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Magnetic properties and ^{57}Fe Mössbauer effect in the $U_2Fe_{17-x}Ge_x$ system[1]

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Abstract

The investigation of magnetic properties and ^{57}Fe Mössbauer effect (ME) is reported for the $U_2Fe_{17-x}Ge_x$ system for $2 \leq x \leq 4$. The magnetic investigation, apart from for conventional magnetometric measurements, also includes high field examination up to 14 T. Moreover, the ME data are collected in the temperature range 10–650 K. An attempt to determine the contribution of the uranium to the magnetism of the phases investigated proved to be unsuccessful. The ME results allow us to propose a model of the occupancy of the crystallographic positions by the Fe atoms. The comparison of the properties of bulk and powder samples suggests an importance of magnetic interactions for stability of the crystal structure. © 1997 Elsevier Science S.A.

Keywords: ^{57}Fe Mössbauer Effect; $U_2Fe_{17-x}Ge_x$; Magnetic properties; Uranium

1. Introduction

The iron-rich rare-earth intermetallics with the Th_2Ni_{17} structure have been investigated actively due to their potential application as permanent magnets. They can exist as binaries or pseudobinaries (for review see [1]). The Th_2Ni_{17} structure can be described as the stacking of three different atomic planes perpendicular to the c-axis: the O-plane is formed by transition T elements located at the 6(g) and 12(k) sites; the P-plane is where f-electron atoms at the 2(b) and 2(d) sites and T atoms at the 12(j) site are distributed; the T-plane contains the same atoms as the P-plane but exhibits a different ordering. All these planes are separated by a pair of T atoms at the 4(f) site commonly described as a 'dumbbell'.

The 'U_2T_{17}' binaries do not exist in thermodynamic equilibrium, however, alloying with electron donor elements, such as Al, Si and Ge yields compound formation with crystal structures isotopic with the Th_2Ni_{17}-type where T = Fe [2–6], Co [5,6] and Ni [5]. This examination has shown that these systems exist in broad composition ranges, however, $U_2Fe_{15}Al_2$ [4], $U_2Co_{15}Si_2$ [5] and $U_2Ni_{15}Ge_2$ [5] compounds exhibit strictly limited stoichiometry. The most recent investigation of the $U_2Fe_{17-x}Ge_x$ alloys [6], also on single crystal samples [5] has shown for $2 \leq x \leq 3$ a strong preferential site occupation of the Ge atoms on one 12(k) of the four different Fe atom sites. All the alloys order ferromagnetically with a Curie point T_c going through a maximum at $T_c = 545(5)$ K for $x = 2.5$.

In the present paper we extend the research to ^{57}Fe Mössbauer effect (ME) measurements over a broad temperature range and the magnetization determination in steady magnetic field as high as 14 T at 4.2 K.

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2. Experiment

The samples with $2 \leq x \leq 4$ were obtained by direct melting of the constituent elements in stoichiometric proportion in an arc-furnace under protective argon atmosphere. This procedure is followed by prolonged annealing under vacuum. This operation has to be done carefully because for higher x, annealing produces a surplus of free Fe which is clearly seen as the high temperature tail of the susceptibility and extra lines in the ME spectra (see below). The X-ray analysis shows that the quality of samples is comparable with those of [6] and consistent with the ME results. The temperature [$M(T)$] and the field [$M(H)$] dependencies were obtained at equipment standard in our laboratories. The $M(T)$ plots were determined at temperatures from 4.2 to 650 K and under a magnetic field of 0.5 T whereas $M(H)$ was obtained at $T = 4.2$ K and in magnetic fields up to 14 T. The Curie points were defined as corresponding to the maximum of the first derivative of magnetization, $dM(T)/dT$.

Mössbauer effect (ME) measurements were carried out using standard transmission geometry, with the ^{57}Co (Rh) source kept at room temperature and the temperature of the absorber being changed in the range of 20–600 K in a gas-flow cryostat or in a furnace with helium-flow around the sample. Approximately 60 mg of the prepared material (mixed with MgO powder) was used for the absorber of the diameter of 5 mm. The obtained powder was heavily pressed between two pieces of thin Al-foil. All isomer shifts are given with respect to the metallic iron.

3. Results and discussion

The temperature dependencies of magnetization are fairly close to those obtained previously (see e.g. [6]), therefore, for the sake of brevity, they are omitted here. The magnetization vs. magnetic field up to 14 T at 4.2 K is presented in Fig. 1 for $x = 2.5$ as an example. It is seen that there is no hysteresis and the saturation is obtained above 5 T (50 kOe). Although the numerical values of the saturation moment given in [6] should be considered cautiously (for $x = 2.5$, $p_s = 22.8\ \mu_B\ \mathrm{fu}^{-1}$), our value is in fair agreement ($24.3\ \mu_B\ \mathrm{fu}^{-1}$ at $H = 14$ T). In Fig. 1 the results for polycrystalline and powder samples are shown and at present we cannot find any explanation for why the saturation for the latter is lower than for the former.

Typical room temperature (RT) Mössbauer spectra are presented in Fig. 2 for samples with $x = 2.0$ and 3.5. The outermost lines visible in the spectrum of $x = 2$ sample originate from the magnetically split six-line pattern of metallic α-Fe (probably slightly modified by the presence of U or Ge) and two Zeeman sextets were used to fit them. The existence of metallic iron was evident also from the magnetization vs. temperature, $M(T)$ curves (not shown). The amount of this impurity phase depends on the Ge-content and thermal treatment. Homogenization of the samples seems to improve the quality of the samples with relatively low Ge-index, x, but in the case of the samples with $x > 3$ it leads to the formation of the precipitates of metallic iron.

There are four crystallographic Fe positions in the Th$_2$Ni$_{17}$ structure: 4(f), 6(g), 12(j), and 12(k). Then

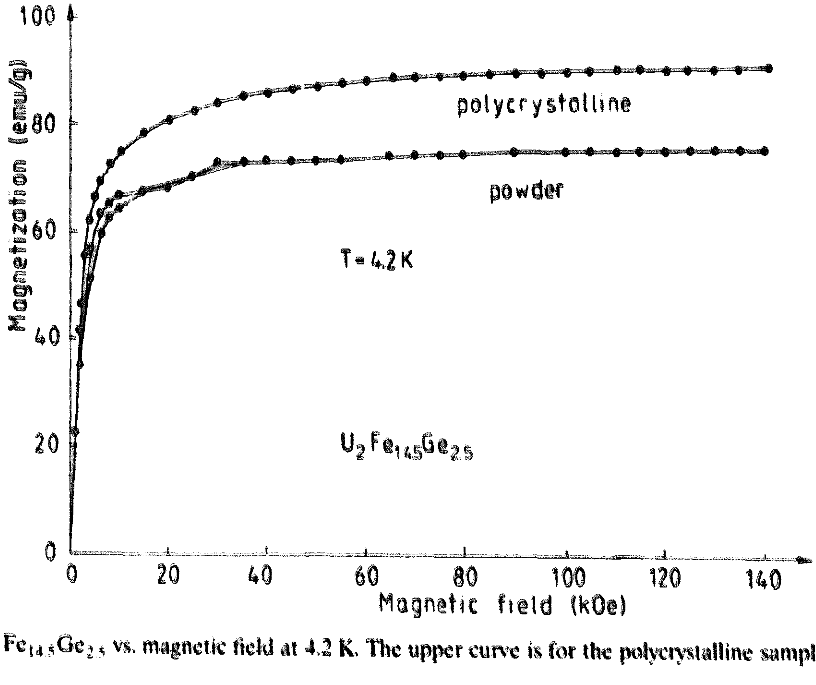

Fig. 1. Magnetization of $U_2Fe_{14.5}Ge_{2.5}$ vs. magnetic field at 4.2 K. The upper curve is for the polycrystalline sample and the lower curve is for powder sample.

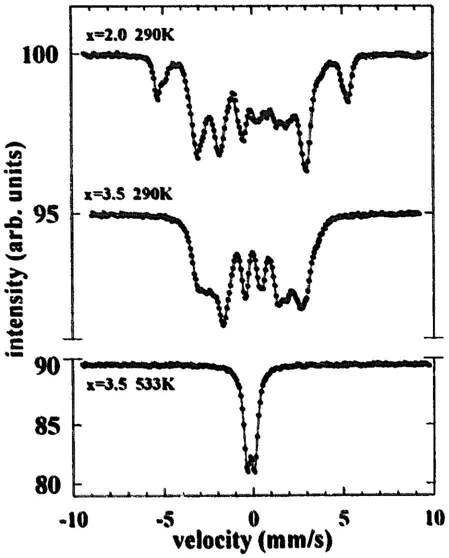

Fig. 2. ^{57}Fe Mössbauer spectra of $U_2Fe_{17-x}Ge_x$ with $x=2$ and 3.5 taken below and above the Curie temperature. Solid lines are fits to the data.

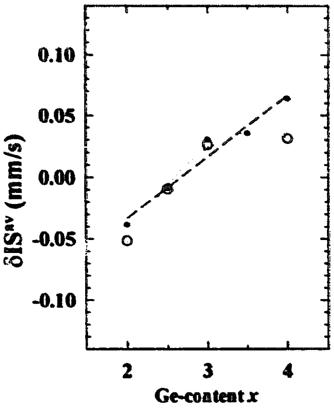

Fig. 3. The average isomer shift δIS^{av} of as-cast (closed symbols) and homogenized (open symbols) samples of $U_2Fe_{17-x}Ge_x$, plotted vs. Ge concentration, x. Lines are guides for the eye.

the ME spectra are fitted with four sextets (Zl,Z2,Z3,Z4, respectively) with different widths of the inner and outer lines, corresponding to the four distributions of magnetic hyperfine fields due to a slightly different crystallographic surrounding. In the case of some spectra two additional sextets were used for the impurity subspectra. The obtained RT values of quadrupole splitting, ΔE_Q for the four positions were approximately + 0.11–0.20 mm s^{-1} (Z2,Z3,Z4) and – 0.17 mm s^{-1} (Z1). The spectra above the Curie temperature (i.e. in paramagnetic state, see Fig. 2 for $x=3.5$ at $T=533$ K) were fitted with a quadrupole doublet with $\Delta E_Q \sim 0.40$ mm s^{-1}. It seems then that the main axis of the electric field gradient is roughly perpendicular to the basal plane of $U_2Fe_{17-x}Ge_x$ in which the magnetic field vector lies [5]. The average RT isomer shift δIS^{av} of non-homogenized and homogenized samples is plotted in Fig. 3 vs. Ge concentration, x. The increase of δIS^{av} with increasing x (with a slope of $\Delta(\delta IS^{av})/\Delta x \approx 0.10$ mm s^{-1}) is clearly observed, indicating the expected increase of the 4 s electron density due to Ge → Fe substitution. The saturation of $\delta IS^{av}(x)$ dependence observed for homogenized samples with $x>3$ suggests that the solubility limit of Ge in homogenized $U_2Fe_{17-x}Ge_x$ has been reached at $x \approx 3$, in good agreement with the conclusion obtained in [6].

The identification of the 4(f) position as corresponding to the Z4 sextet is obvious: the Z4 subspectrum has the smallest relative area (Fig. 4) and the largest hyperfine field H_{hf} (in the case of $x=2$ as-cast sample we obtained 193.6, 172.6, 134.2 and 228.8 kOe for Zl, Z2, Z3 and Z4, respectively). The 4(f) position has $(13-x)$ Fe-nearest neighbors (NN) in comparison to $(10-x)$ for 12(j) and 6(g), and $(9-x)$ for 12(k). The 4(f) position is then expected to have the largest value of H_{hf}. Based on the occupation number (Fig. 4a) we ascribe Z3 to the 6(g) position. In the case of R_2Fe_{17} (R-rare earth) compounds the energy of the magnetic Fe–Fe interactions increases with increasing distance between Fe atoms. Thus, we define r_{av} as the mean distance of Fe–NN. As r_{av} is clearly the smallest for the 6(g) site, the smallest H_{hf} value for this site is expected, and is in fact observed. The largest value of r_{av} in the Th_2Ni_{17} structure of $U_2Fe_{17-x}Ge_x$ corresponds to the 4(f) site. Sites 12(j) and 12(k) then correspond to Z1 and Z2. The value of r_{av} is larger for 12(j) and at the same time this site has a larger number of Fe–NN; both facts should result in a higher value of H_{hf} for the 12(j) site. We therefore relate Z1 to 12(j) and Z2 to 12(k). From the Ge-induced changes of the intensity and the hyperfine magnetic field, H_{hf}, corresponding to each Fe position we conclude that a unique preferred substitution site for Ge in $U_2Fe_{17-x}Ge_x$ does not exist. Increasing the x value leads to a slight increase of the occupation number of 6(g) sites and a significant decrease of the occupation numbers of the 12(k) and 12(j) sites. The occupation of 4(f) sites by Fe is clearly incomplete for all Fe–Ge compositions studied. It could be caused by Ge substituting into this site, but the structural data of [6] strongly exclude such a possibility. We suggest rather that the observed low occupation of 4(f) sites could be due to an inexact stoichiometric substitution of U by a Fe-dumbbell (similarly to the situation encountered in the nitrogenated $Y_2Fe_{17}N_y$ system [7]). Germanium atoms seem hence to occupy preferentially 12(k) sites, and upon further Ge substitution they enter both 12(k) and 12(j) sites. The occupation of 12(k) sites by doped Ge atoms was also

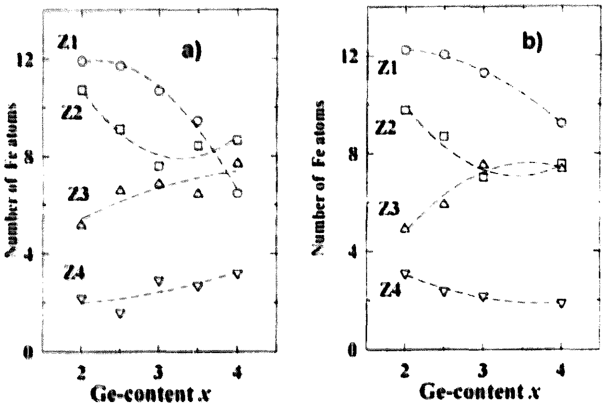

Fig. 4. The relative intensity of the components Z1, Z2, Z3 and Z4 of room temperature Mössbauer spectra of as-cast (a) and homogenized (b) samples $U_2Fe_{17-x}Ge_x$ recalculated to $(34-2x=100\%)$.

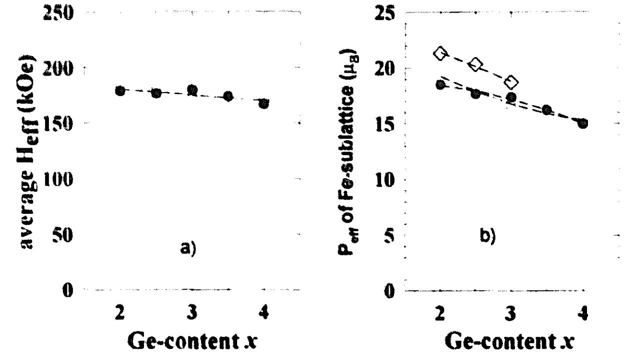

Fig. 5. The average magnetic hyperfine field (a) and the resulting magnetic moment p_{eff} (b) of Fe-sublattice in $U_2Fe_{17-x}Ge_x$ vs. Ge concentration, x; as-cast samples (full circles), homogenized samples (open circles). Open diamonds in (b) represent the results of Chevalier et al. [6] for homogenized samples.

suggested in [6]. In the case of the isostructural $Y_2Fe_{15}Ge_2$ compound, a preferential substitution of 12(k) sites by germanium was also found.

We note here a relatively weak linear decrease of the average $\langle H_{hf}\rangle$ (and also H_{hf} of the Z1–Z4 subspectra) with increasing x, as is shown in Fig. 5a. Assuming that approximately 15 T corresponds to 1 μB (phenomenological conversion factor), we recalculated these data to obtain the effective moments of the Fe-sublattices (in a unit cell) at RT (Fig. 5b). For comparison we have shown, in Fig. 5b, the moments of unit cell obtained in [6] from magnetization measurements. The difference of approximately 10% does not allow us, however, to draw any decisive conclusions concerning the possible contribution of the magnetic moment of uranium. The estimation of the effective moment of the Fe sublattice, p_{eff} (Fe) as mentioned above was based on empirical relation. The presence of metallic Fe-impurity visible in the $M(T)$ plot could lead to overestimation of the effective moment of the unit cell of $U_2Fe_{17-x}Ge_x$. We estimate the resulting error to be in the range 8–10%.

The Curie temperature T_c as obtained from ME data (Fig. 6) increases from approximately 504 K for $x=2$ to 530 K for $x=3.5$. The $M(T)$ measurements in the field of 5 kOe (not shown) yielded slightly higher values of approximately 503–545 K. As can be seen from the inset of Fig. 6, when the temperature approaches T_c, the hyperfine field, H_{hf}, is proportional to $(T_c-\mathrm{T})^{\beta}$ with the critical exponent $\beta\approx0.5$.

An interesting phenomenon was observed in the case of samples used for ME (powders) and containing metallic Fe impurity phase (all homogenized samples and the as-cast ones with $x<3.5$). These samples were unstable above T_c towards the formation of metallic iron (see Fig. 7). We did not observe this instability in the case of ingots made of such materials as well as the powder samples used for magnetometric measurements. Also the other ME samples with $x\geq3.5$ (without metallic Fe but not single phase) were stable up to the highest obtained temperatures (650 K). We exclude here the possibility of the reaction with the Al foil or the formation of any oxides. As the ME samples are ground and then heavily pressed, it probably results in good mechanical contact between metallic Fe precipitates and $U_2Fe_{17-x}Ge_x$ material, which in turn leads to the decomposition of the latter material. The coincidence of the decomposition temperature with T_c suggests that it may be the energy gain due to the magnetic ordering which stabilizes the structure up to T_c. This suggestion is confirmed by Pearson [8] who pointed out that the cell dimensions in the $(\mathrm{R,An})\mathrm{M_6Al_6}$ and $(\mathrm{R,An})\mathrm{M_4Al_8}$ phases indicated relative transition metal sizes in the order Fe < Cu < Mn < Cr, whereas in the elemental metals manganese is larger than chromium which is approximately of the same size as iron. This difference in behavior is related by Pearson [8] to magnetic interactions.

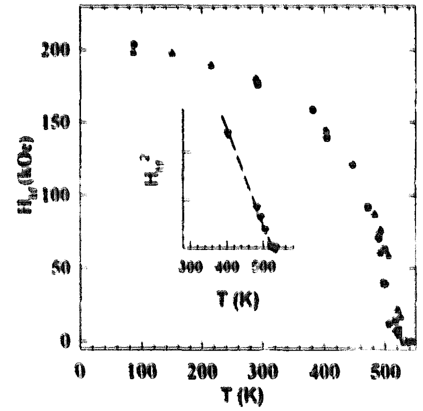

Fig. 6. The average hyperfine field, H_{hf}, for as-cast samples with $x=2$ (circles), 2.5 (squares) and 3.5 (triangles). The inset shows H_{hf}^2 vs. temperature plot for $x=3.5$ as cast sample.

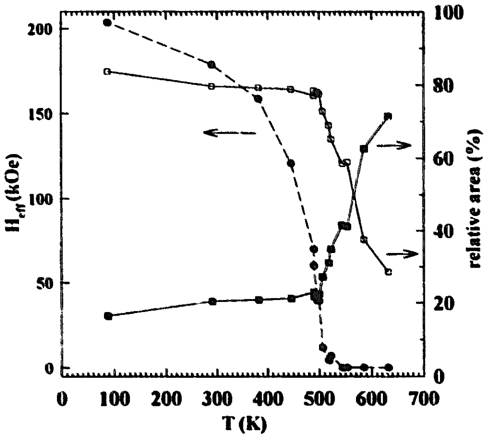

Fig. 7. The temperature dependence of average magnetic hyperfine field, H_{hf} (closed circles, left hand scale) and relative amount of metallic Fe (closed squares, right hand scale) and $U_2Fe_{17-x}Ge_x$ (open squares, right hand scale) for $x = 2$ as cast sample.

4. Conclusions

A series of $U_2Fe_{17-x}Ge_x$ compounds with $2 \leq x \leq 4$ has been synthesized and their magnetic properties investigated using ^{57}Fe ME and dc-magnetization. The ME data show that a unique Ge substitution site does not exist and the doped germanium atoms enter the 12(k) sites initially. Upon further doping, Ge atoms seem to enter the 12(k) and 12(j) sites, mainly. The magnetic moment of iron decreases slowly with increasing Ge concentration, while the Curie point remains unchanged. Magnetic contribution of uranium, if any, remains within experimental error. There is some suggestion of a relation between magnetic interactions and the stability of crystal structure.

References

[1] H.-S. Li, J.M.D. Coey, in K.H.J. Buschow (Ed.), "Handbook of Magnetic Materials" vol. 6, Elsevier Science BV, Amsterdam, 1991, p.1.

[2] T. Berlureau, B. Chevalier, L. Fournès, J. Etourneau, Mat. Lett. 9 (1989) 21.

[3] B. Chevalier, T. Berlureau, P. Gravereau, L. Fournès, J. Etourneau, Solid State Commun. 90 (1994) 571.

[4] B. Chevalier, P. Rogl, J. Etourneau, J. Solid State Chem. 115 (1995) 13.

[5] Y. Shiokawa, M. Hara, Y. Haga, R. Amaro, T. Takahatu, J. Alloys Comp. 213–214 (1994) 512.

[6] B. Chevalier, P. Gravereau, T. Berlureau, J. Etourneau, J. Alloys Comp. 233 (1996) 174.

[7] M. Morariu, M.S. Rogalski, N. Plugaru, M. Valeanu, D.P. Lazar, Solid State Commun. 92 (1994) 889.

[8] W.B. Pearson, J. Less-Common Met. 96 (1984) 103.