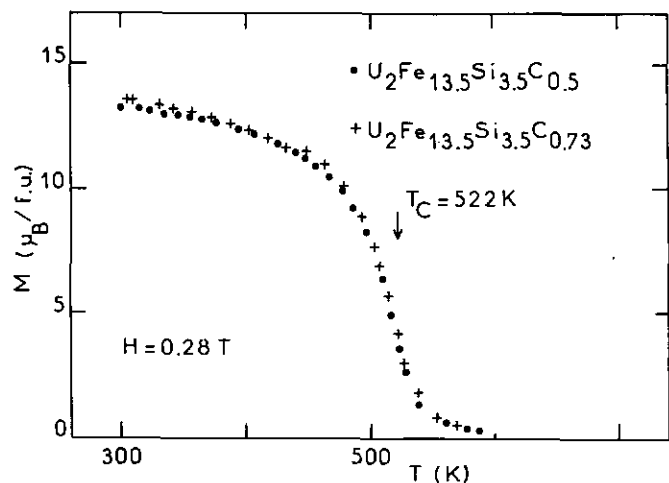

FIG. 3. Temperature dependence of the magnetization of $U_2Fe_{13.5}Si_{3.5}C_y$ ($y = 0.5$ and 0.73) at a field of 0.28 T.
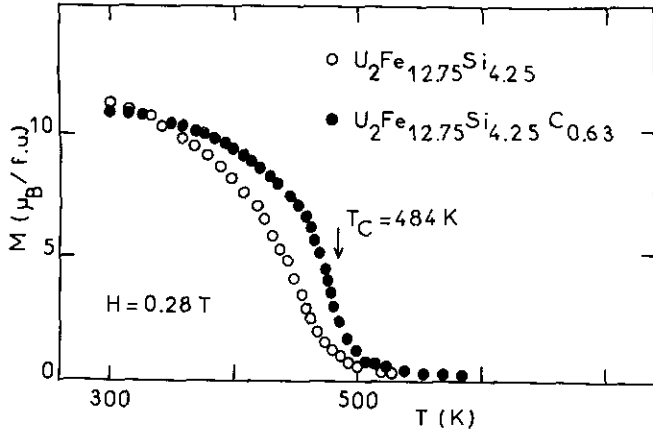
FIG. 4. Temperature dependence of the magnetization of $U_2Fe_{12.75}Si_{4.25}C_y$ ($y = 0$ and 0.63) at a field of 0.28 T.

compounds. Values of T_c are given in Table 1 for all materials investigated thus far. The introduction of interstitial carbon into the lattice of these compounds retains or slightly increases their Curie temperatures. It is interesting to note that the increase in the carbon content in $U_2Fe_{13.5}Si_{3.5}$ induces any change of the T_c value (Fig. 3). On the other hand, the magnetic properties of the R_2Fe_{17} intermetallics are strongly increased by the presence of carbon in their lattice (13, 14). For instance, the coefficient (dT_c/dy) for $Y_2Fe_{17}C_y$ is rather large with ~180 K per inserted carbon atom. The weak influence of the carbon on the magnetic properties of $U_2Fe_{17-x}M_x$ compounds is
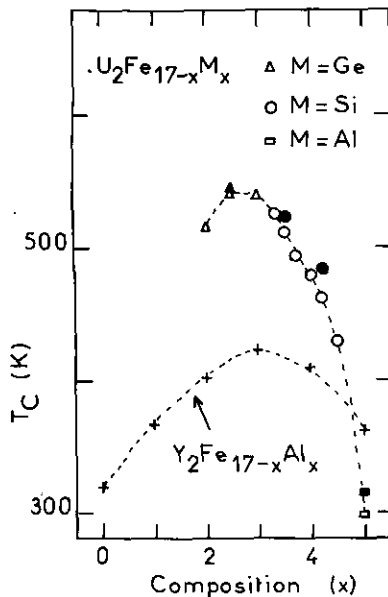
a consequence of the fact that these phases contain a noticeable amount of a nonmagnetic element such as Si, Ge, or Al. As a result some of the Fe–Fe interactions are suppressed.

The composition dependence of the T_c temperature of the various $U_2Fe_{17-x}M_xC_y$ systems studied in the course of the present investigation is compared in Fig. 5 with that of the $Y_2Fe_{17-x}Al_x$ solid solution (15). These latter compounds also crystallize in the hexagonal Th_2Ni_{17}-structure type for $x \leq 3$ but adopt the rhombohedral Th_2Zn_{17}-type for higher aluminum compositions. The $T_c = f(x)$ curve for the $Y_2Fe_{17-x}Al_x$ series goes through a maximum around $x = 3$. This behavior is explained as follows: the initial increase of T_c is due to the unit cell expansion occurring when iron atoms are replaced by larger aluminum atoms. The decrease in T_c for $x > 3$ results from a dilution effect leading to a decrease of the number of the Fe–Fe interations. A similar composition dependence of the T_c temperature is observed for the $U_2Fe_{17-x}M_x$ phases (Fig. 5). It is interesting to note that the germanide $U_2Fe_{14.5}Ge_{2.5}$ has a Curie temperature $T_c = 545$ K comparable to that found for $R_2Fe_{17}C$ carbides such as $Sm_2Fe_{17}C$ ($T_c = 552$ K) or $Gd_2Fe_{17}C$ ($T_c = 582$ K) (5, 13). This result justifies further investigation of these uranium intermetallics with respect to their high Curie temperature.

IV. CONCLUDING REMARKS

The $U_2Fe_{17-x}M_x$ compounds with $M = Al$, Si, and Ge form a new class of materials having a homogeneity range strongly influenced by the nature of the electron donor element M. As in R_2Fe_{17} binary compounds, interstitial carbon atoms can be introduced into the lattice of these materials. But their Curie temperatures are little changed by carbon insertion.

FIG. 5. Composition dependence of the Curie temperature of $Y_2Fe_{17-x}Al_x$ (+) and $U_2Fe_{17-x}M_x$ with $M = Ge$ ($\triangle$), Si(O), and Al ($\square$). The filled symbols refer to the carbon-containing phases.

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