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## Highlights

### Ferromagnetic Ordering in $\text{UFe}_{0.40}\text{Ge}_2$ Studied by $^{57}\text{Fe}$ Mössbauer Spectroscopy

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- $\text{UFe}_{0.40}\text{Ge}_2$  has been confirmed to order ferromagnetically below  $T_C = 37$  K.
- The compound has been studied by Mössbauer spectroscopy.
- The experiments have confirmed that the ferromagnetism in  $\text{UFe}_{0.40}\text{Ge}_2$  is purely long-range in nature.
- The hypothesis of a ferromagnetic cluster glass below  $T_C$  has been discarded.

# Ferromagnetic Ordering in $\text{UFe}_{0.40}\text{Ge}_2$ Studied by $^{57}\text{Fe}$ Mössbauer Spectroscopy

Adam P. Pikul<sup>a,\*</sup>, Rafał Idczak<sup>b,a</sup>, Piotr Sobota<sup>b,a</sup>, Wojciech Nowak<sup>b,a</sup>, Mathieu Pasturel<sup>c</sup>, Vinh Hung Tran<sup>a</sup>

<sup>a</sup>*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-422 Wrocław, Poland*

<sup>b</sup>*Institute of Experimental Physics, University of Wrocław, pl. Maksa Borna 9, 50-204 Wrocław, Poland*

<sup>c</sup>*Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes - UMR 6226, 35042 Rennes, France*

## Abstract

A polycrystalline  $^{57}\text{Fe}$ -isotope-enriched sample of  $\text{UFe}_{0.40}\text{Ge}_2$  was investigated by X-ray powder diffraction, magnetization and Mössbauer spectra measurements. The compound was confirmed to crystallize with the orthorhombic  $\text{CeNiSi}_2$ -type structure (space group  $Cmcm$ ) and with the lattice parameters  $a = 4.0759(2)$  Å,  $b = 15.8107(7)$  Å, and  $c = 4.0379(2)$  Å, being close to those reported previously for a very similar composition. Magnetic properties measurements showed that  $\text{UFe}_{0.40}\text{Ge}_2$  orders ferromagnetically at  $T_C = 37$  K with the effective magnetic moment of  $2.57(3) \mu_B$  and the ordered magnetic moment at 70 kOe of about  $0.64(1) \mu_B$ , being fully consistent with the earlier report on physical properties of  $\text{UFe}_{0.39}\text{Ge}_2$ .  $^{57}\text{Fe}$  Mössbauer spectra measurements performed both in the field-cooled and zero-field-cooled regimes ruled out the formation of ferromagnetic cluster-glass or spin-glass state, and confirmed that the ferromagnetism in the studied system is purely long-range in nature. A small contribution of about  $0.24\text{--}0.36 \mu_B$  to the total magnetic moment from the iron atoms was observed.

**Keywords:** A. Uranium intermetallics, A. Uranium germanides, D. Ferromagnetic ordering, E. X-ray powder diffraction, E. Magnetization measurements, E. Mössbauer spectroscopy

## 1. Introduction

Uranium germanides have attracted much attention from the scientific community, following the discovery of unconventional superconductivity in the ferromagnetically ordered compound  $\text{UGe}_2$  [1], which crystallizes in the orthorhombic  $\text{ZrGa}_2$ -type structure (space group  $Cmmm$ ) [2, 3]. As a result of intense search for other compounds exhibiting the coexistence of ferromagnetism and superconductivity, which so far were considered to be mutually exclusive, two ternary uranium germanides, namely  $\text{URhGe}$  and  $\text{UCoGe}$ , have been reported to be superconducting ferromagnets [4, 5]. They crystallize with the orthorhombic unit cell of the  $\text{TiNiSi}$  type (space group  $Pnma$ ), and their common feature with  $\text{UGe}_2$  is the presence of uranium zig-zag chains within the uranium layers.

Very similar uranium zig-zag chains have also been found in another group of uranium germanides, namely the compounds  $\text{UT}_{1-x}\text{Ge}_2$  (where  $T = \text{Ru, Os, Ni and Fe}$ ), which all crystallize in certain derivatives of the same orthorhombic type of crystal structure. In particular,  $\text{URu}_{0.29}\text{Ge}_2$  and  $\text{UOs}_{0.25}\text{Ge}_2$  form with a monoclinically distorted  $\text{CeNiSi}_2$ -type unit cell (space group  $C2/c$ ) [6, 7]), while  $\text{UNi}_{0.45}\text{Ge}_2$  and  $\text{UFe}_{0.39}\text{Ge}_2$  crystallize in a Ni-deficient  $\text{CeNiSi}_2$  structure type (space group  $Cmcm$ ) [8, 9]. The compounds with Ru, Os and Fe order ferromagnetically at 63 K [6], 45 K [7] and 37 K [9], respectively, and only the Ni-bearing phase was found to order antiferromagnetically at 47 K [8].

The ferromagnetic order in  $\text{UFe}_{0.39}\text{Ge}_2$  at  $T_C = 37$  K occurs in the presence of significant crystallographic disorder. That disorder strongly influences the low-temperature physical properties of the compound (especially its transport properties), suggesting the formation of a ferromagnetic cluster glass [9]. To verify the latter hypothesis, we have investigated that compound by measuring its  $^{57}\text{Fe}$  Mössbauer spectra at various temperatures from the magnetically ordered range and in two different cooling regimes. In the following, we present the results of those experiments along with their analysis for the formation of glassy states.

## 2. Material and Methods

A polycrystalline sample with a nominal composition of  $\text{UFe}_{0.40}\text{Ge}_2$  (that is, to the nearest 0.3%, identical to the previous composition) was prepared by conventional arc melting the elemental components (with purity higher than 99.5% in each case) with about 5 at.% iron substitution by the  $^{57}\text{Fe}$  isotope in purified argon atmosphere. During synthesis, the ingot was turned over and remelted several times to ensure good homogeneity. Subsequently, the specimen was annealed for four weeks at 900 K in an evacuated quartz tube to ensure good homogeneity. The mass loss at the end of the procedure was negligible.

Quality of the product was checked by X-ray powder diffraction (XRD) using a PANalytical X'Pert Pro diffractometer equipped with a  $\text{Cu K}\alpha$  radiation source. The experimental XRD pattern was analyzed by the Rietveld method using the Fullprof software [10]. Magnetic properties of the sample were

\*Corresponding author

Email address: a.pikul@intibs.pl (Adam P. Pikul)

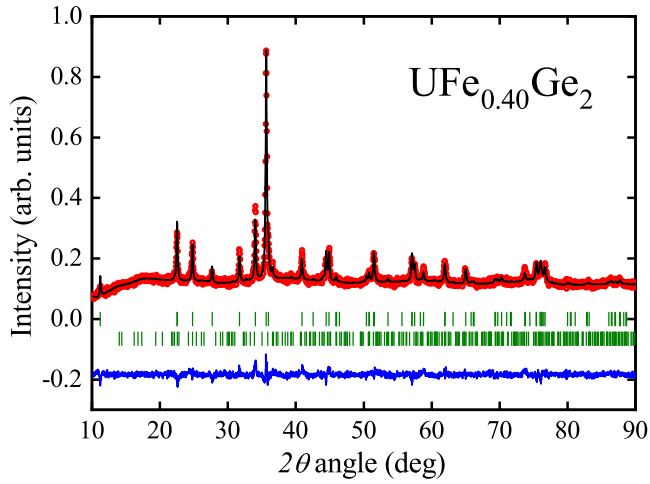


Figure 1: Powder X-ray diffraction pattern of  $\text{UFe}_{0.40}\text{Ge}_2$  (red circles) plotted along with results of the Rietveld refinement of its crystal structure (black curve). Upper and lower green ticks indicate Bragg positions for the major ( $\text{UFe}_{0.40}\text{Ge}_2$ ) and the impurity ( $\text{U}_9\text{Fe}_7\text{Ge}_{24}$ ) phases, respectively. Blue curve shows the difference between the experimental and the theoretical patterns.

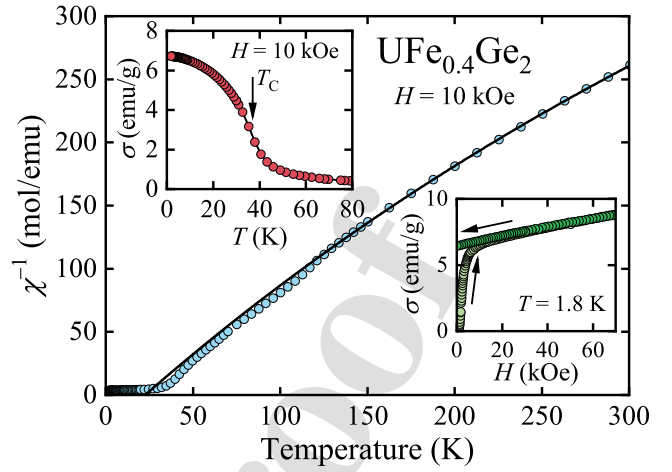


Figure 2: Temperature dependence of inverse magnetic susceptibility  $\chi^{-1}$  of  $\text{UFe}_{0.40}\text{Ge}_2$ ; solid line is a fit of the modified Curie-Weiss law to the experimental data (for details see the text). Upper inset: low temperature variation of mass magnetization  $\sigma$  measured in field-cooling regime; an arrow marks the ferromagnetic ordering temperature  $T_c$ . Lower inset:  $\sigma$  as a function of increasing (open symbols) and decreasing (closed symbols) applied magnetic field  $H$ .

studied using a Quantum Design MPMS-XL SQUID magnetometer in the temperature range 1.8–300 K and in applied magnetic field up to 70 kOe.

The  $^{57}\text{Fe}$  Mössbauer spectra of the powdered  $\text{UFe}_{0.40}\text{Ge}_2$  sample were measured in transmission geometry (TMS) with a conventional constant-acceleration spectrometer, using a  $^{57}\text{Co}$ -in-Rh standard source with a full width at half maximum (FWHM) of 0.22 mm/s. The temperature in the range of 4.3–300 K was controlled using a variable-temperature insert in an Oxford Instruments Spectromag cryostat. The obtained TMS spectra were analyzed using a least-squares fitting procedure to determine the parameters of the hyperfine interactions, such as the magnetic hyperfine field  $B_{\text{hf}}$ , the isomer shift  $IS$ , the quadrupole splitting  $QS$ , the quadrupole shift for the magnetic sextet  $\epsilon$ , the absorption spectral areas  $C$ , and the spectral linewidths  $\Gamma$ . The  $IS$  values presented in this paper refer to the  $\alpha$ -Fe standard at room temperature.

### 3. Results and Discussion

#### 3.1. Crystal structure

The experimental XRD pattern of the  $^{57}\text{Fe}$ -isotope-enriched  $\text{UFe}_{0.40}\text{Ge}_2$  sample (Fig. 1) was readily indexed within the Fe-deficient orthorhombic  $\text{CeNiSi}_2$ -type structure, already solved for that germanide [9], with a small addition of the tetragonal paramagnetic  $\text{U}_9\text{Fe}_7\text{Ge}_{24}$  phase [11]. (The presence of that secondary phase was deliberately allowed, as discussed in Ref. [9]). The Rietveld refinement of those two crystal structures, performed using the crystallographic data reported in Refs. [9] and [11], gave relative amounts of the two phases of about 95 and 5 wt.%, respectively, indicating good quality of the prepared sample. The elevated background due to iron fluorescence could hide Bragg reflections from other secondary

phases (if present at all), but their amount would still be less than 1–2 wt%.

The refined cell parameters for  $\text{UFe}_{0.40}\text{Ge}_2$  are  $a = 4.0759(2)$  Å,  $b = 15.8107(7)$  Å, and  $c = 4.0379(2)$  Å. These values are somewhat closer to those reported by Henriques *et al.* for a similar chemical composition ( $a = 4.083(5)$  Å,  $b = 15.805(5)$  Å, and  $c = 4.030(5)$  Å [12]) than our previous results reported for a polycrystalline sample with the initial composition ' $\text{UFe}_{0.45}\text{Ge}_2$ ' ( $a = 4.0886(1)$  Å,  $b = 15.8339(3)$  Å, and  $c = 4.0505(1)$  Å), suggesting the existence of a small homogeneity domain for the studied phase. Nevertheless, the results show that the sample synthesized for the study described in this paper is essentially identical to the previous sample described in Ref. [9].

#### 3.2. Magnetic properties

Fig. 2 shows results of the magnetic properties measurements carried out for  $\text{UFe}_{0.40}\text{Ge}_2$ . As can be seen, above about 130 K the inverse magnetic susceptibility exhibits featureless and slightly curvilinear behavior characteristic of paramagnets. The experimental data can be easily described by the modified Curie-Weiss law:

$$\chi(T) = \frac{1}{8} \frac{\mu_{\text{eff}}^2}{T - \theta_p} + \chi_0, \quad (1)$$

where  $\mu_{\text{eff}}$  is the effective magnetic moment,  $\theta_p$  stands for the Curie-Weiss temperature, and  $\chi_0$  denotes temperature independent Pauli-like contribution to the total magnetic susceptibility. The least-squares fitting of Eq. (1) to the experimental data resulted in the parameter values:  $\mu_{\text{eff}} = 2.57(3) \mu_B$ ,  $\theta_p = 23(2)$  K, and  $\chi_0 = 8.6(5) \times 10^{-4}$  emu/mol, being fully consistent with those obtained previously for  $\text{UFe}_{0.39}\text{Ge}_2$  ( $\mu_{\text{eff}} = 2.59 \mu_B$ ,  $\theta_p = 30$  K, and  $\chi_0 = 1 \times 10^{-4}$  [9]). The so-estimated value of

$\mu_{\text{eff}}$  is lower than that expected for free  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions (3.62 and  $3.58 \mu_{\text{B}}$ , respectively), but it is large enough to be attributed mainly to the uranium ions. The observed discrepancy may be due to partial delocalization of 5f electrons, magnetocrystalline anisotropy or crystal field effects. The large and positive value of  $\theta_{\text{p}}$  indicates the presence of predominantly ferromagnetic interactions between the magnetic moments.

The pronounced Brillouin-like-shaped anomaly that is visible in the temperature variation of the magnetization,  $\sigma(T)$ , at about 37 K (see the upper inset to Fig. 2) manifests ferromagnetic ordering of  $\text{UFe}_{0.40}\text{Ge}_2$ , being in full agreement with our previous finding [9]. The field dependence of the magnetization,  $\sigma(H)$ , measured at the lowest temperature studied, *i.e.* 1.8 K (see the lower inset to Fig. 2) confirms the ferromagnetic character of the ordering. In the highest field  $\sigma$  reaches a value of  $8.83 \text{ emu/g}$ , which corresponds to the ordered magnetic moment of about  $0.64 \mu_{\text{B}}$ . It is close to the value reported for  $\text{UNi}_{0.39}\text{Ge}_2$  [9] and is within the range of values observed for uranium intermetallics.

The above findings show that the magnetic properties of the sample used in the present study are well defined, and the  $\text{UFe}_{1-x}\text{Ge}_2$  system under study exhibits reproducible magnetic properties.

### 3.3. TMS results

Selected TMS spectra measured for the  $\text{UFe}_{0.40}\text{Ge}_2$  sample are presented in Figs. 3 and 4. As can be seen, the spectra measured at  $T \geq 35 \text{ K}$  (Fig. 3), corresponding approximately to the paramagnetic region of the studied compound, can be described using two paramagnetic components. The major one, with the relative intensity of about 95%, is a well-resolved symmetric doublet. Given the XRD results described in Sec. 3.1 as well as in Ref. [9], this component can be ascribed to the compound  $\text{UFe}_{0.40}\text{Ge}_2$ , in which Fe atoms occupy a single crystallographic site with symmetry lower than cubic. Deep in the magnetically ordered region (Fig. 4), *i.e.* at  $T \leq 30 \text{ K}$ , this component can no longer be described by the doublet, and it must be described by a magnetic sextet with a small hyperfine field  $B_{\text{hf}} = 2.10(3) \text{ T}$ ,  $3.39(1) \text{ T}$  and  $3.55(2) \text{ T}$  for the spectra measured at 30 K, 10 K and 4.3 K, respectively.

The second, minor component of the deconvoluted TMS spectra, with relative intensity being close to 5%, can be described by a single line component (a singlet) with  $IS = 0.06(5) \text{ mm/s}$  at 300 K. As can be seen in Figs. 3 and 4, this component remains a singlet at every other temperature studied, thus showing the absence of a magnetic phase transition at least down to 4.3 K. It can be attributed to the presence of the impurity phase  $\text{U}_9\text{Fe}_7\text{Ge}_{24}$  (see Sec. 3.1 and Ref. [11]), which contains iron atoms and is known to remain paramagnetic down to the lowest measured temperature. It should be noted here that since the hyperfine parameters for the compound  $\text{U}_9\text{Fe}_7\text{Ge}_{24}$  are not available in the literature, the assignment of the singlet to the impurity phase is based on the XRD results (Sec. 3.1) and the fact that TMS measurements performed for some other U-Fe-Ge ternaries revealed similar  $IS$  values at 300 K. In particular,  $IS$  at 300 K for  $\text{U}_2\text{Fe}_3\text{Ge}$  and

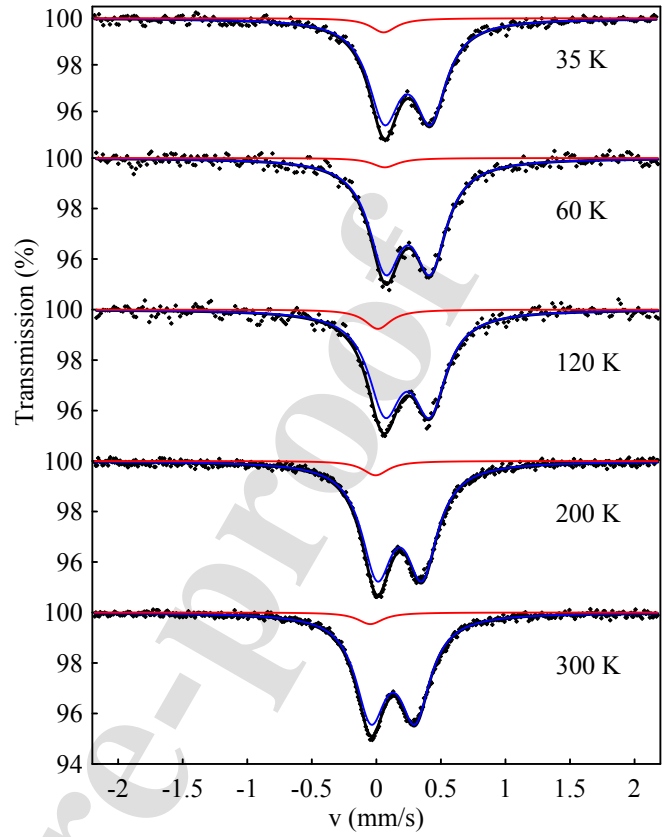


Figure 3: TMS spectra of  $\text{UFe}_{0.40}\text{Ge}_2$  measured at several temperatures from the range 35–300 K and in zero applied magnetic field, fitted by a sum (black curve) of one doublet and one singlet component (blue and red lines, respectively). For details of the fits see the text.

$\text{U}_{34}\text{Fe}_{4-x}\text{Ge}_{33}$  is  $-0.03 \text{ mm/s}$  [13] and  $0.13 \text{ mm/s}$  [14], respectively.

The TMS spectra shown in Figs. 3 and 4 can alternatively be described by only one component: an asymmetric doublet at  $T \geq 35 \text{ K}$  or a Zeeman sextet below 35 K. It should be emphasized, however, that if one excludes the possibility of two components in the measured spectra, then the asymmetry of the quadrupole doublet should be related to the preferred crystal orientation of the sample or to the presence of the Goldanskii-Karyagin effect [15, 16]. The first possibility is very unlikely since the TMS measurements were made on a powdered polycrystalline sample. The second possibility (the Goldanskii-Karyagin effect) is related to vibrational anisotropy in the studied crystal. This effect is temperature dependent, so the spectral asymmetry should decrease with decreasing temperature, which is not the case. In Fig. 3 it is clearly seen that the shapes of the spectra measured at 300 K and 35 K are almost identical, so the Goldanskii-Karyagin effect cannot be responsible for the observed asymmetry of the quadrupole doublet. Taking the above into account, it is more likely that the spectra shown in Fig. 3 consist of two components rather than one doublet with an asymmetry of unknown origin.

The  $IS(T)$  dependence obtained from the above fits to the TMS spectra of  $\text{UFe}_{0.40}\text{Ge}_2$  are shown in Fig. 5(a). In general,

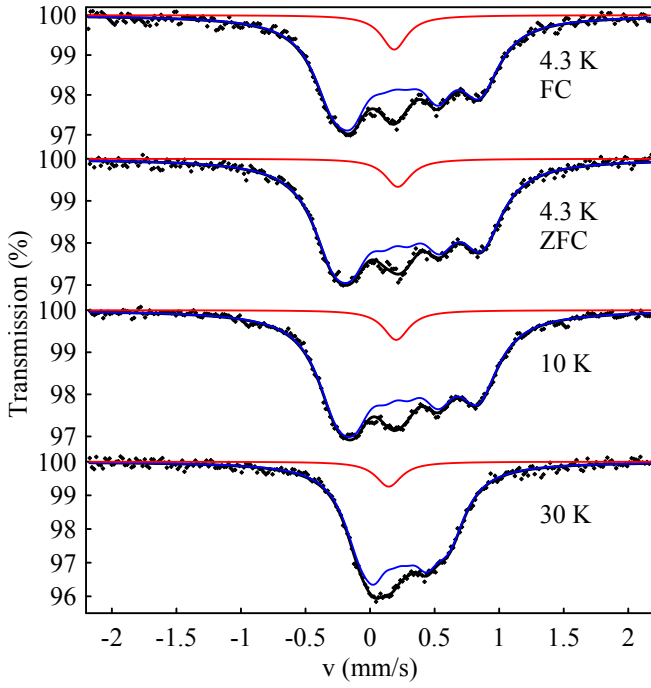


Figure 4: TMS data collected for  $\text{UFe}_{0.40}\text{Ge}_2$  at several temperatures from the magnetically ordered region and in zero applied magnetic field, fitted by a sum (black line) of one sextet and one singlet component (blue and red curves, respectively). FC marks the spectrum measured in zero magnetic field, after cooling the sample in the field of 3 T. For details of the fits see the text.

the isomer shift is dependent on the s-electrons density and is given by the relation [15]:

$$IS = \frac{4\pi}{5} Z e^2 R^2 \left( \frac{\delta R}{R} \right) [|\Psi_A(0)|^2 - |\Psi_S(0)|^2], \quad (2)$$

where  $Z$  is the nuclear charge of the Mössbauer absorber,  $e$  is the elementary charge,  $R$  is the radius of the probe nucleus,  $\delta R$  is the difference between the radii in the ground and excited states, and  $|\Psi_S(0)|^2$  and  $|\Psi_A(0)|^2$  are the s-electrons densities at the probe nuclei in the source and absorber, respectively. At 300 K, the  $IS$  parameter determined for the  $\text{UFe}_{0.40}\text{Ge}_2$  compound is equal to 0.238(4) mm/s. This value lies between that reported earlier for  $\text{U}_3\text{Fe}_2\text{Ge}_7$  (0.21(2) mm/s) [17] and that found for  $\text{U}_3\text{Fe}_4\text{Ge}_4$  (0.27(2) mm/s) [18], indicating a very similar electron density at the iron nuclei in these three systems.

As expected from the second-order Doppler (SOD) effect, the  $IS$  values obtained for  $\text{UFe}_{0.40}\text{Ge}_2$  increase concavely with decreasing temperature. Since the second-order Doppler shift depends on the lattice vibrations of the Fe atoms, the  $IS(T)$  dependence can be expressed in terms of the Debye approximation of the lattice vibrations as [15]:

$$\begin{aligned} IS(T) &= IS(0) + IS_{\text{SOD}}(T) = \\ &= IS(0) - \frac{9}{2} \frac{k_B T}{Mc} \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}, \end{aligned} \quad (3)$$

where  $IS(0)$  denotes the temperature-independent isomer shift,  $M$  is the mass of the nuclei of the absorber (here:  $^{57}\text{Fe}$ ),  $k_B$

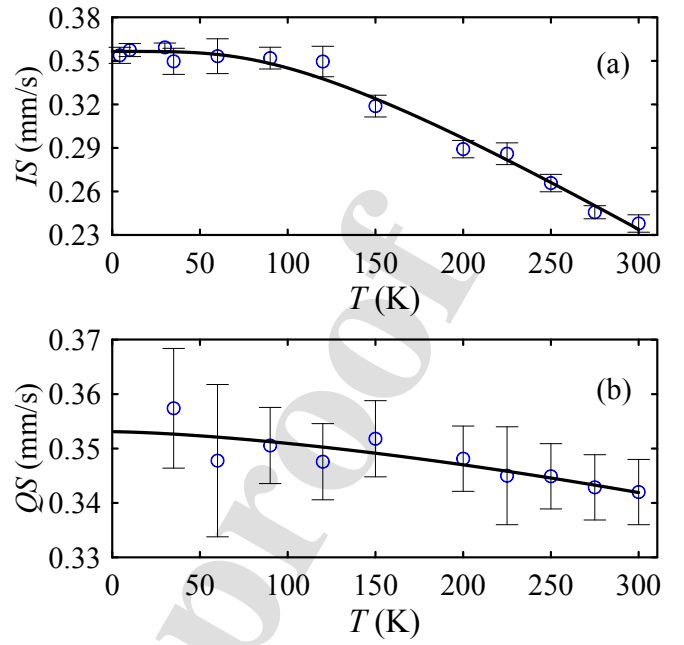


Figure 5: Temperature variations of the  $IS$  (a) and  $QS$  (b) parameters derived from the TMS spectra of  $\text{UFe}_{0.40}\text{Ge}_2$ . Black curves are fits of Eqs. (3) and (4) to the experimental data shown in panels (a) and (b), respectively (for details see the text).

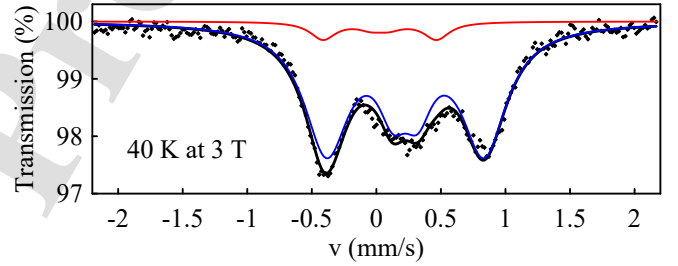


Figure 6: TMS spectrum of  $\text{UFe}_{0.40}\text{Ge}_2$  measured at 40 K and in external magnetic field of 3 T.

is the Boltzmann constant and  $c$  is the speed of light in vacuum. Fitting of Eq. 3 to the experimental  $IS(T)$  values gave  $IS(0) = 0.357(2)$  mm/s and  $\Theta_D = 434(23)$  K. Here, it should be noted that  $\Theta_D$  determined from the TMS data is higher than the corresponding value of  $\Theta_D = 257(5)$  K obtained from heat capacity measurements [9]. This discrepancy can be explained by the fact that the Mössbauer spectroscopy is only sensitive to the immediate neighbourhood of the Mössbauer probe atom ( $^{57}\text{Fe}$ ) and for this reason the estimated  $\Theta_D$  values from the TMS spectra should be treated as the local Debye temperature of the iron sublattice.

The  $QS(T)$  dependence obtained from the TMS spectra of  $\text{UFe}_{0.40}\text{Ge}_2$  are shown in Fig. 5(b). The observed quadrupole splitting fully identifies the presence of the electric field gradient (EFG) which is mainly proportional to the asymmetric charge distribution around the  $^{57}\text{Fe}$  nucleus. The  $QS$  parameter at 300 K is equal to 0.342(2) mm/s, which is comparable to  $QS = 0.32(2)$  mm/s reported previously for  $\text{U}_3\text{Fe}_2\text{Ge}_7$  [17].



Since the structure of  $\text{U}_3\text{Fe}_2\text{Ge}_7$  can be seen as stacking of the  $\text{UFeGe}_2$  and  $\text{UGe}_3$  layers along the  $b$ -axis, the charge distribution around the Fe nuclei in the  $\text{U}_3\text{Fe}_2\text{Ge}_7$  system should indeed be similar to that observed in  $\text{UFe}_{0.40}\text{Ge}_2$ .

In many intermetallic systems, the  $QS(T)$  dependence can be described by the empirical formula [19, 20]:

$$QS(T) = QS(0)(1 - AT^{3/2}), \quad (4)$$

where  $QS(0)$  is the value of  $QS$  at 0 K and  $A$  is a constant. Fitting Eq. 4 to the experimental data yields  $QS(0) = 0.353(2)$  mm/s and  $A = 6(1) \times 10^{-6} \text{ K}^{-3/2}$ . The determined fitting parameters can be treated as material constants, since their physical meaning is not clearly defined.

According to the results of our magnetic properties measurements (see Sec. 3.2 and Ref. [9]), the observed magnetic properties of the  $\text{UFe}_{0.40}\text{Ge}_2$  compound can be ascribed mainly to the uranium ions. However, the appearance of the Zeeman sextets in the TMS spectra measured at  $T \leq 30$  K may suggest that the Fe sublattice establishes long-range magnetic correlations below  $T_C$ . This behavior is similar to that observed in other uranium-iron ferromagnets, *e.g.*  $\text{UFe}_2$  [21],  $\text{U}_2\text{Fe}_3\text{Ge}$  [22] and  $\text{U}_3\text{Fe}_2\text{Ge}_7$  [17]. In all of them, the Mössbauer spectra collected below their magnetic ordering temperatures indicate the presence of small hyperfine field ( $B_{\text{hf}} < 5$  T) at the  $^{57}\text{Fe}$  nuclei.

On the other hand, the magnetic  $^{57}\text{Fe}$  spectra observed below 35 K may be due to the hyperfine magnetic field transferred from the ferromagnetically ordered uranium sites. To shed more light on this problem, we measured the TMS spectrum of  $\text{UFe}_{0.40}\text{Ge}_2$  at 40 K, which is slightly above  $T_C$ , and in external magnetic field  $B_{\text{ext}} = 3$  T, applied parallel to the propagation of the  $\gamma$  radiation beam. As can be seen in Fig. 6, the collected spectrum reveals the presence of two Zeeman components that consist of four lines, since in such a configuration the observed line intensity ratio for the sextet should be 3:0:1:1:0:3 [16]. The first component, with a relative intensity of 7(2)%,  $IS = 0.13(2)$  mm/s and effective hyperfine magnetic field  $B_{\text{eff}} = 2.8(2)$  T, can be attributed to the impurity phase. The second, major component corresponds to  $\text{UFe}_{0.40}\text{Ge}_2$  and can be described by the Zeeman sextet with  $B_{\text{eff}} = 3.78(2)$  T,  $IS = 0.333(7)$  mm/s and  $\epsilon = 0.01(4)$  mm/s. Since  $B_{\text{eff}} = B_{\text{hf}} + B_{\text{ext}}$ , the determined  $B_{\text{eff}} = 3.78(2)$  T confirms that the iron atoms in  $\text{UFe}_{0.40}\text{Ge}_2$  have a small magnetic moment. Assuming that the hyperfine coupling constant for intermetallic compounds is in the range from 10 T/ $\mu_B$  to 15 T/ $\mu_B$  [17, 22, 23], the hyperfine magnetic field  $B_{\text{hf}} = 0.78(2)$  T, obtained from the TMS spectrum measured for  $\text{UFe}_{0.40}\text{Ge}_2$  at 40 K and in  $B_{\text{ext}} = 3$  T, corresponds to the magnetic moment of iron  $\mu_{\text{Fe}}$  of about 0.05–0.08  $\mu_B$ . This estimated value of  $\mu_{\text{Fe}}$  is comparable with  $\mu_{\text{Fe}} \approx 0.2 \mu_B$  inferred from the Mössbauer spectra measurements carried out for  $\text{U}_3\text{Fe}_2\text{Ge}_7$  [17], and is small compared to the effective magnetic moment found for  $\text{UFe}_{0.40}\text{Ge}_2$ . Thus, it does not change our conclusions about the origin of magnetism in the latter compound (see Sec. 3.2 and Ref. [9]).

The values of the  $QS$  and  $\epsilon$  parameters obtained for the paramagnetic and magnetically ordered states of  $\text{UFe}_{0.40}\text{Ge}_2$ , respectively, can be used to determine the angle  $\varphi$  between  $B_{\text{hf}}$  and

the principal axis  $V_{zz}$  of the main electrical field gradient (EFG). Using the commonly used formula [17, 24]:

$$\epsilon = \frac{1}{2}QS(3\cos^2\varphi - 1), \quad (5)$$

and taking  $QS = 0.353$  mm/s and  $\epsilon = 0.08$  mm/s, the angle  $\varphi = 45.3^\circ$  was obtained.

Finally, the TMS technique can be used to confirm or rule out the formation of a ferromagnetic cluster-glass state in the  $\text{UFe}_{0.40}\text{Ge}_2$  system [9]. For this purpose, we measured the Mössbauer spectra of the compound at 4.3 K, that is, deep in the magnetically ordered region, and in two different regimes. The first measurement (denoted as ZFC in Fig. 4) was carried out in zero applied magnetic field and after cooling the sample in zero external magnetic field. The second one (labelled as FC in Fig. 4) was also performed in zero magnetic field, but after cooling the sample in the external field of 3 T, *i.e.* in the nearly-saturated magnetization range.

For the ZFC spectrum, the sextet attributed to  $\text{UFe}_{0.40}\text{Ge}_2$  could be described by  $IS = 0.353(4)$  mm/s,  $\epsilon = 0.08(1)$  mm/s and  $B_{\text{hf}} = 3.55(2)$  T while for FC, the hyperfine parameters are  $IS = 0.349(2)$  mm/s,  $\epsilon = 0.08(1)$  mm/s and  $B_{\text{hf}} = 3.52(2)$  T. Comparing these two sets of values, it can be seen that the two spectra are virtually identical. Moreover, the line intensity ratio estimated for both Zeeman sextets is close to 3:2:1:1:2:3. This means that the magnetic domains in the sample cooled in both the ZFC and FC regimes are randomly oriented, which is expected for the TMS measurements performed on polycrystalline or powdered samples in the absence of an external magnetic field [16].

Let us now consider the expected response from the hypothetical cluster-glass formation. In the FC regime, the sample was cooled down to 4.3 K in magnetic field applied parallel to the  $\gamma$ -ray beam propagation. Again, in this configuration, the observed line intensity ratio for the sextet should be 3:0:1:1:0:3 [16]. If we assume that below  $T_{\text{rmc}}$  a ferromagnetic cluster-glass state really forms, then in the FC regime the magnetic moments should be frozen at 4.3 K and aligned parallel to the applied field. And then also the line intensity ratio for the magnetic sextet in the FC spectrum should be close to the 3:0:1:1:0:3 mentioned above, not 3:2:1:1:2:3 as inferred from the experimental spectrum. This means that the magnetic moments are already magnetically ordered within randomly oriented domains, so the external magnetic field does not affect their local arrangement. Thus, it can be concluded that no behavior indicating the freezing of the magnetic moments (as should be the case in cluster glass or spin glass) is observed, and the compound  $\text{UFe}_{0.40}\text{Ge}_2$  orders purely ferromagnetically at  $T_C$ .

## 4. Conclusions

We have measured the transmission Mössbauer spectra on a polycrystalline,  $^{57}\text{Fe}$ -isotope-enriched sample of  $\text{UFe}_{0.40}\text{Ge}_2$ , which has been positively verified for the crystal structure and

magnetic properties described previously for  $\text{UFe}_{0.39}\text{Ge}_2$ . Analysis of the collected TMS spectra have confirmed that the compound orders ferromagnetically below  $T_C$  of about 37 K, while they have shown no sign of the previously postulated formation of magnetic glassy states. This suggests that the crystallographic disorder present in  $\text{UFe}_{1-x}\text{Ge}_2$  mainly affects the transport properties of the system rather than its magnetic ground state. Further experiments, preferably performed on a single-crystalline sample, are needed to confirm this conclusion.

## CRediT authorship contribution statement

**Adam Pikul:** Conceptualization, Formal analysis, Writing – Original Draft, Review & Editing; **Rafał Idczak:** Investigation, Formal analysis, Writing – Original Draft, Review & Editing; **Piotr Sobota:** Investigation; **Wojciech Nowak:** Investigation; **Vinh Hung Tran:** Writing – Review & Editing; **Mathieu Pasturel:** Formal analysis; Writing – Original Draft, Review & Editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- [1] S. S. Saxena, P. Agarwal, K. Ahilan, F. M. Grosche, R. K. W. Haselwimmer, M. J. Steiner, E. Pugh, I. R. Walker, S. R. Julian, P. Monthoux, G. G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, J. Flouquet, Superconductivity on the border of itinerant-electron ferromagnetism in  $\text{UGe}_2$ , *Nature* 406 (2000) 587–592. doi:https://doi.org/10.1038/35020500.
- [2] K. Oikawa, T. Kamiyama, H. Asano, Y. Ōnuki, M. Kohgi, Crystal structure of  $\text{UGe}_2$ , *J. Phys. Soc. Jpn.* 65 (1996) 3229–3232. doi:https://doi.org/10.1143/JPSJ.65.3229.
- [3] P. Boulet, A. Daoudi, M. Potel, H. Noël, G. Gross, G. André, F. Bourée, Crystal and magnetic structure of the uranium digermanide  $\text{UGe}_2$ , *J. Alloys Compd.* 247 (1) (1997) 104–108. doi:https://doi.org/10.1016/S0925-8388(96)02600-X.
- [4] D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J.-P. Briston, E. Lhotel, C. Paulsen, Coexistence of superconductivity and ferromagnetism in  $\text{URhGe}$ , *Nature* 413 (2001) 613–616. doi:https://doi.org/10.1038/35098048.
- [5] N. T. Huy, A. Gasparini, D. E. de Nijs, Y. Huang, J. C. P. Klaasse, T. Gortenmulder, A. de Visser, A. Hamann, T. Görlach, H. v. Löhneysen, Superconductivity on the Border of Weak Itinerant Ferromagnetism in  $\text{UCoGe}$ , *Phys. Rev. Lett.* 99 (2007) 067006. doi:https://doi.org/10.1103/PhysRevLett.99.067006.
- [6] M. Pasturel, A. Pikul, G. Chajewski, H. Noël, D. Kaczorowski, Ferromagnetic ordering in the novel ternary uranium germanide  $\text{URu}_{0.29}\text{Ge}_2$ , *Intermetallics* 95 (2018) 19–23. doi:https://doi.org/10.1016/j.intermet.2018.01.011.

- [7] M. Szlowska, M. Pasturel, A. Pikul, H. Noël, D. Kaczorowski, poster at the International Conference on Strongly Correlated Electron Systems SCES 2019 in Okayama, Japan, Sep. 23–28, 2019 (unpublished).
- [8] M. Pasturel, M. Szlowska, J. Ćwik, D. Kaczorowski, A. P. Pikul, Antiferromagnetic ordering in the ternary uranium germanide  $\text{UNi}_{1-x}\text{Ge}_2$ : Neutron diffraction and physical properties studies, *Intermetallics* 131 (2021) 107112. doi:https://doi.org/10.1016/j.intermet.2021.107112.
- [9] M. Szlowska, M. Pasturel, D. Kaczorowski, A. Pikul, Ferromagnetism in structurally disordered  $\text{UFe}_{0.39}\text{Ge}_2$ , *J. Alloys Compd.* 892 (2022) 162032. doi:https://doi.org/10.1016/j.jallcom.2021.162032.
- [10] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B* 192 (1) (1993) 55–69. doi:https://doi.org/10.1016/0921-4526(93)90108-1.
- [11] M. S. Henriques, D. Berthebaud, L. C. J. Pereira, E. B. Lopes, M. B. C. Branco, H. Noël, O. Tougaard, E. Šantavá, L. Havela, P. A. Carvalho, A. P. Gonçalves, Structural and physical properties of the  $\text{U}_9\text{Fe}_7\text{Ge}_{24}$  uranium germanide, *Intermetallics* 19 (7) (2011) 841–847. doi:https://doi.org/10.1016/j.intermet.2010.12.004.
- [12] M. S. Henriques, D. Berthebaud, A. Lignie, Z. El Sayah, C. Moussa, O. Tougaard, L. Havela, A. P. Gonçalves, Isothermal section of the ternary phase diagram  $\text{U-Fe-Ge}$  at 900°C and its new intermetallic phases, *J. Alloys Compd.* 639 (2015) 224–234. doi:https://doi.org/10.1016/j.jallcom.2015.03.145.
- [13] M. S. Henriques, D. I. Gorbunov, J. C. Waerenborgh, L. Havela, A. B. Shick, M. Diviš, A. V. Andreev, A. P. Gonçalves, Unusual 5f magnetism in the  $\text{U}_2\text{Fe}_3\text{Ge}$  ternary laves phase: a single crystal study, *J. Phys.: Condens. Matter* 25 (6) (2013) 066010. doi:10.1088/0953-8984/25/6/066010.
- [14] M. Henriques, D. Berthebaud, J. Waerenborgh, E. Lopes, M. Pasturel, O. Tougaard, A. Gonçalves, A novel ternary uranium-based intermetallic  $\text{U}_{34}\text{Fe}_{4-x}\text{Ge}_{33}$ : Structure and physical properties, *J. Alloys Compd.* 606 (2014) 154–163. doi:https://doi.org/10.1016/j.jallcom.2014.03.189.
- [15] P. Gülich, E. Bill, A. Trautwein, Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications, Springer, Berlin, Heidelberg, 2011. doi:https://doi.org/10.1007/978-3-540-88428-6.
- [16] N. N. Greenwood, Mössbauer Spectroscopy, Springer, Dordrecht, 1971. doi:https://doi.org/10.1007/978-94-009-5697-1.
- [17] M. S. Henriques, D. I. Gorbunov, J. C. Waerenborgh, M. Pasturel, A. V. Andreev, M. Dušek, Y. Skourski, L. Havela, A. P. Gonçalves, Synthesis and Structural/Physical Properties of  $\text{U}_3\text{Fe}_2\text{Ge}_7$ : A Single-Crystal Study, *Inorg. Chem.* 54 (2015) 9646–9655. doi:https://doi.org/10.1021/acs.inorgchem.5b01736.
- [18] D. Berthebaud, O. Tougaard, M. Potel, E. B. Lopes, J. C. Waerenborgh, A. P. Gonçalves, H. Noël, Crystal structure and electronic properties of the new compound  $\text{U}_3\text{Fe}_4\text{Ge}_4$ , *J. Alloys Compd.* 554 (2013) 408–413. doi:https://doi.org/10.1016/j.jallcom.2012.11.162.
- [19] Z. M. Stadnik, P. Wang, H.-D. Wang, C.-H. Dong, M.-H. Fang, Magnetic ordering in  $\text{TiFe}_{1.3}\text{Se}_2$  studied by Mössbauer spectroscopy, *J. Alloys Compd.* 561 (2013) 82–86. doi:https://doi.org/10.1016/j.jallcom.2013.01.085.
- [20] M. A. Albedad, F. Nejdassattari, Z. M. Stadnik, J. Przewoźnik,  $^{57}\text{Fe}$  Mössbauer spectroscopy and magnetic study of  $\text{Al}_{13}\text{Fe}_4$ , *J. Alloys Compd.* 619 (2015) 839–845. doi:https://doi.org/10.1016/j.jallcom.2014.08.225.
- [21] S. Tsutsui, M. Nakada, Y. Kobayashi, S. Nasu, Y. Haga, Y. Ōnuki,  $^{238}\text{U}$  and  $^{57}\text{Fe}$  Mössbauer Spectroscopic Study of  $\text{UF}_2$ , Hyperfine Interactions 133 (2001) 17–21. doi:https://doi.org/10.1023/A:1012272310063.
- [22] S. K. Dhar, K. V. Shah, P. Bonville, P. Manfrinetti, F. Wrubl, Structure and magnetic properties of  $\text{U}_2\text{Fe}_3\text{Ge}$ , *Solid State Commun.* 147 (5) (2008) 217–220. doi:https://doi.org/10.1016/j.ssc.2008.05.016.
- [23] S. M. Dubiel, Relationship between the magnetic hyperfine field and the magnetic moment, *J. Alloys Compd.* 488 (1) (2009) 18–22. doi:https://doi.org/10.1016/j.jallcom.2009.08.101.
- [24] G. Filoti, M. D. Kuz'min, J. Bartolomé, Mössbauer study of the hyperfine interactions and spin dynamics in  $\alpha$ -iron(II) phthalocyanine, *Phys. Rev. B* 74 (2006) 134420. doi:https://doi.org/10.1103/PhysRevB.74.134420.



- $\text{UFe}_{0.40}\text{Ge}_2$  has been confirmed to order ferromagnetically below  $T_c = 37$  K.
- The compound has been studied by Mössbauer spectroscopy.
- The experiments have confirmed that the ferromagnetism in  $\text{UFe}_{0.40}\text{Ge}_2$  is purely long-range in nature.
- The hypothesis of a ferromagnetic cluster glass below  $T_c$  has been discarded.

Adam Pikul: Conceptualization, Formal analysis, Writing -- Original Draft, Review & Editing;  
Rafał Idczak: Investigation, Formal analysis, Writing -- Original Draft, Review & Editing;  
Piotr Sobota: Investigation;  
Wojciech Nowak: Investigation;  
Vinh Hung Tran: Writing -- Review & Editing;  
Mathieu Pasturel: Formal analysis; Writing -- Original Draft, Review & Editing.

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