Independence of magnetic behavior for different structural states in melt-spun $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \leq x \leq 6$)

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Independence of magnetic behavior for different structural states in melt-spun $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ $(0 \leqslant x \leqslant 6)$

Z Śniadecki[1], B Idzikowski[1,4], J-M Greneche[2], P Kerschl[3], U K Rößler[3] and L Schultz[3]

[1] Institute of Molecular Physics, Polish Academy of Sciences, M Smoluchowskiego 17, PL-60-179 Poznań, Poland
[2] UMR CNRS 6087, Université du Maine, F-72085 Le Mans, France
[3] IFW Dresden, PO Box 270116, D-01171 Dresden, Germany

E-mail: idzi@ifmpan.poznan.pl

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Abstract

Structural and magnetic properties of rapidly quenched alloys from the $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ $(0 \leqslant x \leqslant 6)$ series produced by melt-spinning are investigated by x-ray diffraction (XRD) at room temperature (RT), magnetic measurements in the temperature range from 1.7 to 350 K, and ^{57}Fe Mössbauer spectrometry at 77 and 300 K. Significant similarities in magnetic properties were found between mixed (crystalline and amorphous) $DyMn_3Ge_3Fe_3Al_3$ and fully amorphous $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ alloys showing essentially the same thermal magnetization behavior with a slight decrease of magnetization. Mössbauer spectra confirm a reduction of magnetic polarization in the transition–metal substructure by the substitution of FeAl by MnGe. The present alloys display complex magnetic behavior which originates from different antiferromagnetically coupled magnetic sublattices (Dy- and Fe–Mn sublattice) and the dilution of the Fe sublattice by Mn atoms. In addition, a spin-cluster-glass-like structure is proposed to describe the dynamic effects which occur in the $DyMn_3Ge_3Fe_3Al_3$ alloy, resulting from the competing exchange couplings in this mixed Fe–Mn sublattice.

1. Introduction

The $REMn_{6-x}Ge_{6-x}Fe_xAl_x$ $(0 \leqslant x \leqslant 6)$ compounds with complex magnetic ordering are derived from a ternary system combining the transition metals (TM) Fe and Mn, the rare-earth element (RE) Dy and a metalloid or other metal (M) Ge or Al. In the $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ series, the limiting compounds $DyMn_6Ge_6$ $(x = 0)$ and $DyFe_6Al_6$ $(x = 6)$ have hexagonal crystal structure ($HfFe_6Ge_6$-type in equilibrium, $P6/mmm$ space group) and tetragonal crystal structure (akin to $ThMn_{12}$-type, partially disordered $CeMn_4Al_8$-type, $I4/mmm$ space group), respectively. Different crystalline structures and also amorphous states appear during rapid solidification between $0 \leqslant x \leqslant 6$ as a result of the destabilization of the parent crystal structures [1]. The occurrence of these different structural types in the alloy series gives a unique possibility to study the influence of atomic order on the complex magnetic properties of such RE–TM–M alloys. The parent compound $DyMn_6Ge_6$ ($HfFe_6Ge_6$-type equilibrium structure) is a helimagnet with simultaneous ordering of the Dy and Mn sublattices with a high transition temperature $T_N = 423$ K [2–4] and a reorientation transition below 100 K to a conical helix [3, 5]. $DyFe_6Al_6$ with the tetragonal crystal structure akin to $ThMn_{12}$-type ($I4/mmm$) has a ferrimagnetic structure with ordering at 340 K [6, 7]. A broad maximum of magnetization versus temperature $M(T)$ curves is found at 240–270 K. At $T \leqslant 40$ K spontaneous magnetization vanishes due to a compensation of moments in each of the RE and Fe sublattices ([7] and references therein). It was suggested that this magnetic transition is related to competing exchange couplings in the (partially) disordered Fe sublattices and a modulated non-collinear magnetic order within the Fe sublattices [7], while the Dy–Fe coupling maintains locally a ferrimagnetic structure.

[4] Author to whom any correspondence should be addressed.

This ordering of Fe moments and other properties of $DyFe_6Al_6$ were established mainly from ^{57}Fe Mössbauer spectra [7]. Thus, in the two limiting ternary compounds $DyMn_6Ge_6$ and $DyFe_6Al_6$, one has competing exchange couplings within the TM sublattices, antiparallel orientation of the Dy and the TM sublattice moments and magnetic anisotropy effects mainly due to the Dy sublattice. The competing exchange couplings are responsible for the appearance of the helimagnetic order in $DyMn_6Ge_6$ and for the conjectured modulated non-collinear state with effectively compensated sublattice magnetizations in $DyFe_6Al_6$. The magnetic anisotropy of Dy explains the easy-plane-type of the magnetic behavior in these uniaxial compounds. It is also believed to be responsible for the more subtle effects, like the reorientation transition within the helical states in $DyMn_6Ge_6$. As we have shown previously, fully amorphous states with magnetic properties can be generated in the $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \leqslant x \leqslant 6$) series [1, 8]. In this work, we describe the characterization of the magnetic properties in this alloy series from thermal magnetic measurements and Mössbauer spectroscopy data.

2. Experimental methods

The master alloys were prepared by arc-melting of the pure elements (4N or more) under Ar atmosphere. The ingots were subsequently melt-spun on a single-roller apparatus with a wheel surface velocity of 20 m s^{-1} and then investigated in the as-quenched state.

Structural information was obtained by XRD either using a Philips X'Pert or a TUR M-62 diffractometer both with Co Kα ($\lambda = 1.788\,97$ Å) radiation. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves were measured in an MPMS-5 (Quantum Design) at 0.1 T (the lowest value of applied magnetic field which allows the observation of the magnetic phase transitions in $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \leqslant x \leqslant 6$) alloys) between 1.7 and 300 K. The transmission Mössbauer experiments were performed at 77 K and room temperature (RT) using a constant acceleration conventional spectrometer with a ^{57}Co source. The hyperfine structure was modeled by means of the least-squares refinement procedure involving magnetic and quadrupolar components with Lorentzian lines. The isomer shift values are quoted relative to that of α-Fe at RT.

3. Results and discussion

Figure 1(a) shows XRD patterns obtained for all melt-spun $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ (alloys for $3 < x < 6$ were described already in [8]). The $DyFe_6Al_6$ ($x = 6$) has the tetragonal partially disordered $CeMn_4Al_8$-type ($I4/mmm$ space group) structure both in the as-quenched and annealed states. A simultaneous substitution of Fe and Al by Mn and Ge atoms leads to a small shift of tetragonal Bragg peak positions for $x = 5$, but for larger substitution a new type of structure (not analyzed here) arises in the as-quenched state for $DyMn_2Ge_2Fe_4Al_4$ ($x = 4$) and $DyMn_3Ge_3Fe_3Al_3$ ($x = 3$). For $x = 3$ the same series of Bragg peaks arises more weakly on an unstructured background in the XRD pattern. The structure of this as-quenched material, therefore, appears to be nanocrystalline or mixed crystalline and amorphous. The observed diffraction patterns are consistent with amorphous states for the $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($1 \leqslant x \leqslant 2.5$) alloys [1]. Finally, the second parent compound $DyMn_6Ge_6$ ($x = 0$) in the as-quenched state exhibits the metastable hexagonal $TbCu_7$-type crystal structure ($P6/mmm$) [9]. The XRD pattern for the mentioned crystal structure (figure 1(a), $x = 0$) is shown with Miller indices, while a black arrow points out an unidentified peak. Depending on preparation conditions, the $TbCu_7$-type structure can be obtained as a disordered version of the hexagonal $CaCu_5$-type structure in $RETM_x$ alloys with $x > 5$, whereby RE atoms are randomly substituted by TM dumbbells, see, for example, [10–12]. In effect, the $TbCu_7$ structure is structurally closely related to a $CaCu_5$-type structure [9]. The extra peak is likely related to a phase fraction with an ordered hexagonal $CaCu_5$-like structure and a concomitant change of the lattice parameters. Subsequent annealing favors the formation of $HfFe_6Ge_6$-type crystal structure ($P6/mmm$), which again is derived from the $TbCu_7$-type structure.

As observed in figure 1(b), irreversibilities between FC and ZFC $M(T)$ curves indicate complex magnetic behavior at rather elevated temperature, for all $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \leqslant x \leqslant 6$) samples in the as-quenched state. The ferrimagnetic ordering temperature for $DyFe_6Al_6$ is about 315 K, which is close to the temperatures reported earlier [8]. One can see also a broad maximum of magnetization between 230 and 260 K. With a further decrease of temperature, magnetization decreases and finally vanishes as shown by measurements of spontaneous $M(T)$ [7]. The phase transition below the broad maximum of magnetization occurs due to the change of ferrimagnetic into effectively antiferromagnetic order [13]. For the substituted sample $DyMnGeFe_5Al_5$ ($x = 5$) with the same tetragonal structure a decrease of ordering temperature to about 260 K is observed and the magnetization is generally lower for this system. Negative magnetization in $M(T)$ curves occurs due to antiferromagnetic coupling between two sublattices (the Dy sublattice and the mixed Fe–Mn sublattice). One sublattice is ordered ferromagnetically at high temperatures, while the other one becomes ordered with decreasing temperature and, at 135 K, an overcompensation of the net moment of the high temperature ordered sublattice takes place.

In the samples with higher substitution of FeAl by MnGe, i.e. for $DyMn_2Ge_2Fe_4Al_4$ ($x = 4$), $DyMn_3Ge_3Fe_3Al_3$ ($x = 3$) and $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ ($x = 2.5$), a shift of magnetization maximum to lower temperatures is observed. The onset of irreversibility may be ascribed to an inhomogeneous magnetic state and clustering owing to the dilution by Mn atoms of the Fe sublattice, which orders ferromagnetically at high temperature. Here again crossing of FC and ZFC magnetization curves indicates complex magnetism involving different antiferromagnetically coupled sublattices, namely the Fe–Mn and Dy substructures, with different temperature dependence of spontaneous polarization. The $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ ($x = 2.5$), which is fully amorphous, shows very similar magnetization behavior as for the crystalline $x = 4$ and mixed (amorphous and crystalline)

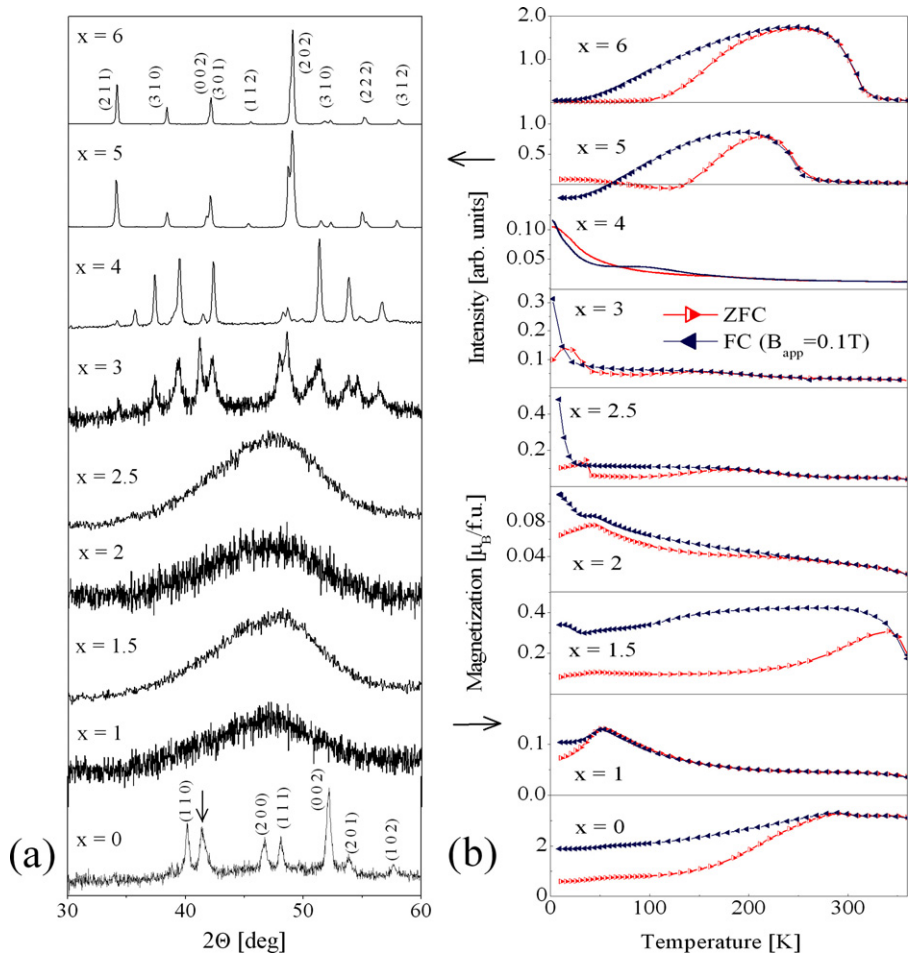

Figure 1. (a) XRD patterns of $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \leqslant x \leqslant 6$) in the as-quenched state. For $x = 0$ indices identify the peaks of the $TbCu_7$-type crystal structure (the black arrow marks an unidentified peak) and for $x = 6$ the peaks are related to partially disordered $CeMn_4Al_8$-type structure. (b) Field-cooled (blue + left pointing triangle) and zero-field-cooled (red + right pointing triangle) magnetization data $M(T)$ at 0.1 T of the as-quenched $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \leqslant x \leqslant 6$).

(This figure is in colour only in the electronic version)

$x = 3$ compounds. For the set of fully amorphous samples rather different types of magnetization behavior are seen with irreversibilities of the $M(T)$ at elevated temperatures near 300 K and relatively high magnetization values for $x = 1.5$, while the samples with $x = 1$ and 2 display irreversibilities only at lower temperatures and suppressed magnetization. For $DyMn_6Ge_6$ one can see a significant increase of $M(T)$ in the whole range of temperatures and a magnetic transition at about 300 K [1]. Remarkably, for the whole series of samples, low temperature anomalies in the magnetization indicate contributions of the Dy sublattice to the magnetic properties. The mixing of the Mn–Fe subsystem seems to suppress the magnetization of the TM sublattice for the intermediate range of compositions, in particular for the partially amorphous and crystalline samples with $x = 2.5$–4.

The $DyFe_6Al_6$ crystallizes in the partially disordered $CeMn_4Al_8$-type crystal structure, which is derived from the $ThMn_{12}$-type. It has four crystallographic sites: the 2*a* site is fully occupied by Dy atoms, the 8*f* and 8*i* contain only Fe and Al, respectively, while the 8*j* is randomly occupied by Fe and Al atoms [14, 15]. As shown in figures 2(a) and (b), the 77 K Mössbauer spectra of $DyFe_6Al_6$ consist of a broadened line sextet resulting from different Fe species while an additional central quadrupolar feature is observed at RT. This complex magnetic structure is attributed to different atomic surroundings of Fe atoms in the crystalline structure. The spectra had to be fitted with several magnetic sextets with hyperfine fields ranging from 8 to 18 T for the spectrum measured at 77 K and from 4 to 12 T for the spectra at RT. For the RT spectrum an additional quadrupolar component had to be included (the fraction of which is estimated from the absorption area at about 6%) [7]. The mean values of the hyperfine parameters are listed for all samples in table 1. When the MnGe content becomes larger, i.e. for x in the range from 1 to 2, the Mössbauer spectra show pure quadrupolar structures at both 300 and 77 K consistent with a paramagnetic state. These spectra can be *a priori* well described by means of two quadrupolar doublets with broad lines but a second fitting model involving quadrupolar splitting distributions linearly correlated with the isomer shift to describe the asymmetry was also successfully established. The distributions of quadrupolar splitting, which remain rather narrow, are consistent with

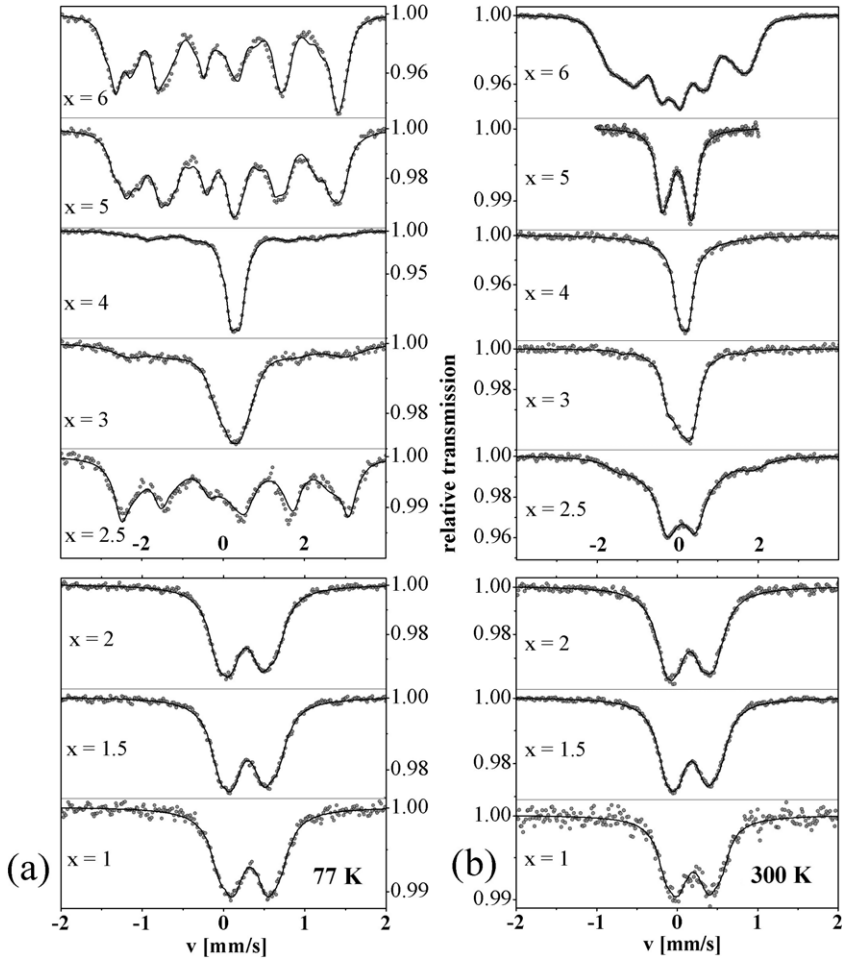

Figure 2. Mössbauer spectra of as-quenched $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($1 \leqslant x \leqslant 6$) at 77 K (a) and 300 K (b).

Table 1. Hyperfine field (B_{hyp}), paramagnetic fraction (PF), isomer shift (IS) and quadrupolar shift (2ε) or splitting (QS) values estimated from Mössbauer measurements of as-quenched $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($1 \leqslant x \leqslant 6$) alloys at 77 and 300 K. Values marked with '$*$' were obtained for the $x = 3$ sample from measurements in external magnetic fields $B_{ext} = 0.04$ T and 0.3 T at 77 and 300 K, respectively (details in the text).

x	$\langle B_{hyp}\rangle$ (T) 77 K ±0.5	$\langle B_{hyp}\rangle$ (T) 300 K ±0.5	PF (%) 77 K ±2	PF (%) 300 K ±2	$\langle IS\rangle$ (mm s^{-1}) 77 K ±0.02	$\langle IS\rangle$ (mm s^{-1}) 300 K ±0.02	$\langle 2\varepsilon\rangle$ or $\langle QS\rangle$ (mm s^{-1}) 77 K ±0.02	$\langle 2\varepsilon\rangle$ or $\langle QS\rangle$ (mm s^{-1}) 300 K ±0.02
6	14.7	8.0	0	6	0.20	0.09	0.10	0.15
5	13.4	0	0	100	0.22	0.12	0.11	0.28
4	4.5	0	67	100	0.41	0.30	0.13	0.12
3	6.1	4.9	64	95	0.34	0.24	0.14	0.12
	7.6*	1.8*	55*	83*	0.33*	0.25*	0.16*	0.14*
2.5	13.5	2.6	17	74	0.34	0.22	0.12	0.47
2	0	0	100	100	0.39	0.28	0.49	0.47
1.5	0	0	100	100	0.41	0.30	0.49	0.46
1	0	0	100	100	0.43	0.31	0.50	0.45

an amorphous state, as previously concluded from x-ray diffraction. For intermediate MnGe content ($2.5 \leqslant x \leqslant 5$), the 77 K Mössbauer spectra exhibit a mixture of magnetic and quadrupolar components. Thus, the hyperfine structure results from a distribution of magnetic hyperfine fields and a rather broad single line at the center of the spectrum. Except for a ribbon with $x = 5$, the Mössbauer spectra taken at 300 K are qualitatively similar but the hyperfine field distribution is obviously shifted to lower fields, while the central quadrupolar feature is significantly increased. The Fe magnetic structure of these alloys progressively orders when the temperature decreases. The Fe sublattice for $x = 4$ and 5 orders magnetically below 300 K.

The systematic trends in the Mössbauer spectra essentially reflect the dilution of Fe sites. With increasing MnGe content, the Fe atoms increasingly are surrounded by other nonmagnetic

atoms and, therefore, Fe remains in the paramagnetic state. Furthermore, the exchange interactions within the Fe substructure are weakened with the MnGe substitutions. This is in agreement with $M(T)$ measurements where magnetization at 77 K decreases significantly (figure 1(b)) for $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($2.5 \leqslant x \leqslant 5$). Low values of magnetization (about 0.1 μ_B/f.u.) for $x = 3$ and 2.5 are observed at 77 K and RT. In spite of this fact, sextets exist at both temperatures for these alloys. This suggests that there are still Fe atoms which interact with a sufficient number of magnetic atoms in their surroundings and Fe magnetic components are still visible in the Mössbauer spectra (figures 2(a) and (b), for $x = 3$ and 2.5). With increasing MnGe content, the hyperfine structure can be described by a smaller number of magnetic components. This effect can be connected with a decreasing number of different atomic surroundings, i.e. a reduced number of magnetic nearest neighbors. A paramagnetic contribution with decreasing weight down to 77 K was observed, indicating chemical disorder at some Fe positions [16], which leaves a larger fraction of Fe atoms without significant magnetic couplings in the TM sublattice. A larger number of Fe atoms takes part in magnetic ordering at 77 K. For the $x = 3$ alloy, Mössbauer spectra measured in the applied field exhibit the occurrence of dynamic effects: indeed, the presence of an external magnetic field applied perpendicular to the γ beam ($B_{ext} = 0.04$ T for 77 K and 0.3 T for 300 K) favors the decrease of the paramagnetic fraction from 95 (without field) down to 83% and from 64 down to 55% at 300 and 77 K, respectively (see details in table 1). Such a feature suggests rather a spin-cluster-glass-like structure, which may occur in the mixed TM sublattice involving competing exchange couplings between Fe and Mn ions. For alloys with larger Mn and Ge contents there are no magnetic components directly visible in ^{57}Fe Mössbauer spectrometry due to the lack of magnetic coupling. Rather, high magnetization values which are still observed, especially for $DyMn_{4.5}Ge_{4.5}Fe_{1.5}Al_{1.5}$, should be related to two separate magnetic orderings of the Mn-rich substructures, which do not couple to Fe ions anymore, and of the Dy sublattice. The major part of the magnetic response should be related to Mn in these structures. It is likely that there is no (strong) exchange coupling to Fe in the Mn-rich TM sublattice so that Fe remains in the paramagnetic state, while there is a true long-range ordering of Mn atoms. Mössbauer spectra of $DyMnGeFe_5Al_5$ ($x = 5$) measured at RT and 77 K exhibit different hyperfine structures, which are consistent with the ordering temperature at 260 K, as observed in figure 1(b). In $DyMn_2Ge_2Fe_4Al_4$ ($x = 4$) the situation is similar but the quadrupolar splitting vanishes to zero. The lower paramagnetic contribution for 'mixed' and fully amorphous alloys ($x = 3$ and 2.5) can be explained by the presence of Fe clusters in an amorphous matrix. For alloys with $x = 1$, 1.5 and 2 there are only nonmagnetic components in the spectra. In table 1 the values of hyperfine fields, paramagnetic fractions and quadrupolar shift and splitting values for each composition are summarized. The values of isomer shift and quadrupolar shift/splitting were allowed to vary freely during the fitting procedure and are averaged for each magnetic or quadrupolar component.

4. Conclusions

In conclusion, for compositions ranging between those of the parent compounds in the $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ alloy series, the structural instability is growing and the formation of amorphous structure is observed. This process is accompanied by relatively small changes in magnetic structures of these alloys. With the substitution of FeAl by MnGe atoms, the Mössbauer spectra indicate a reduced participation of Fe, which seems to decouple from the magnetic Mn and Dy sublattice. At high enough Mn substitution the vanishing of magnetic components (sextets) in the Mössbauer spectra is observed. Mössbauer spectra collected at 77 and 300 K are consistent with magnetization measurements. For $x = 5$ the occurrence of negative magnetization in $M(T)$ curves could be attributed to the antiferromagnetic coupling between two sublattices (Dy sublattice and the mixed Fe–Mn sublattice). The Fe–Mn sublattice is ordered ferromagnetically at high temperatures already, while the other RE sublattice becomes ordered with decreasing temperature and an overcompensation of net moment is visible at 135 K. Complex magnetic behavior is observed also for other compositions in this alloy series, mainly due to the presence of different antiferromagnetically coupled sublattices with a different temperature dependence of spontaneous polarization. For the $x = 3$ alloy, Mössbauer spectra measured in an applied field give evidence of the occurrence of some dynamic effects indicating a spin-cluster-glass-like structure. It may originate from the mixed TM sublattice with competing exchange couplings between Fe and Mn ions.

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