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Magnetism influenced by structural disorder in melt-spun $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ (x = 2.5, 3)

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Abstract Different chemical and/or geometrical orders were found in melt-spun $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ with x = 2.5 and 3 having fully amorphous and mixed (crystalline and amorphous) structure, respectively. Thermal variations in magnetization *M* from liquid helium up to room temperature for both samples are similar. Magnetization value at zero field cooled curve reaches about 0.1 μ_B per formula unit at 2 K and then increases. Two maxima are visible, the first at 50 K (a sharp effect) and the second very broad ranging from 150 to 200 K. ^{57}Fe Mössbauer spectrometry investigation revealed a remaining magnetic component in addition to a prevailing quadrupolar feature. Application of a weak external magnetic field causes an increase in the mean hyperfine magnetic field B_{hyp} and the volume fraction of magnetic component. This observation was confirmed by results of *M(T)*, *M(H)* and AC magnetic susceptibility measurements. In short-range ordered crystallographic zones characteristic of melt-spun $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ (x = 2.5, 3) alloys, the related magnetic ordering, called the mictomagnetism or the cluster spin glass appears.

Keywords Rare earth transition metal alloys · Magnetic metallic glasses · Rapid solidification · Mössbauer spectrometry · Cluster spin glass

1 Introduction

The intermetallic compounds $DyMn_{6-x}Ge_{6-x}Al_xFe_x$ with limiting compositions $x = 0$ ($DyMn_6Ge_6$) and $x = 6$ ($DyFe_6Al_6$) crystallize in hexagonal and tetragonal

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structures, respectively. Metastable crystalline as well as amorphous states appear as a consequence of phase competition during the rapid quenching process [1]. The plethora of magnetic states characteristic of amorphous structures, includes the spin glass-type states. It can follow from the statistical distribution of magnetic ions interacting *via* RKKY-type couplings, including some antiferromagnetic ones, as encountered in magnetically frustrated alloys. Such frustrations were observed even in heavy fermion systems, where the f electron or conduction electron hybridization under the influence of topological disorder can suppress Kondo interactions. It is a very local effect depending on the structural environment around the f ions. Therefore, lattice distortions or disorder connected with metastability of the material structure play an important role both when the ground state is magnetic or not. The spin glass ordering is characterized by a cusp in the magnetic susceptibility as a function of temperature observed at the freezing temperature T_f. It comes from a thermal blocking of the fluctuating magnetic moments.

2 Experimental details

The alloys in the form of ribbons were prepared by melt spinning (details in [1]). Subsequently, they were investigated in the as-quenched and annealed states. Heat treatment was performed at temperature $T_a = 505^\circ$ C for time $\tau = 15$ min. Magnetization curves, $M(H)$ loops and AC magnetic susceptibility were measured in MPMS-5 and PPMS (Quantum Design). The transmission ^{57}Fe Mössbauer effect experiments were performed at room temperature (RT) using a constant acceleration conventional spectrometer with a ^{57}Co source. The hyperfine structure was modelled by means of the least square refinement procedure involving magnetic and quadrupolar components with Lorentzian lines. The values of the isomer shift are quoted relative to that of α-Fe at RT.

3 Results and discussion

Figure 1 shows XRD patterns obtained for melt-spun $DyMn_{6-x}Ge_{6-x}Al_xFe_x$ with $x = 2.5$ and 3 samples, having an amorphous and mixed (crystalline and amorphous) structure, respectively. For $x = 3$ three crystalline phases can be distinguished: the tetragonal phase of $CeMn_4Al_8$-type (space group *I4/mmm*), AlFe-type phase (space group *Pm-3m*) and $DyMn_2Ge_2$ (space group *I4/mmm*). The amorphous residue reaches about 15 % of total volume. The volume contribution of $CeMn_4Al_8$-type phase is close to 38 % and that of AlFe phase is 21 %, while that of $DyGe_2Mn_2$ phase reaches 26 %. The lattice constants are: $a = 8.676 \pm 0.002$ Å, $c = 5.100 \pm 0.002$ Å for $CeMn_4Al_8$, $a = 2.926 \pm 0.001$ Å and $a = 3.955 \pm 0.001$ Å, $c = 10.775 \pm 0.003$ Å for AlFe and $DyGe_2Mn_2$, respectively.

For $x = 2.5$ in the as-obtained state the spectrum is typical of amorphous structure. From the Gauss curve fitting the smallest interatomic distances and sizes of coherently scattered domains were determined [2] as 0.28 and 0.83 nm, respectively. $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ in the first step of crystallisation forms a multiphase alloy with dominant contributions of two phases. The angular positions of the peaks corresponding to one of these phases are close to those characteristic of $DyMn_2Ge_2$

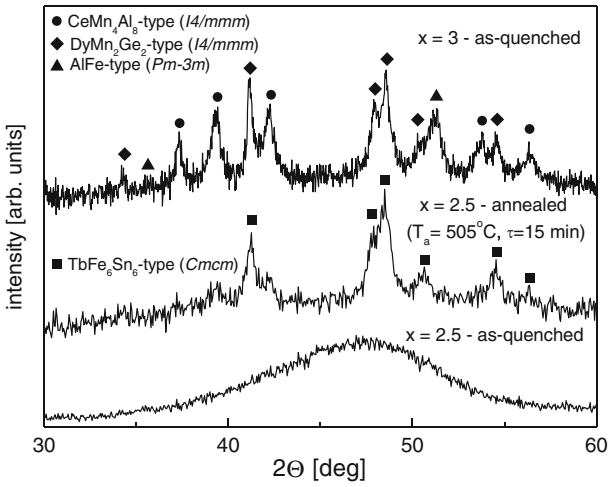

Fig. 1 X-ray diffraction (XRD) patterns of $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($x = 2.5, 3$) in as-quenched and annealed states. Heat treatment was performed at temperature $T_a = 505°$ C for time $\tau = 15$ min. Identified phases are marked

structure observed for the alloy with $x = 3$. However, it probably is a structure of $TbFe_6Sn_6$-type with space group *Cmcm*. Moreover, similarly as for RFe_6Ge_6 alloys [3], the presence of two additional crystallographic sites was observed at the interstitial positions of the elementary cell of $TbFe_6Sn_6$-type structure. Cited authors have suggested that R and Ge atoms occupy the 4*c* (0.5, 0.128(1), 0.25) and 8*g* (0.8477(2), 0.1248(6), 0.25) sites, at the expense of the population of the site 4*c* (0, 0.122(1), 0.25) and 8*g* (0.3477(2), 0.1252(6), 0.25). On top of that, the presence of atoms of a few elements in the alloy (Fe, Al, Mn and Ge) is a source of chemical disorder also in the other crystallographic sites leading to changes in the peak intensities. The lattice constants of the $TbFe_6Sn_6$ phase for the annealed sample $x = 2.5$ are $a = 8.379 \pm 0.002$ Å, $b = 17.719 \pm 0.004$ Å, $c = 5.060 \pm 0.001$ Å.

Thermal variations of magnetization from liquid helium up to room temperature for $DyMn_3Ge_3Fe_3Al_3$ ($x = 3$) and $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ ($x = 2.5$) samples are similar (published by us in [1]). Magnetization value at zero field cooled (ZFC) curve reaches about 0.1 μ_B per formula unit at 2 K and then increases. Two maxima are visible, the first at 50 K (a sharp effect) and the second very broad ranging from 150 to 200 K. The transition to the paramagnetic state occurs above 400 K. The intersection of the field cooled (FC) and ZFC magnetization curves indicates complex magnetism involving different antiferromagnetically coupled sublattices (the Fe-Mn and Dy-substructures) with different spontaneous polarization dependence as a function of temperature. Low temperature anomalies in the magnetization for both samples indicate a strong contribution of the Dy-sublattice to the magnetic properties.

300 K ^{57}Fe Mössbauer spectrum presented in Fig. 2 reveals the remaining magnetic component in addition to the prevailing quadrupolar feature. This investigation of the $DyMn_3Ge_3Fe_3Al_3$ alloy suggests the existence of magnetic fluctuations as it was previously observed at 77 K [4]. Application of a weak external magnetic field results in an increase in the mean hyperfine magnetic field B_{hyp} and the magnetic fraction. The Mössbauer spectra strongly indicate a Zeeman splitting and similar situation is expected for $x = 2.5$. For $DyMn_3Ge_3Fe_3Al_3$ alloy at 300 K the content of the magnetic fraction increased from MF = 5 % without field to 17 % in

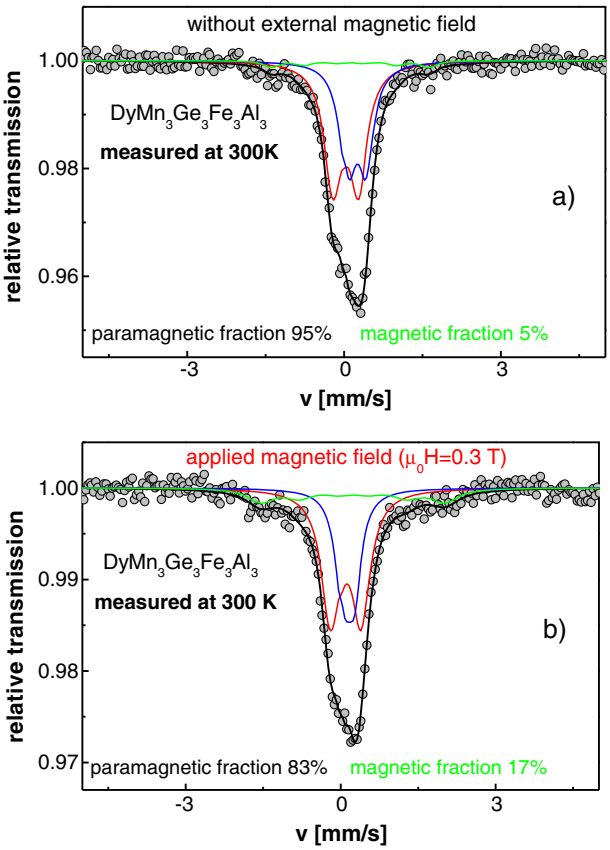

Fig. 2 The Mössbauer spectra of $DyMn_3Ge_3Fe_3Al_3$ sample measured at 300 K without (**a**) and with applied magnetic field (**b**) of induction $\mu_0 H = 0.3$ T

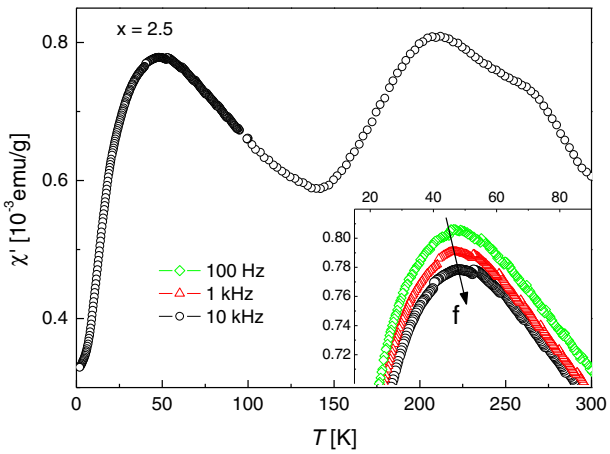

Fig. 3 Real component χ' of AC magnetic susceptibility as a function of temperature measured at $\omega = 0.1$, 1 and 10 kHz as-quenched for $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$. The inset shows $\chi'(T)$ in the vicinity of the freezing temperature

$\mu_0 H = 0.3$ T as it was already reported [4]. For the sample with mixed structure ($x = 3$) AC susceptibility measurements already confirmed the presence of spin dynamics (Fig. 4 in [4]).

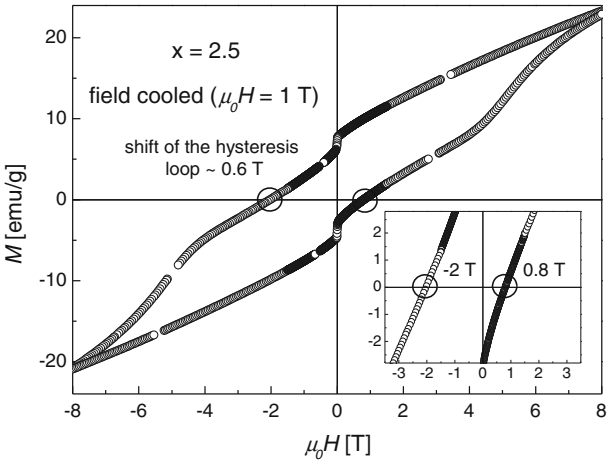

Fig. 4 Magnetization $M(H)$ as a function of magnetic field for the $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ sample initially cooled in the field $\mu_0 H = 1$ T down to $T = 2$ K (measurement performed at 2 K). The inset is magnification of the inert part of hysteresis $M(H)$ to show its asymmetry

The Vogel-Fulcher law $\tau = \tau_0 \exp\left[E_a k_B^{-1} \left(T_f - T_0\right)\right]^{-1}$ [5] and critical slowing-down power law $\tau = \tau_0 \left(T_f T_g^{-1} - 1\right)^{-z\nu}$ [6] were helpful in characterization of the spin dynamics observed in $DyMn_3Ge_3Fe_3Al_3$. Both approximations give comparable values for the spin flipping time necessary to obtain the equilibrium state $\tau_0 = 8 \times 10^{-7}$ and 1×10^{-9} s, respectively. Additionally the product of the dynamic critical exponent yielded $z\nu \approx 3.5$ values characteristic of cluster spin glass systems (for ordinary spin glasses $z\nu \approx 8$). One can observe similar behaviour also for $DyMn_{3.5}Ge_{3.5}Fe_{2.5}Al_{2.5}$ (Fig. 3.). There is a cusp in the temperature dependence of the real part of magnetic susceptibility with a shift in freezing temperature T_f measured at different frequencies shown in inset in Fig. 3.

As illustrated in Fig. 4 an essential result confirming the occurrence of the mictomagnetic ordering and competing exchange interactions with different signs was obtained from the $M(H)$ measurements. A marked shift of the loop (asymmetry) along the abscissa axis $\mu_0 H$ was observed when measured after a preliminary cooling of the sample down to $T = 2$ K in a magnetic field of induction of 1 T.

It is possible to observe a small exchange bias on $M(H)$ curve by measuring a shift (asymmetry) in the hysteresis loop on the axis of the applied field following the cooling of the sample below T_f in the presence of a magnetic field. It is related to the freezing of the moments of the magnetic clusters close to the temperature T_f upon cooling in a relatively weak magnetic field of the order of 1 T. Such a behavior is characteristic of systems with competing (negative/positive) exchange interactions, including the spin glass-type ones, as previously described by C.M. Hurd [7].

4 Conclusions

The above presented and discussed results confirm the occurrence of mictomagnetic ordering in the alloy investigated. With decreasing Fe content ($x = 2.5$) an increase in the hyperfine field strength B_{hyp} as well as in the volume of the magnetic fraction in the alloy is observed.

The presence of clusters with frustrated magnetic interactions was also investigated by us in structurally disordered metastable cobalt, iron or yttrium containing systems [8, 9], *e.g.*, in polycrystalline structures with Y and Co.

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