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Synthesis, Crystal Structure, and Magnetic Properties of UFe_5Sn

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The UFe_5Sn compound was synthesized by arc melting, followed by annealing at 800°C. The crystal structure was determined by single-crystal X-ray diffraction and refined to a residual value of $R = 0.035$ ($R_w = 0.031$). This compound crystallizes in the orthorhombic $CeCu_5Au$-type structure, space group *Pnma*, with lattice parameters $a = 8.082(3)$ Å, $b = 4.869(1)$ Å, and $c = 10.448(3)$ Å. Magnetization measurements were performed in the 5–300 K temperature range and under fields up to 5.5 T. The results indicate a weak ferromagnetic behavior at room temperature. Two magnetic anomalies are observed at 248 and 180 K, respectively, and the ferromagnetic character strongly increases below the highest temperature anomaly. © 2000 Academic Press

Key Words: **UFe_5Sn; uranium intermetallic; magnetic intermetallic; $CeCu_5Au$-type structure.**

INTRODUCTION

Since the discovery of the $NdFe_{14}B$ compound (1,2) the study of R–Fe–M (R = lanthanide, light actinide; $M = d$ or p element) systems has received a new impetus with the objective of finding new magnetic compounds with fundamental and technological applications. The experimental investigations have focused mainly on R–Fe–M systems with M = Al, Si, Ga, Ge, Sn, Pb, and a transition metal (3,4). While many of these systems with lanthanides have been extensively studied, those with actinides remain largely unexplored. So far, very little work has been done on the U–Fe–Sn ternary system, and only one ternary compound, U_2Fe_2Sn, has been identified in this system (5).

In the course of a systematic study of the U–Fe–Sn ternary phase diagram, a new iron-rich compound, with UFe_5Sn nominal composition, was discovered (6). Herein we report on the crystallographic structure determination, from powder and single-crystal X-ray diffraction data, and on the magnetic properties, studied by magnetization measurements, of the new intermetallic compound UFe_5Sn.

EXPERIMENTAL

Samples with UFe_5Sn nominal composition, each weighing ~0.4 g, were prepared by arc-melting ingots of the constituents with purity higher than 99.9% on a water-cooled copper crucible under Ti-gettered high-purity argon atmosphere. The surface of the uranium ingots was cleaned in diluted HNO_3 prior to use. Repeated melting was used in order to ensure a better homogeneity. The weight losses were less than 0.5 wt%.

Each button was wrapped in molybdenum foil, sealed in evacuated quartz ampules, and annealed for 100 hours at 900°C, followed by rapid cooling to room temperature.

A microstructural analysis of the samples was performed with a SEM/EDS (JEOL-JSM 840) apparatus on polished surfaces. Quantitative analysis of the observed phases was made by EDS analysis of the atomic characteristic X rays excited by the electron beam operating at 15 kV.

The samples were examined by X-ray powder diffraction using an INEL CPS 120 diffractometer. Silicon powder was added to the material and used as an internal standard. The room-temperature lattice parameters were obtained by least-squares fits using the program UnitCell (7).

A single crystal suitable for X-ray measurements was isolated from the polycrystalline material, glued on the top of a glass fiber, and mounted on the goniometer head. X-ray single-crystal diffraction data were collected using a four-circle diffractometer, Enraf-Nonius CAD-4, with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The lattice parameters were also obtained by least-squares refinement of the 2θ values of 25 centered reflections (from various regions of the reciprocal space).

The data were recorded at room temperature in an ω–2θ scan mode ($\Delta\omega = 0.80 + 0.35\,\mathrm{tg}\,\theta$). Three reflections were monitored as intensity and orientation standards at 360-minute intervals during data collection; no variation larger than 5% was observed. The intensities of the 2063 measured

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TABLE 1
Crystallographic and Experimental Data of the X-Ray Single-Crystal Measurement

Formula	UFe_5Sn
Formula weight (g/mole)	635.954
Color	Metallic gray
Crystal size (mm)	$0.1 \times 0.06 \times 0.06$
Crystal system	Orthorhombic
Space group (11)	*Pnma*, No. 62
Lattice parameters (Å)	
a	8.082(3)
b	4.869(1)
c	10.448(3)
Volume (Å^3)	412.7(2)
Z	4
Calculated density (g/cm^3)	10.27
Radiation λ (Å)	0.71069
μ (MoKα) (cm^{-1})	602
Scan mode	ω–2θ
2θ range (°)	2–70
Reflections measured	2063
Observed reflections ($I > 3\sigma(I)$)	1386
Independent reflections	750
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.035
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2)]^{1/2}$	0.031
$w = 4F^2/[\sigma^2(F^2) + (0.06F^2]^2]$	
Goodness of fit	1.24

TABLE 2
Positional Parameters, Isotropic Thermal Parameters, and Their Estimated Standard Deviations

Atom	Site	x	y	z	B (Å^2)
U	4*c*	0.24882(7)	0.250	0.55889(5)	0.42(1)
Fe1	8*d*	0.0681(2)	0.5028(3)	0.3138(1)	0.48(2)
Fe2	4*c*	0.0624(3)	0.250	0.1037(2)	0.76(3)
Fe3	4*c*	0.3144(3)	0.250	0.2471(2)	0.47(3)
Fe4	4*c*	0.4061(3)	0.250	0.0201(2)	0.79(3)
Sn	4*c*	0.1342(1)	0.250	0.85932(8)	0.38(1)

reflections (with $2^\circ \leq 2\theta \leq 70^\circ$) were corrected for absorption by an empirical method based on Ψ scans (8), and for Lorentz and polarization effects. The 1386 observed reflections ($I > 3\sigma(I)$) were averaged, resulting in 750 independent reflections.

The diffraction data are compatible with an orthorhombic system, space group *Pnma*. The structure was refined employing the program MOLEN (9) and assuming a $CeCu_5Au$-type structure (10). The extinction factor, scale factor, six isotropic temperature factors, and 13 position parameters (x and z for all the sites and y for the 8*d* position) were refined. Crystallographic and experimental data of the structural determination are listed in Table 1.

Magnetization measurements were performed on the polycrystalline samples after zero field cooling (ZFC) and field cooling (FC). The measurements were carried out in the 5–300 K temperature range and under fields up to 5.5 T using a SQUID magnetometer (Quantum Design MPMS).

RESULTS AND DISCUSSION

The EDS elemental analysis of the new phase confirmed that its composition is close to the nominal U:5Fe:Sn ratio of the elements.

All the peaks of the X-ray powder diffractograms could be indexed according to the orthorhombic structure. The analysis of the silicon peaks' positions points to an insignificant zero-shift. The refinement of the lattice parameters using the 22 most intense reflections of the orthorhombic structure in the range $10^\circ \leq 2\theta \leq 60^\circ$, down to a residual $R(2\theta) = 0.027$, gives $a = 8.091(3)$ Å, $b = 4.873(2)$ Å, and $c = 10.469(4)$ Å, and a cell volume of 412.7(2) Å^3.

The X-ray single-crystal diffraction data are in agreement with the data from powder samples. The refinement of the lattice parameters yields values similar to those obtained from the powder measurements ($a = 8.082(3)$ Å, $b = 4.869(1)$ Å, and $c = 10.448(3)$ Å). The least-squares procedure for refinement of positional and isotropic thermal parameters for all atoms converged to $R = 0.035$ and $R_w = 0.031$, confirming for UFe_5Sn the $CeCu_5Au$-type structure, where uranium replaces cerium, iron substitutes for copper, and tin replaces gold. The refined atomic positions and isotropic thermal parameters are presented in Table 2.

The unit cell of UFe_5Sn is illustrated in Fig. 1. In UFe_5Sn the uranium atoms are located on one 4*c* site, the tin atoms are on another 4*c* site, and the iron atoms are on four different sites, three 4*c* and one 8*d*. The $CeCu_5Au$-type structure can be described as an ordered version of the $CeCu_6$-type structure (12). Due to normalization using the program Structure Tidy (13) the origin is shifted by 0.5, 0,

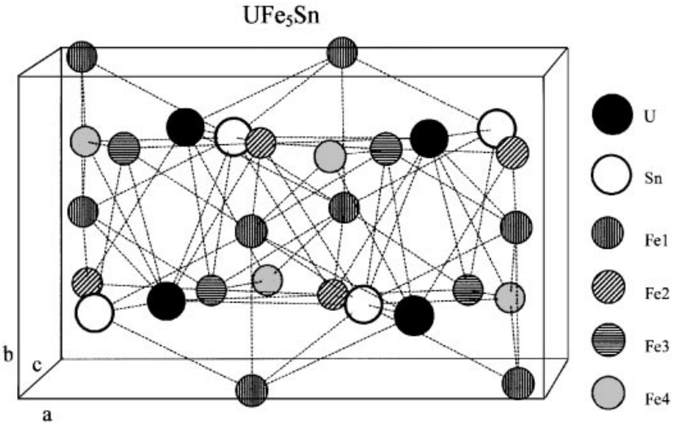

FIG. 1. Unit cell of UFe_5Sn.

TABLE 3
Interatomic Distances (*d*) and Nearest-Neighbors (NN) Numbers

	NN	Atoms	*d* (Å)		NN	Atoms	*d* (Å)
U	2	Fe4	2.767(1)	Fe3	2	Fe1	2.442(2)
	1	Fe4	2.890(1)		2	Fe1	2.474(2)
	2	Fe2	2.911(1)		1	Fe4	2.484(3)
	1	Fe2	3.051(2)		1	Fe2	2.528(3)
	2	Fe1	3.127(1)		1	Fe2	2.539(3)
	2	Fe3	3.171(1)		2	Sn	2.734(1)
	2	Fe1	3.195(1)		2	U	3.171(1)
	1	Sn	3.230(1)		1	U	3.301(1)
	1	Sn	3.273(1)				
	2	Fe1	3.276(1)	Fe4	2	Fe1	2.478(2)
	1	Fe3	3.301(2)		1	Fe3	2.484(3)
	2	Sn	3.342(1)		2	Fe1	2.498(2)
					1	Sn	2.766(2)
Fe1	1	Fe1	2.407(3)		2	U	2.767(1)
	1	Fe3	2.442(2)		1	U	2.890(2)
	1	Fe1	2.462(3)		2	Fe4	2.899(2)
	1	Fe3	2.474(2)		1	Fe2	2.912(3)
	1	Fe4	2.478(2)				
	1	Fe4	2.498(2)	Sn	1	Fe2	2.619(2)
	1	Fe2	2.517(2)		2	Fe1	2.719(2)
	1	Sn	2.719(2)		2	Fe1	2.732(2)
	1	Sn	2.732(2)		2	Fe3	2.734(1)
	1	U	3.127(1)		1	Fe4	2.766(2)
	1	U	3.195(1)		2	Fe2	2.932(1)
	1	U	3.276(1)		1	U	3.230(1)
					1	U	3.273(1)
Fe2	2	Fe1	2.517(2)		2	U	3.342(1)
	1	Fe3	2.528(3)				
	1	Fe3	2.539(3)				
	1	Sn	2.619(2)				
	2	U	2.911(1)				
	1	Fe4	2.912(3)				
	2	Sn	2.932(1)				
	1	U	3.051(2)				

0.5 relative to those reported for $CeCu_6$. In $CeCu_5Au$ the gold atoms occupy one of the copper 4*c* sites.

The numbers of nearest neighbors and interatomic distances (up to 3.40 Å), obtained in the X-ray refinement for the different crystallographic positions, are listed in Table 3. The nearest-neighbor coordination polyhedra for U, Fe1, Fe2, Fe3, Fe4, and Sn in UFe_5Sn are shown in Fig. 2. The coordination numbers (*CN*), deduced using the maximum gap method (14), are 19 for uranium, 14 for tin, 13 for Fe2, and 12 for Fe1, Fe3, and Fe4.

The uranium–(nearest neighbor) interatomic distances are usually long, well above the sum of the metallic radii (1.26 Å for iron, 1.58 Å for tin, and 1.53 Å for uranium, for a coordination number of 12 (15)). The only exceptions are two Fe4 atoms that are at 2.767 Å, close to the R_U–R_{Fe} sum, 2.79 Å. The higher uranium coordination number, when compared with the *CN* of 12 of the given metallic radii, partially explains the observed long distances. No other uranium atoms are on the U nearest coordination sphere.

The interatomic distances between Fe1 and the nearest iron (2.407–2.517 Å) and tin (2.719–2.732 Å) atoms are approximately equal to or below the metallic radii sum, 2.52 Å and 2.84 Å, respectively. The uranium atoms are at distances of 3.127–3.276 Å, longer than that sum, 2.79 Å.

The Fe3 and Fe4 atoms have next-nearest neighbors at distances below and above the sum of the metallic radii. Five iron (2.442–2.484 Å) and two tin atoms (2.734 Å) are below and two iron (2.528–2.539 Å) and three uranium atoms (3.171–3.301 Å) are above these sums in the case of Fe3. For a Fe4 central atom, five iron (2.478–2.498 Å), one tin (2.766 Å), and two uranium atoms (2.767 Å) are below and three iron (2.899–2.912 Å) and one uranium atom (2.890 Å) are above the sum of the metallic radii.

In the case of Fe2, and due to its higher coordination number, a slight increase of the interatomic distances could be expected. However, the two Fe2 atoms are at distances considerably larger (3.412 Å) than the sum of the metallic radii (2.52 Å) and cannot be considered next-nearest neighbors. These large distances are probably fixed by the uranium and tin atoms located at the corners of the rhombic faces (Fig. 3). A slight increase of the interatomic distances for the next-nearest neighbors Fe1 and Fe3 (2.517–2.539 Å) is observed. For the remaining atoms the distances are well above this sum (uranium at 2.911–3.051 Å, tin at 2.932 Å, and iron at 2.912–3.412 Å) except in the case of one tin (2.619 Å).

The distances from the Sn atom to its 14 atoms of the nearest coordination sphere are of two types. The Sn–Fe distances are usually below the metallic radii sum, 2.84 Å, the only exceptions being the two Fe2 atoms at 2.93 Å, and all of the Sn–U distances are above the radii sum, 3.16 Å.

The above variations suggest the following:

- reduced hybridization effects between uranium and the other atoms and, consequently, the possibility of an appreciable uranium magnetic moment (the shortest distance between uranium atoms, 4.89 Å, is well above the Hill limit, ~3.4 Å);
- strong interactions between Fe1 and the next-nearest neighbor iron and tin atoms;
- medium interactions between Fe3/Fe4 and the next-nearest neighbors;
- weak interactions between Fe2 and its next-nearest neighbors, except in the case of one tin atom; and
- strong interactions between tin and the next-nearest neighbor iron atoms.

The average interatomic distances between each type of nearest neighbor (uranium, tin, iron) and U, Fe1, Fe2, Fe3, Fe4, and Sn are listed in Table 4. These values can be indicative of the average volumetric constraints of the

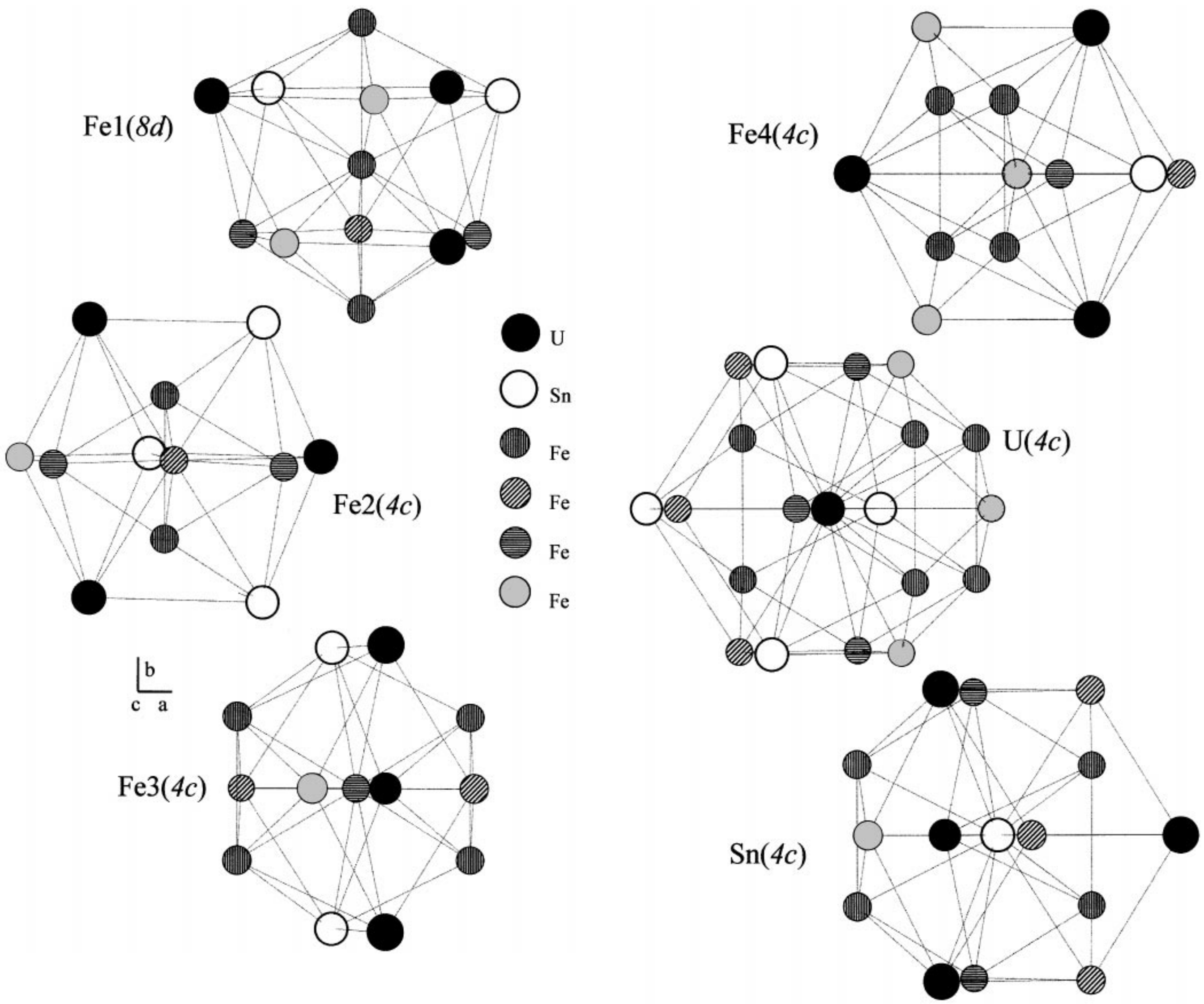

FIG. 2. Next-nearest-neighbors coordination polyhedra in the UFe_5Sn crystal structure.

crystallographic site and comparison between different sites can be made if they have close numbers of each type of nearest neighbors. Fe1 and Fe3 have nearly identical values of the average interatomic distances, indicating that the average volumetric constraints are probably similar for these two sites. This can be confirmed by the fact that the two sites have identical values of the isotropic thermal parameters (Table 2). In the case of the Fe2 and Fe4 sites both have higher average interatomic distances and also higher isotropic thermal parameters, when compared with the Fe1 and Fe3 sites. The direct comparison with the uranium and tin positions is not straightforward, due to their different coordination and number of each type of nearest neighbor.

The variation of magnetization with temperature for various magnetic fields is shown in Fig. 4. For fields up to 0.1 T,

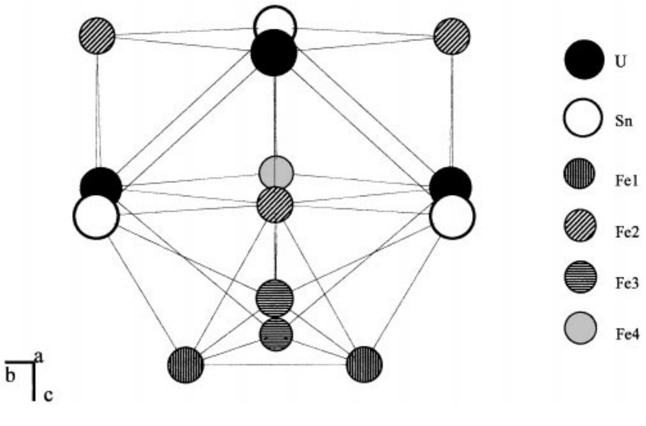

FIG. 3. Coordination polyhedra of the Fe2 site in the UFe_5Sn crystal structure, emphasizing the relationship between the Fe2 position and the uranium–tin rhombic faces.

TABLE 4
Number (N) and Average Interatomic Distances (d_{av}) for Each Type of Nearest Neighbor, Uranium, Tin, and Iron

	Uranium		Tin		Iron	
Atom	N	d_{av} (Å)	N	d_{av} (Å)	N	d_{av} (Å)
U	0	—	4	3.30	15	3.08
Fe1	3	3.20	2	2.72	7	2.47
Fe2	3	2.96	3	2.83	5	2.60
Fe3	3	3.21	2	2.73	7	2.48
Fe4	3	2.81	1	2.77	8	2.64
Sn	4	3.30	0	—	10	2.76

two magnetic transitions can be observed below room temperature: a ferromagnetic-type transition, at 248(3) K (T_A), and a less pronounced anomaly, at 180(2) K (T_B), which is smoothed out for higher measurement fields.

The dependence of magnetization on applied field, for values up to 5.5 T, for various temperatures is shown in Fig. 5. For temperatures below 248 K the curves are typical of a ferromagnet; the magnetization increases rapidly at low fields (< 0.5 T) and the extrapolated spontaneous magnetization for $T = 0$ K yields $m = 5\ \mu_B$/fu.

For larger applied fields a linear variation is observed; the slope which is very small for temperature values around 200 K increases with decreasing temperatures for $T < 150$ K. At 280 K ($> T_A$), the $M(H)$ curves still show a small ferromagnetic component ($\cong 0.5\ \mu_B$/fu), indicating that order still exists above room temperature.

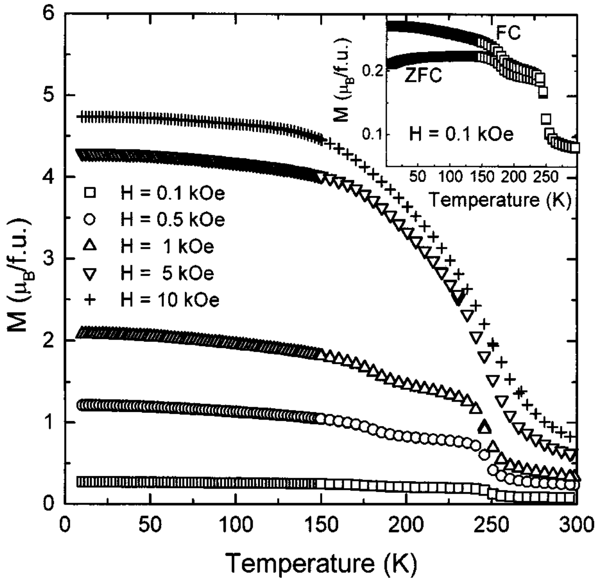

FIG. 4. Temperature dependence of the magnetization for UFe_5Sn, obtained at different applied fields (squares, 0.1 kOe; circles, 0.5 kOe; up-triangles, 1 kOe; down-triangles, 5 kOe; crosses, 10 kOe). The inset shows in detail the temperature dependence of the magnetization obtained at $H = 100$ Oe.

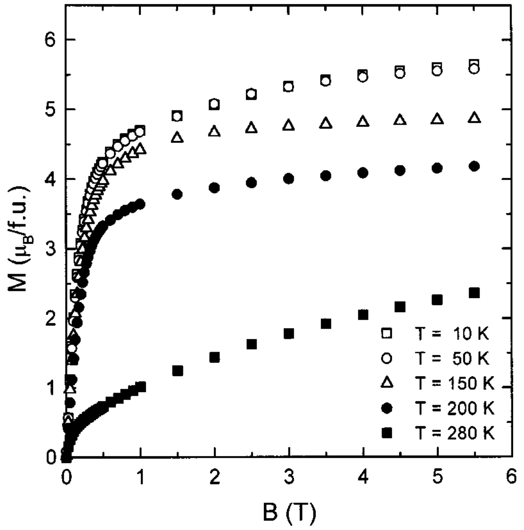

FIG. 5. Magnetization versus magnetic field for UFe_5Sn at different temperatures (open squares, 10 K; open circles, 50 K; up-triangles, 150 K; closed circles, 200 K; closed squares, 280 K).

The transition at $T = 248$ K is in principle related to ferromagnetic ordering of the iron atoms. The anomaly at 180 K can reflect either a rearrangement of magnetic moments or another type of ordering occurring in the system, like ordering of the uranium moments, as suggested by the increase in the magnetic susceptibility at high fields for the lower temperatures. However, one cannot exclude the possibility of the existence of small amounts of the UFe_{2-x} phase, for which the ordering temperature has been reported to vary between 147 and 195 K (16,17).

CONCLUSION

A new uranium intermetallic compound, UFe_5Sn, was synthesized and its structure studied by X-ray diffraction. This compound was found to crystallize in the orthorhombic $CeCu_5Au$-type structure, an ordered phase isomorphous with the $CeCu_6$-type structure.

The analysis of the next-neighbor environments suggests reduced hybridization between uranium and the other atoms (and, consequently, the possibility of an appreciable uranium magnetic moment) and variable interactions between the different iron atoms. The magnetization results indicate a weak ferromagnetic behavior at room temperature and two magnetic anomalies at 248 and 180 K; the ferromagnetic character strongly increases below the highest temperature anomaly. These results point to complex magnetic interactions in this compound that need to be further investigated after obtaining large single crystals suitable for magnetization and neutron diffraction experiments.

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