Evidence of uranium magnetic ordering on U_2Fe_3Ge

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A B S T R A C T

A new ternary uranium intermetallic compound, U_2Fe_3Ge, was synthesized and investigated. This compound crystallizes in the $MgZn_2$-type structure ($a = 5.1870(3)$ Å and $c = 7.8501(5)$ Å, space group $P6_3/mmc$), with uranium–uranium distances well below the Hill limit. Magnetization measurements indicate a ferromagnetic-type transition at 55(1) K. Mössbauer studies show that the magnetic ordering is due only to the uranium sub-lattice, pointing to U_2Fe_3Ge as a new exception to Hill's rule.

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1. Introduction

Uranium based intermetallic compounds are well known for their interesting and unusual physical properties. The coexistence of magnetic order and superconductivity at ambient pressure, reported for only two compounds, URhGe [1] and UCoGe [2], is an example of exotic physical phenomena shown by uranium intermetallics, since according to the BCS theory, superconductivity and magnetic order are mutually exclusive, as the magnetic interactions impede phonon-mediated singlet superconductivity.

The large diversity in the physical properties of uranium compounds is mainly due to the particular nature of the 5f states. Their energy and spatial extension are responsible for a considerable hybridization of the 5f electrons with the valence states of the neighbouring atoms in the crystal lattice, and hence for their participation in bonding.

The correlation between magnetic behaviour and the actinide interatomic spacing was first pointed out by Hill [3], who conjectured that the overlap of the f-electron wave functions between the uranium atoms determines whether the uranium behaviour is magnetic or non-magnetic (and often superconducting). Most of the compounds behave as Hill expected: for U–U spacing ≤ 3.5 Å 5f wave functions overlap and form an electronic broad band with a relatively low density of states at the Fermi level, E_F, and thus non-magnetic, heavy-fermion behaviour and conventional superconductivity are favoured. α-U is one example of this type of behaviour. For larger U–U spacings, there is no direct overlap and uranium magnetic order can be expected. However, because Hill's rule does not take into account details of the density of states, frequently determined by the 5f-ligand hybridization, there are several exceptions to this rule. The heavy-fermion superconducting compounds are clear exceptions to Hill's rule: the f-electrons condense into a superconducting state although the spacing between the uranium atoms in those compounds is fairly large. UPt_3 and UBe_{13} are examples of heavy-fermion superconductors beyond the Hill limit. The existence of uranium magnetism on compounds with U–U distances lower than the Hill limit is much rarer. UNi_2 is the only clear exception to this rule, as it is a Laves phase crystallizing in the $MgZn_2$-type structure with $d_{U-U} < 3.2$ Å that shows weak itinerant ferromagnetism below ~ 20 K [4]. Another compound that was claimed to be an exception of this type to the Hill's rule is $U_2V_3Ge_4$, with $T_C \sim 60$ K, but no structural details were reported [5], and therefore the correct U–U distances are not known.

Following the previous work on the U–Fe–Al system [6], where several new compounds with unusual physical properties were discovered [7], similar studies on the U–Fe–Ge ternary system were performed in order to identify the possible existence of new interesting ternary compounds and to explore the phase relations

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Table 1
Parameters for data collection and structural refinement of U_2Fe_3Ge

Chemical formula	U_2Fe_3Ge
Space group	$P6_3/mmc$ (No. 194)
Cell parameters (Å)	
a	5.1870(3)
c	7.8501(5)
Volume (Å^3)	151.39(2)
Wavelengths (Å)	Cu K$_\alpha$
Data range and counting step (deg 2θ)	10°–70°, 0.03
Counting time (s)	50
Number of reflections	56/2
Number of refined parameters	20
Rietveld reliability factors (%)	
R_P	7.04
R_{WP}	10.0
R_E	4.29
χ^2	5.38
R_{Bragg}	7.00
R_F	6.36

Fig. 1. U_2Fe_3Ge unit cell.

Fig. 2. Observed (squares) and calculated (continuous line) X-ray diffraction patterns for the U_2Fe_3Ge sample. Vertical ticks are related to the Bragg angle positions in the $P6_3/mmc$ space group. The lower profile gives the difference between the observed and the calculated data.

at selected temperatures. Preliminary results on the study of the 900 °C isothermal section confirmed the four phases previous reported in literature, UFeGe [8], UFe_2Ge_2 [9], UFe_6Ge_6 [10] and $U_2Fe_{17-x}Ge_x$ [11], and also revealed many other new phases [12]. One of the new intermetallic compounds found in this system was U_2Fe_3Ge. In this paper the results of the structural and physical characterization of U_2Fe_3Ge, by means of powder X-ray diffraction, magnetic and Mössbauer spectroscopy measurements are presented.

2. Experimental details

Ternary intermetallic samples of U_2Fe_3Ge were synthesized by arc-melting the proper amounts of the elements (purity >99.9% w/w) on a water-cooled copper earth and under a titanium-gettered high purity argon atmosphere. To ensure homogeneity, the melting procedure was repeated at least three times. Weight losses during the melting were found to be less than 1%.

The as-cast polycrystalline powdered samples were examined by X-ray powder diffraction at room temperature. The scans were performed using a Philips X'PertPro diffractometer (Bragg–Brentano assembly, monochromatized Cu Kα radiation, $10° < 2\theta < 70°$, step width 0.03°, and 50 s of counting time/step). Phase identification was made from the powder data using the program PowderCell [13], and the Rietveld refinement of the crystal structure was done with the help of the FULLPROF [14] program. An experimentally determined $K\alpha_1/K\alpha_2$ intensities ratio of 0.5, a factor $\cos\theta = 0.7998$ for the monochromator polarization correction and a Pseudo-Voigt profile shape function were used. The background was manually refined and introduced in the input file. A total of 20 parameters were refined in the final cycles of the least squares refinement. Further details on data refinement are given in Table 1. The samples were analyzed by scanning electron microscopy (SEM), with energy dispersive x-ray spectroscopy (EDS), using a Jeol JSM-7001F field emission microscope. At least three EDS point analysis were obtained for each phase. These analyses were carried out at 25 kV, with a spatial resolution of 2.5 μm for iron and germanium, and of 1 μm for uranium.

Magnetization measurements were performed in a S700X SQUID magnetometer (Cryogenic Ltd) from 2 to 300 K under magnetic fields up to 5 T. Magnetization was studied in fixed and free powder samples as a function of magnetic field and temperature.

Mössbauer spectra were collected at room temperature and at 4.2 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in a Rh matrix.
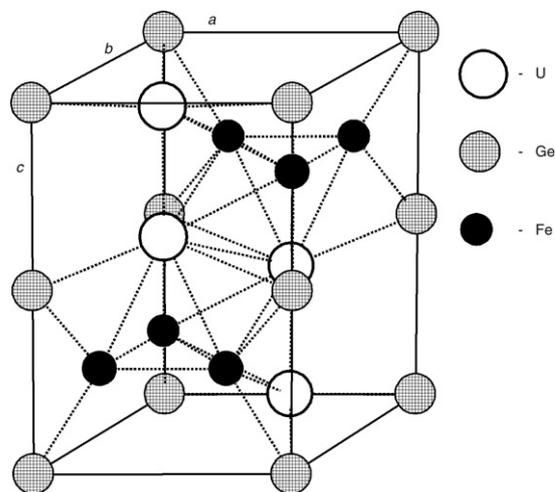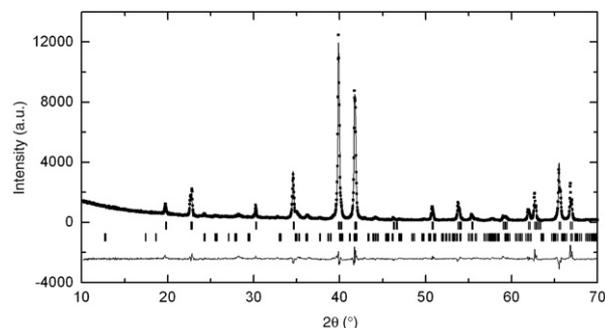
The velocity scale was calibrated using α-Fe foil. The absorbers were obtained by pressing the powdered samples (5 mg of natural Fe/cm^2) into perspex holders. Isomer shifts are given relative to metallic α-Fe at room temperature. Low-temperature spectra were collected using a bath cryostat with the sample immersed in liquid He. The spectra were fitted to Lorentzian lines using a non-linear least-squares method [15].

3. Results and discussion

A comparison between simulated and experimental diffractograms indicates that U_2Fe_3Ge crystallizes in the $MgZn_2$-type structure (Fig. 1) [12]. Assuming that the uranium, iron and germanium atoms are located at the 4f, 6h and 2a crystallographic positions, respectively, the intensity and the peak positions in the experimental powder patterns are in good agreement with those calculated, and this structure model was used in the subsequent calculations. As shown in Fig. 2, besides the presence of U_2Fe_3Ge as the major phase, there is also a small amount (<5% vol.) of the low temperature UFeGe phase that was also considered in the Rietveld refinement. Below 500 K the UFeGe compound crystallizes in the monoclinic UFeGe-type structure, a distortion of the high temperature TiNiSi-type [8]. The apparent contradiction in observing the low temperature modification in an as-cast sample was already pointed out in a previous work on UFeGe [16].

The refinement of the lattice parameters for U_2Fe_3Ge results in $a = b = 5.1870(3)$ Å and $c = 7.8501(5)$ Å, very close to the previously reported values ($a = 5.185(4)$ Å and $c = 7.853(5)$ Å [12]). No significant deviation from the full occupancy could be

Table 2
Atomic coordinates and thermal parameters for U_2Fe_3Ge

Atom	Site	x	y	z	B (Å^2)
U	4f	1/3	2/3	0.0717(2)	3.4(2)
Fe	6h	0.827(1)	0.654(3)	1/4	4.1(2)
Ge	2a	0	0	0	1.0(2)

Table 3
Selected interatomic distances (d, Å) and coordination number (C.N.) of atoms for the U_2Fe_3Ge compound

Atom			d, Å	C.N.	Atom			d, Å	C.N.
U	–	1 U	2.799	16	Fe	–	2 Fe	2.495	12
	–	3 Fe	2.907			–	2 Ge	2.504	
	–	6 Fe	2.948			–	2 Fe	2.692	
	–	3 Ge	3.047			–	2 U	2.907	
	–	3 U	3.200			–	4 U	2.948	
Ge	–	6 Fe	2.504	12					
	–	6 U	3.047						

observed during the refinement, and therefore uranium, iron and germanium site occupations were fixed in the last cycles at the 4f, 6h and 2a positions, respectively. The least-squares structure refinement converged to final $R_{Bragg} = 0.07$ and $R_F = 0.0636$, confirming that the U_2Fe_3Ge as-cast sample is composed mainly (>95 % vol.) of a phase which has the $MgZn_2$-type structure. The refined crystallographic parameters, including the atomic positions and isotropic thermal parameters are given in Table 2. The comparison between the observed and the calculated patterns and the difference curve are shown in Fig. 2. SEM/EDS analyses confirm the existence of only two phases, with the major phase being U_2Fe_3Ge and amounting to a >98% volume concentration, in agreement with the powder X-ray diffraction results.

In U_2Fe_3Ge the germanium atoms are positioned at the edges and at the corners as shown in Fig. 1, and the iron atoms are placed in a triangular arrangement at $\frac{1}{4}$ and $\frac{3}{4}$ along the c axis. The interatomic distances for each crystallographic position together with the number of nearest neighbours, are listed in Table 3. The U–U nearest neighbour distances are 2.799 Å (along the c axis) and 3.200 Å, both well below the Hill critical distance of ∼3.5 Å. In addition, uranium has iron atoms at distances above 2.9 Å, higher than the sum of their metallic radii (1.26 Å for iron and 1.53 Å for uranium, for a coordination number of 12 [17]). This indicates a strong overlap of the 5f–5f states of uranium and reduced hybridization between the 5f–3d states of uranium and iron, respectively. As a consequence, non-magnetism in the uranium and iron atoms can be expected [18].

The UFeGe low temperature phase was magnetically characterized by Havela et al. [16] and it shows a paramagnetic behaviour with the features of spin fluctuations. Taking into account the small amount of this phase in the sample and its non-magnetic character it is reasonable to assume that it has no noticeable influence on the magnetic characterization of the U_2Fe_3Ge compound.

The temperature dependence of the U_2Fe_3Ge magnetization, measured on a free powder sample under a 3 T magnetic field is presented in Fig. 3. According to the observed minimum on the temperature derivative of the magnetization, the sample undergoes a ferromagnetic-like transition at $T_C = 55(1)$ K. No signs of other magnetic transitions can be seen in the temperature range analyzed. At temperatures above 100 K the susceptibility data is well adjusted by a modified Curie–Weiss law, $\chi - \chi_0 = C/(T - \theta)$ (C = Curie constant, θ = Curie–Weiss temperature and χ_0 = temperature-independent susceptibility). The U_2Fe_3Ge compound has a paramagnetic Curie–Weiss temperature of $\theta = 58.6$ K, $\chi_0 = 6.63 \times 10^{-8}$ m^3 mol^{-1}, and $C = N_A\mu_{eff}^2/3k_B = 1.84 \times 10^{-5}$ m^3 K mol^{-1} (N_A = Avogadro's constant and k_B = Boltzmann constant). The Curie–Weiss temperature is in good
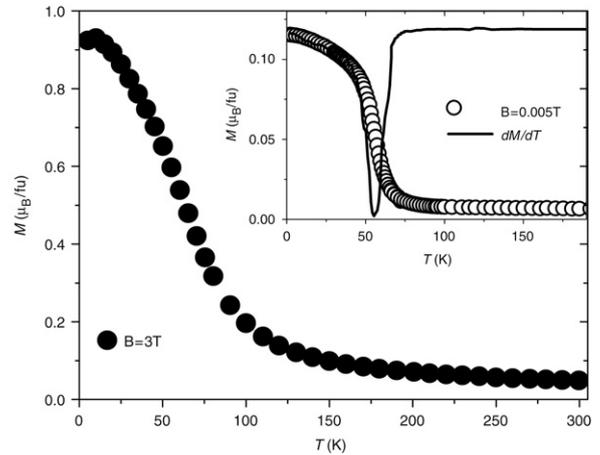
Fig. 3. Temperature dependence of the magnetization for the U_2Fe_3Ge compound. Inset shows in detail a low field ($B = 0.005$ T) measurement and its temperature derivative.
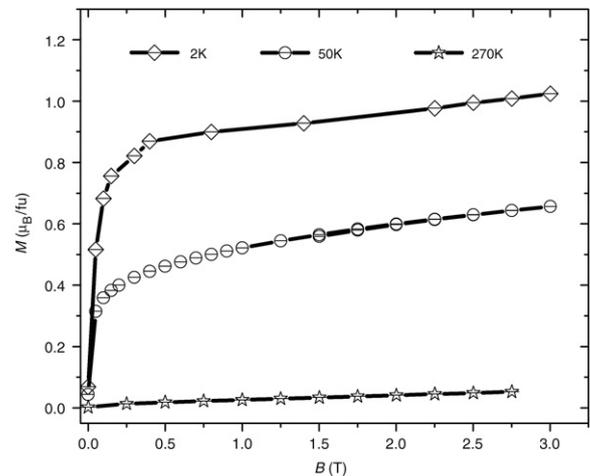
Fig. 4. Magnetic field dependence of the magnetization for the U_2Fe_3Ge compound.

agreement with the Curie temperature obtained from the ferromagnetic-like transition (55 K) and its positive value indicates that ferromagnetic interactions rule this compound. The effective magnetic moment deduced from the Curie constant is $\mu_{eff} = 3.42\mu_B/f.u.$ (formula unit), or $2.42\mu_B/U$ if it is assumed that only uranium atoms contribute to the magnetism. This value is lower than the expected moment for the free U^{3+} or U^{4+} configurations ($\mu_{eff}(U^{3+}) = 3.62\mu_B$ and $\mu_{eff}(U^{4+}) = 3.58 \mu_B$, calculated for free uranium ions on the basis of the Russel–Saunders coupling [18]). Analogous low effective magnetic moments are found in intermetallic compounds of uranium in which the 5f states are located very close to the Fermi level and tend to be partially delocalized [19].

The temperature dependence of the magnetization is identical for both the free and fixed powder samples, exhibiting no significant hysteresis.

Fig. 4 shows the magnetization as a function of the applied magnetic field, $M(B)$ for the free powder sample at different temperatures. At temperatures lower than T_C a rapid increase of the magnetization at low fields is observed which is typical of a ferromagnetic material. A small linear field dependence of the magnetization is observed for $B > 1$ T, which corresponds to an approximation to saturation since the sample does not reach saturation for fields up to 5 T. By the linear extrapolation of the high-field linear dependence to zero field, $M(B \rightarrow 0)$ one can obtain the 'spontaneous magnetization', M_{sp}, at 2 K as $M_{sp} = 0.85\mu_B/f.u$ for the U_2Fe_3Ge compound.
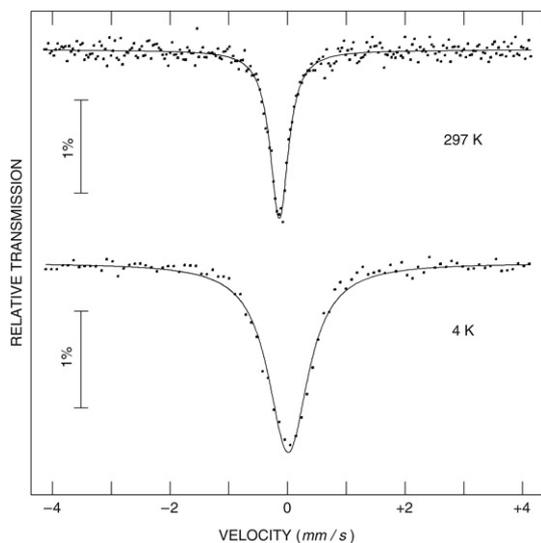
Fig. 5. Mössbauer spectra of U_2Fe_3Ge taken at different temperatures.

Table 4
Estimated parameters from the Mössbauer spectra of the U_2Fe_3Ge sample

T (K)	IS (mm/s)	QS (mm/s)	LW (mm/s)
297	−0.03	0.06	0.36
4.2	0.12	0.10	0.80

IS: isomer shift relative to metallic α-Fe at 295 K;
QS: quadrupole splitting;
LW: line-width; estimated errors are ≤ 0.02 mm/s.

Mössbauer spectra taken at room temperature and at 4 K consist of single absorption peaks (Fig. 5). The room temperature spectrum may be analysed as a single quadrupole doublet in agreement with XRD data, the iron atoms occupying a single crystallographic site with non-cubic symmetry. The estimated quadrupole splitting (Table 4) is lower than the line widths, thus explaining why the two peaks of the doublet are not resolved. No magnetic splitting is detected at 4 K. This indicates that neither the long-range magnetic ordering nor the standard spin-glass behaviour of the iron sublattice is associated with the magnetic anomaly detected by magnetization measurements. Assuming that the iron magnetic moments, μ_{Fe}, are non-zero, the strong broadening of the absorption peak at 4 K suggest a slowing down of the μ_{Fe} relaxation due to magnetic ordering of the uranium sub-lattice.

All the above results suggest that the U_2Fe_3Ge compound is the second example of uranium magnetism on compounds with U–U spacings lower than the Hill limit. However, for the other Hill's rule exception compound, UNi_2, which also crystallizes in the hexagonal $MgZn_2$ structure, a ferromagnetic transition was found at ~20 K, with a much smaller ordering moment, $0.081\mu_B/U$ [20]. UNi_2 is a well known compound described as a weak itinerant 5f ferromagnet. Within a simple band approach, the ferromagnetism of UNi_2 is outstanding from the high density of 5f-electron states at the Fermi level [21]. The origin of the uranium magnetism in U_2Fe_3Ge is still unknown, band structure calculations are now under way.

4. Conclusions

U_2Fe_3Ge is a hexagonal new Laves-phase compound that crystallizes in the $MgZn_2$-type structure, space group $P6_3/mmc$, with $a = 5.1870(3)$ Å and $c = 7.8501(5)$ Å unit cell parameters. In this compound the uranium atoms are located at the 4f crystallographic positions, the U–U nearest neighbour distances being 2.799 Å and 3.200 Å, both well below the Hill critical distance (~3.5 Å). The magnetization experiments point to a ferromagnetic-like behavior below 55(1) K. Mössbauer studies indicate that the ternary intermetallic U_2Fe_3Ge is a new exception to the Hill rule, with the magnetic moments only located on the uranium atoms.

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